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Faculty of Science
Department of Chemistry

A study on The Removal of Some Phenolic Compounds from Wastewater

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A Study on The Removal of Some Phenolic Compounds From Wastewater

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ABSTRACT

The removal by means of Advanced Oxidation Processes (AOPs) is an attractive option for the treatment of industrial wastewater containing phenolic compounds in an environmental . The present work would summarize some AOPs technologies focusing only on heterogeneous catalytic removal of phenol and highlighting the catalysts activity and reaction conditions. The catalysts used were H-ZSM-5,H-Mordenite and Bentonite. H-ZSM-5,H-Mordenite doped with Platinum (Pt) were prepared and characterized by using X-ray diffraction analysis (XRD), thermal analysis, Scanning electron microscopy, High Resolution Transmission electron microscopy, pluse titration measurements, nitrogen adsorption desorption at -196°C.the experimental parameters affecting the removal efficiency were time, temperature, pH, initial phenol concentrations, catalyst dose and the effect of irradiating with Ultraviolet (UV –C) were studied . The optimum conditions for the removal of each catalyst were investigated .

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List of abbreviations

abbreviation	**Full name**
AOPs	advanced oxidation processes
CWPO	catalytic wet peroxide oxidation
CWAO	catalytic wet air oxidation
EPER	European Pollutant Emission Register
EPRTR	European Pollutant Release and Transfer Register
IPCS	International Programme in Chemical Safety
EHC	Environmental health criteria documents
BOD	biochemical oxygen demand
COD	chemical oxygen demand
EPA	Environmental Protection Agency
ZSM-5	Zeolite Scony Mobile-5
XRD	X-Ray Diffraction Analysis XRD
SEM	Scanning electron microscopy
HR-TEM	High Resolution Transmission electron microscopy

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OBJECTIVES OF THE STUDY

The problems of scarcity and the bad use of water have been increased because of the industrial activity, from where effluents with high toxicity and biodegradation difficulties are coming from. For that reason, it is essential to treat these effluents before they are released to the municipal wastewater treatment plants. From the wide variety of chemical processes focussed on the treatment of industrial effluents with high content of organic compounds so this study aims to:

- Prepare aluminosilicata materials and nano sized Pt/H-ZSM-5 and Pt/H-Mordenite with different concentrations.
- Characterize these catalysts.
- Remove phenol by using these catalysts.
- Study the different factors affecting on the removal processes (Temperature, initial pH, initial phenol concentration, Catalyst dose and UV-C irradiation).
- Get the optimum conditions for the removal process for each catalyst.

Chapter 1

Introduction

INTRODUCTION

The problems of scarcity and the bad use of water have been increased because of the industrial activity, from where effluents with high toxicity and biodegradation difficulties are coming from. For that reason, it is essential to treat these effluents before they are released to the municipal wastewater treatment plants. From the wide variety of chemical processes focussed on the treatment of industrial effluents with high content of organic compounds, it is found the advanced oxidation processes (AOPs), which develop technologies such as the oxidation of organic compounds, e.g. the catalytic wet peroxide oxidation (CWPO). The improvement of this process is based on the variation either of the catalyst or the oxidant source because they directly affect the operational conditions and cost. The last decades have shown a reevaluation of the issue of environmental pollution, under all aspects, both at regional and at international level. The progressive accumulation of more and more organic compounds in natural waters is mostly due to the development and extension of chemical technologies for organic synthesis and processing **[1]**.

Population explosion, expansion of urban areas increased adverse impacts on water resources, particularly in regions in which natural resources are still limited. Currently, water use and reuse has become a major concern. Population growth leads to significant increases in default volumes of wastewater, which makes it urgent imperative to develop effective and affordable technologies for wastewater treatment.

There's no doubt that the water problems in the world in general & in Egypt in particular became an urgent need to be solved. So, it was necessary to do a lot of researches to choose the best way to depend on. Egypt has been suffering from severe water scarcity in recent years. One of the most promising ideas to overcome this crisis is the treatment and reuse of industrial wastewater. Industrial effluents are often highly toxic, containing heavy metals and toxic organic matter such as phenol **Figure 1.**

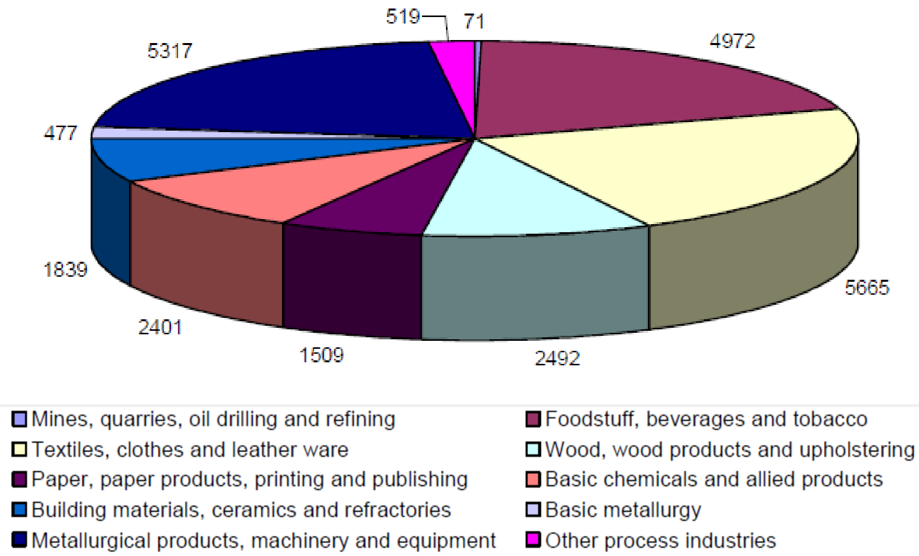


Figure 1: Distribution of enterprises for the different industrial sectors in Egypt**[2]**.

1.1. Water pollution

Water is considered the most important natural resource for man to develop his prosperity as well as his essential needs. Industrialization is considered the cornerstone of the development strategies due to its significant contribution to the economic growth and human welfare, however in most developing countries it led to serious environmental degradation **[3]** .

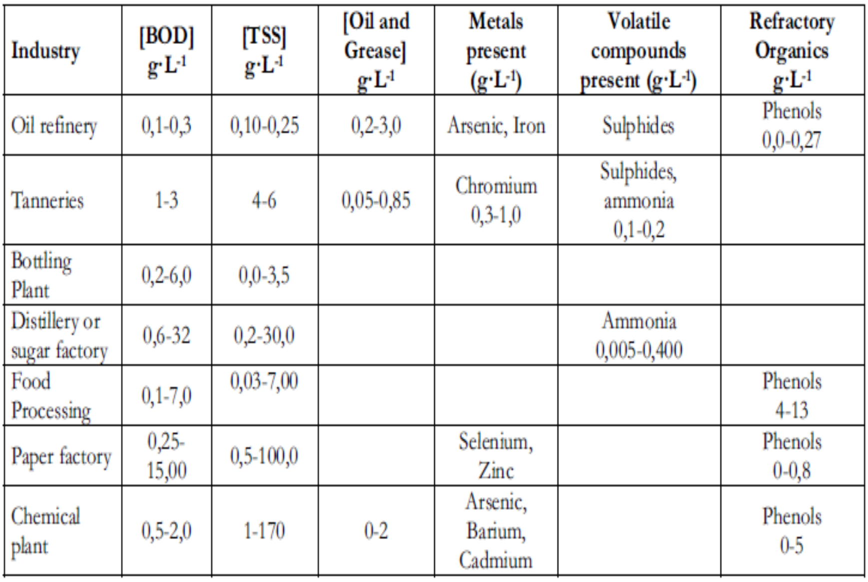
The decreasing availability of water and the human impact impulse human beings to control pollutants and contamination of water resources. Sources of water pollution can be found on stationary sources such as sewage treatment plants, factories and ships and non-point sources, more diffusive, includes agricultural run-off, mining activities and paved roads. That is why, the **European Pollutant Emission Register** (EPER) was established to control and prevent integrated pollution. According to EPER decision, every Member State should report every three years the industrial emissions into air and water. This report should include 50 pollutants with their respective values and comparison with the permissible levels of the EPER decision. Moreover, the threshold values were selected in order to include about the 90% of the emissions of the industries facilities looked at. The first report was published in 2001, the second reporting year was 2004 and data was provided in June 2006, besides instead to being the third EPER reporting 2007, it was replaced by the **European Pollutant Release and Transfer Register** (European PRTR). Therefore, the updated and available data is still being 2004 EPER report. From 50 pollutants considered at the EPER decision, 26 concerned to water. An overview provides the organisation of these pollutants in five groups. The threshold values for each pollutant are defined. If emissions exceed these values, such emissions must be reported**[4].**

There are a variety of pollutants on EPER list, although Phenols are taken as representative pollutants of industrial wastewaters because the removal of pollutants from industrial wastewater is one of the most important issues nowadays. **The International Programme in Chemical Safety** (IPCS) provides reports called Environmental health criteria documents (EHC). Each EHC makes critical reviews on the chemicals or the combinations of chemicals and physical and biological agents on human health and the environment. Each EHC follows a standard outline, so it is expected to find all the necessary information of pollutants **[5]**.

1.2. Industrial wastewaters

Industrial wastewater has a wide range of pollutant concentrations. These wastes are high in **biochemical oxygen demand** (BOD), dissolved salts, odour, phenol, and sulphur compounds. For instance, food processing industries, distilleries, and soft drink industries are characterised by very high BOD concentration, suspended solids, dissolved solids, variable pH, and a high level of organic matter. Even though they have low BOD strength, wastewaters from chemical industries are important because they are frequently toxic to aquatic organisms at very low concentrations. In addition, the biodegradability assessment of industrial wastewater is used on treatment processes to optimise the maximum pollutant removal efficiency. This efficiency is represented by the ration of BOD and **chemical oxygen demand** (COD), which is widely used to determine the degradability of contaminated water. For instance a BOD/COD ratio of 0,4 is generally considered the cut-off point between biodegradable and difficult to biodegrade waste. In order to know the levels of possible contamination the United Nations Environment programme on its division of technology, industry and economics reported the typical industrial wastewater pollutant characteristics, **Table 1.**

Table 1. Typical industrial wastewater pollutant characteristics**[6].**



Industry	[BOD] $g\cdot L^{-1}$	[TSS] $g\cdot L^{-1}$	[Oil and Grease] $g\cdot L^{-1}$	Metals present ($g\cdot L^{-1}$)	Volatile compounds present ($g\cdot L^{-1}$)	Refractory Organics $g\cdot L^{-1}$
Oil refinery	0,1-0,3	0,10-0,25	0,2-3,0	Arsenic, Iron	Sulphides	Phenols 0,0-0,27
Tanneries	1-3	4-6	0,05-0,85	Chromium 0,3-1,0	Sulphides, ammonia 0,1-0,2	
Bottling Plant	0,2-6,0	0,0-3,5				
Distillery or sugar factory	0,6-32	0,2-30,0			Ammonia 0,005-0,400	
Food Processing	0,1-7,0	0,03-7,00				Phenols 4-13
Paper factory	0,25-15,00	0,5-100,0		Selenium, Zinc		Phenols 0-0,8
Chemical plant	0,5-2,0	1-170	0-2	Arsenic, Barium, Cadmium		Phenols 0-5

Source: CEP report No. 40, 1998, p9.

1.3 Pollutants

The continuous industrial development and the characterisation of the effluents coming from industries highlight the production of refractory compounds like phenols. So that, it is our commitment to evaluate the treatment of refractory compounds to propose feasible technologies and reduce the contamination caused by industrial activity. Removing pollutants from industrial process waters and wastewaters is becoming an important area of research as the amount and quality of freshwater available in the world continues to decrease due to growing water demands and/or long periods of drought. Increasingly stricter wastewater discharge standards continue to be introduced worldwide in an effort to reduce the environmental impacts of industrial processes. Chemical and petroleum industries generate a wide variety of highly toxic organic wastes. Among organic pollutants phenol and phenol derivatives **[7]**.

Phenol and phenolic compounds are a kind of priority pollutants, often occur in the aqueous environment due to their widespread use in many industrial processes as a basic raw materials for the manufacture of plastics, dyes, drugs, antioxidants and pesticides **[8]** .

Some of the toxic members of phenolic compounds are the chlorinated and nitro substituted phenols that are used as pesticides and antibacterial [7]. These compounds have high stability, high toxicity and non-biodegradable. They pose severe problems to the environment because they are carcinogens and mutagens. For example, 2,4-dichlorophenol may cause some pathological symptoms and change human endocrine systems their mode of exposure is through the skin and gastrointestinal **[9]**.

Thus, they are considered as common environmental contaminants. The total production of phenols reached 7.8 million tons in 2001 and phenolic compounds such as p-nitrophenol (PNP) and p-chlorophenol (PCP) impact unpleasant odours and tastes to drinking water and are harmful to humans and living organisms. Their presence even at low concentrations can be obstacles to the acceptance of recycled water by the community **[10]**.

Due to their toxicity and adverse effects on the environment, phenolic compounds are listed as priority pollutants by the **United States Environmental Protection Agency** (EPA). For example 2-chlorophenole listed in number 24 and phenol listed in number 65 **[11]**.

For these reasons the elimination of phenolic compounds from wastewater effectively has been in urgent demand.

1.4 Refractory compounds – phenols

In accordance with organic chemistry, phenols also called phenolics are a class of chemical compounds consisting of a hydroxyl group (-OH) attached to an aromatic hydrocarbon group. The simplest or representative compound of this group is phenol (C_6H_5OH). Although similar to alcohols, phenols have unique properties and they are not classified as alcohols (since the hydroxyl group is not bonded to a saturated carbon atom). They have relatively higher acidities because the aromatic ring's tight coupling with the oxygen and a relatively loose bond between the oxygen and hydrogen. The polar nature of O-H bond (due to the electronegativity difference of the atoms) results in the formation of hydrogen bonds with other phenol molecules or other H- bonding systems (e.g. water).

Therefore, phenolic compounds show high melting and boiling points with high solubility in aqueous media. The abatement of water pollutants like phenols has several alternatives for its treatment. So, a lot of research works have been made due to phenol is strong bactericide even at mild concentrations and frequently is selected as a model compound **[12]**. The election of a specific wastewater treatment will be based on the characteristics of the treated effluent and the expected product. Moreover, phenol-contaminated wastewaters attract particular interest because, aside from being, phenol confers a particularly disagreeable taste and odour to water, even at concentrations below 0,001 mg /L **[13]**. Then the main reason to concern is that prolonged exposures to phenol may be genotoxic for humans and animals. Finally, the necessity to reduce the level of pollutants discharged by industry into municipal sewer systems is urgent because into general pretreatment regulations phenols are listed within several of the categorical standards.

Phenol was chosen as the studying object, for it is typical in phenolic compounds, moreover, it is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic compounds **[14]**.

1.5 Phenol – As a model compound

Phenol is formed during the natural decomposition of organic materials, although the major part of phenol present in the environment comes from anthropogenic origin. So, in order to identify this model compound, **Table 2** represent the physical and chemical properties of phenol.

Some chemical and physical properties of phenol (so called phenic acid or carbolic acid). Phenol was first isolated from coal tar in 1834 by German chemist Runge, it is an aromatic compound. At ambient temperature and pressure it is a hygroscopic crystalline solid, when pure, solid phenol is white but it is mostly colored due to the presence of impurities. Phenol is very soluble in ethyl alcohol, in ether, and in several polar solvents as well as hydrocarbons such as benzene. In water it has a limited solubility and behaves as weak acid. As a liquid phenol attacks rubber, coating, and some forms of plastics. Hot liquid phenol attack aluminum, magnesium, lead and zinc metals it characterized by a typical pungent sweet, medicinal, or tar- like odour **[15]**. It is a combustible compound.

Phenols do not have an H atom attached to the C atom carrying the OH group. Therefore, their reaction with oxidizing agents is quite different from that of primary or secondary alcohols. Only very strong oxidizing reagents, such as permanganate, dichromate or Fremy's salt $(KSO_3)_2NO$, oxidize simple phenols to 2,5-cyclohexadien-1,4-ones(benzoquinones).

There is an interaction between the delocalized electrons in the benzene ring and one of the lone pairs on the oxygen atom. This has an important effect on both the properties of the ring and of the -OH group**[16]**.

One of the lone pairs on the oxygen overlaps with the delocalised ring electron system. Giving a structure rather like this:

The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene itself.

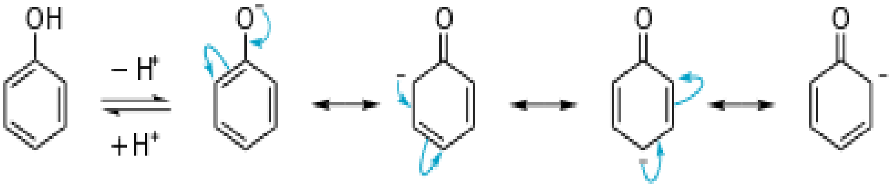


Figure 2. Delocalised ring electron system for phenol

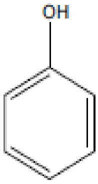
It also helps to make the -OH group's hydrogen a lot more acidic than it is in alcohols **[17]**.

Statistic information according to the **Environmental health criteria** (EHC), no data are available on atmospheric phenol levels. Background levels are expected to be less than 1 µg.m^3. Either urban or suburban levels vary from 0.1 to 8 µg▪ m3, while concentrations in source-dominated areas (industry) were reported to be up to two orders of magnitude higher. Phenol has been detected in rain, surface water and ground water, but data are very scarce. Elevated phenol levels have been reported in sediments and ground waters due to industrial pollution **[18]**.

Occupational exposure to phenol may occur during the production of phenol and its products, during the application of phenolic resins (wood and iron or steel industry) and during a number of other industrial activities. The highest concentration (up 0.1 to 88 µg.m^3) was reported for workers in the ex-USSR quenching coke with phenol containing wastewater. Most other reported concentrations did not exceed 19 mg.m^3 (Law 10/1993-Spain and IPCS, 1994)**[19]**

.Additionally, the EPER reports the amounts of Phenol emissions to air, water or WWTP, showing the high quantities of phenol and its compounds to treat.

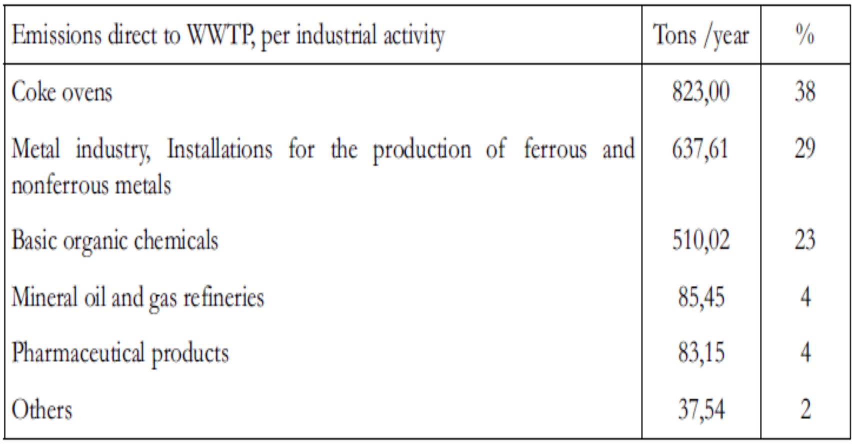
Table 2. Identity, physical and chemical properties of phenol[15].

Phenol	
Molecular formula	C_6H_5OH
Molar mass	94,11 $g{\cdot}mol^{-1}$
Density	1,07 $g{\cdot}cm^3$
Melting point	40,5 °C
Boiling point	181,7 °C
Solubility in water	8,3 $g{\cdot}100\ mL^{-1}$ (20 °C)

Due to industrial activity increment, it is possible to notice in **Table 3.** That Coke ovens, metal industry and basic organic chemicals are main wastewater producers. Then, if high levels of phenols emission continuously increment and treatment in between industrial releases and wastewater treatment plants does not exist, the world will be seriously aware of an imminent environmental contamination because industrial activity will increase pollution, then water resources will be totally cut-off as consequence and human beings will have health problems **[4]**.

The concentration of pollutants on industrial wastewater depends on the industrial source, because when exists high concentration of toxic materials, it is necessary to apply specific processes for their separation, transformation, and further decomposition.

Table 3. EPER-report of phenols emission indirect to water[4].



Emissions direct to WWTP, per industrial activity	Tons /year	%
Coke ovens	823,00	38
Metal industry, Installations for the production of ferrous and nonferrous metals	637,61	29
Basic organic chemicals	510,02	23
Mineral oil and gas refineries	85,45	4
Pharmaceutical products	83,15	4
Others	37,54	2

Different processes based on biological, physical, chemical and their combinations are available to achieve this goal, however each technique has limitations and different applicability, effectiveness and cost.

1.6 Phenol industrial syntheses and sources

Currently, phenol is produced at a rate of about 6 million ton/yr worldwide, with a significantly increasing trend **[20]** .The so called Hock processes, i.e., the three-step cumene synthesis and oxidation processes (such as the Sunoco-UOP, the KBR and the GE -Lummus processes), consisting in the simultaneous syntheses of phenol and acetone from benzene, propylene and oxygen, produces about 95%of the phenol used in the world. These processes **[21]** involve:(i) alkylation of benzene with propene to form cumene, catalyzed by phosphoric acid, aluminum chloride or,recently,by beta or MCM22 zeolite ;(ii) oxidation of cumene to cumene hydro peroxide(CHP)with air proceeding via a free-radical mechanism that is essentially auto catalyzed by CHP ;(iii) cleavage of cumene hydro peroxide to phenol and acetone , catalyzed by sulphuric acid.

Several alternative industrial synthesis of phenol exist **[22]** i.e., through chlorobenzene (reaction with caustic soda at 350◦C) or by sodic benzen solfonate alkaline fusion or by oxidation of toluene via benzoic acid. Phenol is also present in benzole and coal tar produced during coal coking. It may be separated from these by products by extraction with caustic solutions as sodiumphenate.It is shipped in the molten state at elevated temperatures or in the solid or crystalline form; it is also available as an aqueous solution. Phenol and many substituted phenols are natural components of many substances (e.g., tea, wine and smoked foods), and phenol is also emitted from the combustion of fossil fuels and tobacco. It is also present in animal wastes and decomposing organic material and may be formed in air as a product of benzene photo oxidation. Bacteria in the environment quickly breakdown phenol, and so levels in air (1-2 days) ,water (9 days) and soil(2-5days)are generally quite low **[23]** .

1.7 Phenol industrial applications

As a pure substance, phenol is used as a disinfectant, for the preparation of some cream and shaving soap for its germicidal and local anesthetic properties, in veterinary medicine as an internal antiseptic and gastric anesthetic, as a peptizing agent in glue, as an extracting solvent in refinery and lubricant production, as a blocking agent for blocked isocyanate monomers, as a reagent in chemical analysis and as a primary petrochemical intermediate. Its largest use (35%) is to produce phenolic resins like phenol-formaldehyde resins (Bakelite) which are low-cost thermosetting resins applied as plywood adhesive, construction, automotive and appliance industries. By reaction with acetone it may also be converted into bisphenol A, a monomer for epoxy-resins (28%). It is also used to produce cyclohexanone and cyclohexanone-cyclohexanol mixtures by selective catalytic hydrogenation. Cyclohexanone is later converted into its oxime and further to caprolactame, the monomer for nylon 6 (16% of phenol applications). The mixture cyclohexanone-cyclohexanol is oxidized by nitric acid to adipic acid, one of the monomers for the production of nylon-6,6. Phenol is also used to produce polyphenoxy and polysulphone polymers, corrosion-resistant polyester and polyester polyols**[24]**.

Phenol may be converted into xylenols, alkylphenols, chlorophenols, aniline, and other secondary intermediates in the production of surfactants, fertilizers, explosives, paints and paint removers, textiles, rubber and plastic plasticizers and antioxidants, and curing agents and so on. Phenol is also a building block for the synthesis of pharmaceuticals, such as, e.g., aspirin **[25]**.

1.8 Phenol and health

The sterilizing activity of phenol was discovered by the English surgeon Joseph Lister in 1865. The germicidal activity of phenol appears associated to its protein denaturing ability. It has lipofile properties, so it binds itself to the batteric proteine by hydrogen bonds. On the otherhand, phenol has relevant health effects for humans **[26]** .The manufacture and transportation of phenol as well as its many uses may lead to worker exposur to this substance ,through inhalation, ingestion, eye or skin contact, and absorption through the skin. Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosisand death can result from overexposure to it. Internally, phenol affects the liver, kidneys, lungs, and vascular system. The ingestion of 1g of phenol is deadly for man. The Nazi used phenol toxicity for refining extermination techniques, making phenol injections for killing the prisoners. Death was coming up in a few seconds and the method was considered to efficacious and economic. No evidence exists to indicate that phenol has any carcinogenic potential **[27]**.

1.9 Abatement technologies for phenol in wastewaters

Phenols are present in wastewater of various industries such as refineries (6- 500 mg /L), coking operations (28-3900 mg /L), coal processing (9-6800 mg /L) and manufacture of petrochemicals 3-1220 mg /L). Besides, phenols are the main organic constituents present in condensate streams in coal gasification and liquefaction processes**[28]**

Moreover, other sources of wastes containing phenols are pharmaceutical, plastic, wood products, paint and pulp and paper industries (0,1-1600 mg /L). It can be mentioned that olive oil mill wastewaters present richness in phenol and polyphenol derivatives, causing a significant problem in the Mediterranean area. Phenol-containing wastewater may not be conducted into open water without treatment because of the toxicity of phenol. It also contributes to off-flavours in drinking and food processing waters. Due to the toxic nature of some of these compounds the Environmental Protection Agency has set a water purification standard of less than 1 part per billion (ppb) of phenol in surface waters. In Italy, in agreement with the recommendations of the European Union,the limit for phenols in potable and mineral waters is 0.5µg/l (0.5ppb), while the limits for wastewater emissions are 0.5mg/l (0.5ppm) for surface waters and 1mg/l for the sewerage system (law no. 152/2006) **[24]** .

Because of the high concentration of toxic materials in industrial wastewaters, it is necessary to apply specific processes for their separation, transformation, and further decomposition. Different processes based on thermal, biological, physical, chemical and their combinations are available to achieve this goal, however each technique has limitations, different applicability, effectiveness and cost. Besides, the wide variety of technologies for phenol degradation from wastewater was compared, providing evidence for the strong research efforts carried out in recent time to develop new and improved technologies, moreover some phenol intermediates or derivatives are also water pollutants, so that the different technologies applied to phenol can be performed for its derivatives as well **[29]**.

Developing green and sustainable technology for the effluent treatment is very important research area in this era of industrial and social development. Many researchers have carried out the research in this field. One of the important pollutants from this point of view is phenol. It has its presence in the effluent from major chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. Phenol causes harmful side effects such as sour mouth, diarrhea, impaired vision, excretion of dark urine. It is also toxic for fishes.

The toxic levels usually range between the concentrations of 10-24 mg/L for human and the toxicity level for fish between 9-25 mg/L. Lethal blood concentration of phenol is around 150-mg/100 ml. Various treatment processes used for the removal and/or recovery of phenols are hot gas or steam stripping, adsorption, ion exchange solvent extraction, oxidation, phase transfer catalysis and biological treatment processes. Phenolic waste water is treated using activated carbon in the fixed bed/ moving bed/ fluidized bed **[30]** .

1.10 Various methods for phenol removal

Various methods are used for removal of the phenol from wastewater such as adsorption, photodecomposition, volatilization and other various biological and non-biological methods. In the present study attempt is done to present the survey of the research on the phenol removal by various methods. The methods such as Polymerization, electrocoagulation, extraction, photodecomposition, advanced oxidation and ion exchange were used effectively by various investigators. These methods are reported to be efficient for the phenol removal. Suitable method for phenol removal can be selected based on availability of the material, extent of separation required and properties of phenolic effluent **[31]**.

1.10.1 Polymerization

Stanisavljević and Nedić **[32]** have carried out a research on phenol removal by polymerization. They carried out the phenol removal in a reaction step which was polymerization of phenol in presence of an enzyme horseradish peroxidase (HRP). They used hydrogen peroxide along with the peroxidase enzyme. The native enzyme (E) is oxidized by peroxide (H_2O_2) to an active intermediate enzymatic form. This accepts an aromatic compound into its active site and carries out its oxidation. A free radical is produced and released into solution leaving the enzyme in the compound state. This compound oxidizes a second aromatic molecule, releasing another free radical product and returning the enzyme to its native state, thereby completing the cycle. The Free radicals formed during the cycle diffuse from the enzyme into the bulk solution where they react to form polyaromatic products. These polymers are water-insoluble and may be removed by solid liquid operations. It was observed that phenol conversion in all experimented conditions was greater than 90%. The high efficiency observed is in accordance with conditions optimized to guarantee 90% polymerization using purified HRP. There is a compromise between the reduction in variable costs by the use of fewer enzymes and the increase in capital investment at the time of building the treatment facility. The effect of horseradish peroxidase (HRP) and H_2O_2 concentrations on the removal efficiency of phenol, defined as the percentage of phenol removed from solution as a function of time, has been investigated by Vasudevan and Lee **[33]**. They found that the phenol is almost completely precipitated within 10 minutes. . The removal efficiency increases with an increase in the concentration of HRP, but an increase in the time of treatment cannot be used to offset the reduction in removal efficiency at low concentrations of the enzyme, because of inactivation of the enzyme. Nicell *et al.* **[34]** have carried out the search on phenol polymerization and precipitation using polyethylene glycol as additive. They observed that the presence of polyethylene glycol enhance enzyme performance for the treatment of synthetic wastewaters containing a range of phenol concentrations between 0·5 and 16 milli molar (47 to 1500 mg/l) at neutral pH. Results demonstrated a significant improvement in catalyst lifetime in the presence polyethylene glycol in both batch and continuous stirred tank reactor configurations.

1.10.2 Electro coagulation

Abdelvahab *et al.* **[35]** have carried out the research on electrochemical removal of phenol from oil refinery waste. They explored the possibility of using electro coagulation for phenol removal. They used the cell with horizontally oriented aluminum cathode and a horizontal aluminium screen anode. They studied the phenol removal with respect to various parameters such as pH, operating time, current density, initial phenol concentration and addition of NaCl. According to them removal of phenol during electro coagulation was due to combined effect of sweep coagulation and adsorption. The results showed that, at high current density and solution pH of 7, remarkable removal of 97% of phenol after 2hour can be achieved. Also they observed that the rate of electro coagulation increases with decrease in phenol concentration and the maximum removal rate was attained at 30 mg /l phenol concentration. The study showed that, electro coagulation of phenol using aluminum electrodes is a promising process. Effect of the variables like pH, operating time, current density, initial phenol concentration and addition of NaCl on phenol removal by coagulation was studied by Zazouli and Taghavi **[36]**. They observed maximum phenol removal percentage at a pH value of 7. They also observed that increasing the concentration of phenol led to decrease in the removal efficiency. They also observed that the removal rate of phenol increased with increasing current density, and the highest current density (25 mA/cm^2) had the maximum removal efficiency.

1.10.3 Extraction

The extraction of phenol from simulated sebacic acid waste water was tried by Rao *et al.[***37].** They used 1-hexanol, 1-heptanol and 1- octanol as solvent for phenol removal. It was observed that 1-octanol showed lesser phenol removal efficiency compared to other two solvents. Xu *et al.* **[38]**have carried out investigation on extraction of phenol in wastewater with annular centrifugal contactors. They carried out the experimental study on treating the wastewater containing phenol with QH-1 extractant (the amine mixture) and annular centrifugal contactors. They observed that the extraction rate of the three-stage cascade was more than 99%. When 15% NaOH was used for stripping of phenol in QH-1(the amine mixture), the stripping efficiency of the three-stage cascade was also more than 99% under the experimental conditions.

1.10.4 Photodecomposition

Investigation of the photodecomposition of phenol in near-UV-irradiated aqueous TiO_2 suspensions was carried out by Ilisz *et al.***[39]**.They investigated The effects of charge-trapping species on the kinetics of phenol decomposition. They observed that the heterogeneous degradation of phenol followed apparently zero-order kinetics up to 70% conversion. The results of the experiments in the presence of Ag^+ indicated that the phototransformation of phenol can proceed via direct electron transfer, neither dissolved O_2 nor its reduced forms play a significant role in the degradation mechanism. Akbal and Onar **[40]** have studied photocatalytic degradation of phenol. They carried out the investigation to study photocatalytic degradation of phenol in the presence of UV irradiated TiO_2 catalyst and H_2O_2. They concluded that photocatalytic degradation can be effective method for phenol removal.

1.10.5 Biological Methods

Marrot *et al.* **[41]** have carried out the research on biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor. They investigated the effect of adaption of mixed culture on phenol degradation. They found that biological treatment was economical and practical for removal of phenol. High concentrations of phenol are inhibitory for growth. Biological and enzymettric treatments were used for phenol removal by Bevilaqua *et al.***[42]**. The systems studied were conventional batch aerobic biological followed or preceded by enzymatic treatment. They employed the Tyrosinase as enzyme.. They observed that biological treatment effectively degrades phenol upto concentration of 420 mg/l. Enzymatic polishing of biotreated effluent removed up to 75% of the remaining phenol in a four-hour reaction with 46 U.m/L of tyrosinase and 50 mg/l of chitosan (used as coagulant). The research on detection of phenol degrading bacteria and pseudomonas putida in activated sludge by polymerase chain reaction was carried out by Movahedyan**[43]**. According to results in this study, the best phenol-degrading bacteria that can utilize 500 – 600 mg/l phenol completely after 48 hours incubation belong to Pseudomonas Putida strains. It is clear that use of isolated bacteria can lead to considerable decrease of treatment time as well as promotion of phenol removal rate.

1.10.6 Electro-Fenton (EF-Fere) method

An improved Electro-Fenton (EF-Fere) method using H_2O_2 amendments and electrogenerated ferrous ions was investigated to treat phenol-containing wastewater by Jiang *et.al.* **[44]**. The degradation process of phenol was carried out in an EF-Fere system, which was composed of a power source, a cylindrical electrolytic cell and a H_2O_2 dosing system. The electrolysis was controlled by an electrochemical working station. For the phenol degradation experiments conducted in the EF-Fere electrolytic system, the maximum COD removal efficiency of phenol-containing wastewater is achieved at the condition of 800 mg/L initial ferric ions concentration, 1.0A electric current with continuous H_2O_2 addition mode. Furthermore, SnO_2 film anode and UV irradiation in the EF-Fere system are beneficial to COD removal efficiency.

1.10.7 Advanced oxidation processes (AOPs)

Rubalcaba *et al***. [45]**. have used advanced oxidation processes coupled to a biological treatment for phenol remediation. Results showed promising research ways for the development of efficient coupled processes for the treatment of wastewater containing toxic or biologically non-degradable compounds. Similar research has been carried out by Esplugas *et al.* **[46]**. Though Fenton reagent was most effective for degradation of phenol,. lower costs were obtained with ozonation. In the ozone combinations, the best results were achieved with single ozonation. Phenol degradation in presence of chlorides and sulphates was carried out by Siedlecka *et al.***[47]**. They studied the degradation of three representatives of phenolic compounds in presence of chlorides and sulphates, namely phenol, 2 chlorophenol and 2 nitrophenol. The presence of anions influenced the degradation rates. Relatively low degradation rates were observed for 2 chlorophenol. The biodegradability of phenol was increased by chloride while that of other two derivatives was increased by presence of sulphates.

1.10.7.1. Wet Air Oxidation and Catalytic Wet Air Oxidation

Wet Air Oxidation (WAO) is an established technology that involves the liquidphase oxidation of dissolved organics or oxidizable inorganic compounds**[48-50]**, which purpose is to enhance the contact between molecular oxygen and the organic matter. Unfortunately air, as oxygen source, is poorly soluble in water, rather un-reactive at low temperatures; therefore, it needs high temperature (200-350^{o}C) and pressure (70-230 atm) to be effective **[48]**, becoming an expensive process **[51-52]**. Therefore, the use of catalysts improved the reaction and decreased the operational conditions.

1.10.7.2. Wet Peroxide Oxidation and Catalytic Wet Peroxide Oxidation

Advance oxidation processes (AOPs) have been defined as those aqueous phase oxidation processes, which are based primarily on the participation of the hydroxyl radical mechanism(s) resulting in the destruction of the target pollutant or contaminant compound **[53]**. AOPs include several techniques, some of which are ozonation, fenton or fenton-like, photocatalysis, and wet oxidation, from which ozonation and fenton-like are the most used **[21]**.

Ozonation consists in molecular ozone acting directly on the nucleophilic sites and unsaturated bonds of the organic compounds. Ozone decomposition in aqueous solution develops through the formation of •OH radicals. Moreover the increase of pH to the aqueous O3 solution will thus result into higher rates of •OH radical production **[21]**. Ozonation has been widely used for drinking water desinfection-bacterial sterilization, odor and algae, but its application to wastewater treatment is limited due to its high-energy demand **[54]**.

Wet oxidation is possible with a cheap oxidant like hydrogen peroxide. Once again the use of a catalyst improves the process but decreases the operational total cost. For instance, the use of hydrogen peroxide needs a promoter in order to generate •OH radicals capable to attack the phenolic ring, that is the case of Fenton reagent (H_2O_2/Fe^{+2}) **[49-51]** or Fenton-like reactions **[52,53]**.

Fenton reaction is a process based on an electron transfer between H_2O_2 and a metal acting as a homogeneous catalyst. Moreover, Fenton and related reactions are viewed as potentially convenient and economical ways to generate oxidizing species for treating chemical wastes. From a group of bulk oxidants, hydrogen peroxide is inexpensive, safe and easy to handle, and posses no lasting environmental threat since it readily decomposes into water and oxygen **[54]**. Likewise iron is comparatively inexpensive, safe and environmentally friendly. Researches on application of Fenton chemistry to wastewater started its development in 1894, when Henry J. Fenton reported that H_2O_2 could be activated by Fe(II) salts. Nowadays, the number of scientific articles has increased exponentially and the Fenton reagent group can be divided in two groups called Catalytic Wet Peroxide Oxidation (CWPO) using homogeneous and heterogeneous catalysts. Then, the efficiency of WAO can improve considerably by the use of catalysts, either in homogeneous or heterogeneous phase. Then, the WAO with the presence or mediation of catalysts is called catalytic wet air oxidation (CWAO), obtaining higher catalytic efficiency and lower energy requirements (120-250^{o}C, 5-25 atm) **[61-63]** and employing materials, as reported on the review of Levec *et al.* **[64]** or like the activated carbon review reported by Stuber *et al.* **[52]**.

1.10.7.3. Catalytic Wet Peroxide Oxidation (CWPO) - Homogeneous catalysis

From the group of AOPs, the Wet Peroxide Oxidation (WPO) has a special interest since the use of hydrogen peroxide promotes milder operating conditions **[54,55]**. Therefore, WPO process is an adaptation from Fenton's reaction that operates around 120°C, besides it was developed in order to decrease the running cost of wet oxidation, using hydrogen peroxide instead of molecular oxygen. For instance, an advantage for using a liquid oxidizing agent (hydrogen peroxide) is the elimination of the mass transfer problems of WAO process when using molecular oxygen **[66]**. This process was successfully operated however the necessity for recovering the catalyst after reaction was controlled by a precipitation of the transition metal (Fe^{+2}) at pH 9 and filtration **[67]**.

The conventional homogeneous Fenton reaction, which is an attractive treatment method for a large number of hazardous and organic materials, uses Iron (II) salt to produce high generation of hydroxyl radicals. In addition, because of the simplicity of equipment and mild operation conditions it has been postulated as the most economic oxidation alternative. The mechanism of hydrogen peroxide generation has been established in the literature **[60]**, therefore its catalytic decomposition by means of Fe^{2+} at acid pH is expressed on Equation **(1)**.

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

For instance, several processes based on different variations of Fenton concept have been developed in past decades with the use of metals like copper or manganese to treat refractory compounds **[67]**. Moreover, the reaction efficiency depends on the acidic pH and stoichiometric excess of hydrogen peroxide. It was reported that hydrogen peroxide to iron molar ratios employed in water treatment typically lie in the range of 100/1000 **[60]**.

1.10.7.4. Catalytic Wet Peroxide Oxidation (CWPO) - Heterogeneous catalysis

The application of conventional homogeneous Fenton reaction gets complications by typical problems such as catalytic separation, regeneration, etc. In order to overcome these problems, it was proposed the use of heterogeneous catalysts on Fenton process, which is also called heterogeneous Fenton **[68]**. Thus, catalyst for the heterogeneous Fenton e.g. solids containing transition metal cations have been synthesised and tested. Therefore, interesting results were reported when using transition metals as active phase and zeolites **[69]**, pillared clays**[70,71]** or activated carbon **[72]** as supports. Although, the main problem of these catalysts comes from the leaching of the active phase when oxidation is carried out at low pH, below 3. On the other hand, it was reported that heterogeneous Fenton oxidation is also suitable for adsorption **[73]**. The adsorption occurs when the catalytic support attracts the toxic compounds to its surface**[74]**, where the metal cations have been immobilised. Therefore, the catalytic matrix allows the simultaneous sorption and oxidation of soluble contaminants. For this reason, when working with CWPO it is highly important the development of the catalyst.

Among the various AOPs, photo catalysis has been accorded great importance over the last few years due to its potential to destroy a wide range of organic pollutants at ambient temperatures and pressures, without the production of harmful products.

The major mechanism in the removal is due to oxidation by hydroxyl radicals produced in this process **[75]**.Oxidation of phenol furnishes more hydroxylated aromatic compounds that can be oxidized to quinones while further oxidation give a complex mixture of organic compounds as reported schematically in **Figure 3 .**

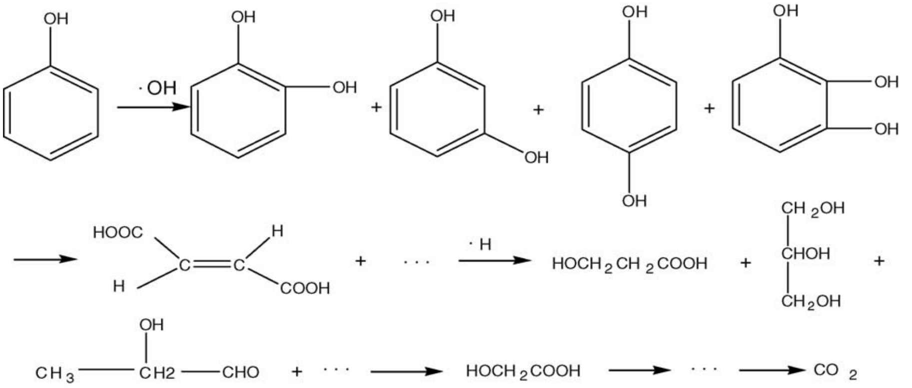


Figure 3. Simplified scheme for phenol oxidation**[75].**

In the case of the chlorinated phenols, the number and the position on aromatic ring of the chlorine atoms modifies the oxidation efficiency. The oxidation rate constant decreases linearly with increasing number of chlorine content on the aromatic ring. Also, the increase of chlorine content will block some favorable positions susceptible to hydroxyl radical attack **[54].**

1.10.8 Adsorption and Ion exchange

Experiments were conducted to examine the liquid-phase adsorption of phenol from water by silica gel, activated alumina, activated carbon by Roostaei and Tezel **[76]**. Experiments were carried out for the analysis of adsorption equilibrium capacities and kinetics. They found it to be a promising method for phenol removal. The research on phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resins was done by Caetano et.al. **[77].** They evaluated the removal of phenol from aqueous solution by using a nonfunctionalized hyper-cross-linked polymer macronet and two ion exchange resins. The nonfunctionalized resin reported the maximum loading adsorption under acidic conditions, where the molecular phenol form predominates. Ion exchange resins showed the maximum removal in alkaline medium. Desorption of nonfunctionalized resin was achieved by using the solution (50% v/v) of methanol/water with a recovery close to 90%. In the case of the ion exchange resins the desorption process was performed at different pHs. Qadir and Rhan have investigated the removal of phenol by using adsorption **[78].** The treatment of waste with active carbon is considered to be an effective method for the removal of phenol from waste solution because of its large surface area. The experimentation on adsorption isotherms for phenol removal on activated carbon was carried out by Maarof *et al.***[79]**. The adsorption isotherm parameters for the Langmuir and Freundlich models were determined using the adsorption data. It was found that both the Langmuir and the Freundlich isotherms described well the adsorption behavior of phenol on Norit Granular Activated Carbon) NAC 010, while the Freundlich isotherm described very well the adsorption of phenol on NAC 1240. Hycinthe as adsorbent was used for phenol removal by Uddin *et al.***[80].** They carried out the batch kinetic and isotherm studies under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. The inferred that the adsorption of phenol decreased with increasing pH. The results also showed that kinetic data followed closely to the pseudo-second-order model.

1.10.9 Membrane based separation

Membrane-Based Separation of phenol/water mixtures using ionically and covalently cross-linked ethylene-methacrylic acid copolymers was tried succesfully by Mixa and Staudt**[81]**. They performed the Membrane-based separation of phenol/water mixtures with concentrations of phenol between 3 wt% and 8 wt% in the feed with nonmodified as well as cross-linked ethylene-methacrylic acid (E-MAA) copolymers with different amounts of methacrylic acid. They concluded that using nonmodified membranes with higher methacrylic acid monomer content in the polymer, lower fluxes and higher enrichment factors were observed. Also the Investigation of different cross-linked membranes showed that with high phenol concentration in the feed, ionic cross-linking seems to be very promising. Polyurethane urea as pervaporation membrane for the selective removal of phenol was tried by Gupta *et al.***[82]**. They reacted the Hydroxyterminated polybutadiene (HTPB) with 2,4-toluene diisocyanate (TDI) followed by the addition of a diamine chain extender (prepared by the condensation reaction of 4,4′-diaminodiphenylsulfone and terepthalaldehyde) to prepare an imine containing polyurethane urea (PIUU).About 88 percent of phenol was seperated as a condensed permeate. Diaconu *et al.***[83]** have carried out research on use of membrane techniques for phenol separation**.**They presented a separation study of some phenolic compounds frequently encountered in the environment: m-nitrophenol, p-nitrophenol, m-cresol, p-cresol, using the bulk liquid membranes technique. They used chloroform as the organic solvent for the membrane and studied the operational parameters of the transport and also established the optimum separation conditions (the feed phase pH, the receiving phase pH, the time period of the transport). The best transport efficiencies were obtained for m-nitrophenol and p-nitrophenol. The transport efficiencies in the case of these phenolic derivatives were 92% for nitrophenol and 98% for p-nitrophenol.

1.11 Catalysts used in phenol removal

Some papers on oxidation of phenol using Fe or Cu supported titania, ceria, zeolites or active carbon were studied. Also Noble metals supported catalysts were studied such as Ru or Pt.

Maduna Valkaj *et al.* **[84]** study the oxidation of phenol with hydrogen peroxide on Cu/ZSM-5 catalysts. The catalysts samples were prepared by two different methods: by ionic exchange from the protonic form of commercial ZSM-5 zeolite, and by direct hydrothermal synthesis. The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at the atmospheric pressure and the temperature range from 50 to 80°C. for catalyst prepared by direct hydrothermal synthesis and 2.23–3.52wt.% for catalyst prepared by ion exchange method. The initial concentration of phenol and hydrogen peroxide was 0.01 and 0.1moldm−3, respectively. The influence of different methods of Cu/ZSM-5 preparation on their catalytic performance was monitored in terms of phenol conversion and degree of metal leached into aqueous solution.

Liotta L. F. *et al.* **[7]** carried out a research on Fe/ZSM-5 . The catalyst Fe/ZSM-5 has been reported as a promising system for the treatment of phenolic aqueous wastes in presence of H_2O_2, allowing total elimination of phenol and significant total organic carbon (TOC) removal under mild working conditions. Phenol 0.069 M, H2O2 stoichiometric ratio1.5,catalyst 0.35g/L,180 min,70◦C,pH2.5 the removal percent was 77%and TOC 21%.by changing the pH value to 3.5 the removal was 81% . In case of increasing the catalyst load to 1.5g/L the removal was 100% at pH 3.5.

Amin N.A.S. *et al.* **[85]** have carried a research in which HZSM-5 and H-Mordenite were tested at different operating conditions for removal of phenol and COD by ozonation. The process variables include concentration of phenol in solution, ozonated air flow rates, pH of solution, temperature, and reaction time. According to experimental results, combination of zeolite and ozone was able to remove both phenol and COD effectively compared to without ozone.the adsorption capacity of zeolites decreased at higher pH due to the formation of OH radicals, which diminished the surface reactions, but enhanced the bulk removal of phenol.

Muhammad S. *et al.* **[86]** have carried a research on Activated carbon (AC) and Zeolite Socony Mobil-5 (ZSM5) supported ruthenium oxide catalysts. These catalysts were prepared and tested to degrade aqueous phenol in the presence of peroxymonosulphate. It was found that RuO_2/AC was highly effective in heterogeneous activation of per-oxymonosulphate to produce sulphate radicals, presenting higher reaction ratein phenol degradation compared with RuO2/ZSM-5. Degradation efficiency of phenol could be achievedat100%of phenol decomposition and 60% of total organic carbon (TOC) removal in 1 h at the conditions of 50 ppm phenol, 0.2 g catalyst, 1 g Oxone®in 500 mL solution at 25°C using the two catalysts .

Yan Ying *et al.* **[87]** have carried a research on Fe-ZSM-5.this catalyst was prepared for catalytic wet peroxide oxidation (CWPO) of phenol in a fixed bed reactor. The catalyst was prepared by incipient wetness impregnation.The experimental results showed that the Fe-ZSM-5 catalyst achieved the highest activity (99.2% phenol conversion and 77.7% TOC conversion, respectively) with remarkable low iron leaching concentration closed to zero at the temperature of 80C, feed flow rate of 2mL/min and catalyst bed height of 3.8 cm. The Fe-ZSM-5 catalyst showed a perfect stability with low iron leaching concentration (about 1.0 mg/L) and high phenol conversion (above 95.0%) after three successive runs.

Yan Ying *et al.* **[88]** have carried a research on Fe-ZSM-5 and Fe_2O_3/ZSM-5 zeolite catalysts. These catalysts were prepared by hydrothermal synthetic and incipient wetness impregnation .The oxidation reaction with Fe-ZSM-5 was performed well at temperature of 70˚C pH of 4, catalyst concentration of 2.5 g/L and stirring rate of 400 rpm, reaction time of 180 min and the conversion of phenol reached 94.1%.

Investigation of the photodecomposition of phenol using nanomaterial TiO_2 was tried by Z. Guo *et al.* **[14]**.The degradation of 100 mg/L phenol solution under ultraviolet (UV) in the presence of TiO_2 and in the absence of it was analyzed with gas chromatography/mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC). After 12 h of degradation, the products under the two conditions were both derivatized by MSTFA and TMIS, and then analyzed by GC–MS. The results show the main intermediates are the same. They are hydroquinone, resorcinol, catechol, 1,2,3-benzenetriol, (E)-2-butenedioic acid, 2 hydroxy-propaldehyde, glycerol, 3-hydroxypropyl acid, and hydroxy-acetic acid. The chromatogram given by HPLC indicates that the presence of TiO_2 is not in favor of the degradation when the concentration of phenol is 100 mg/L; its catalysis becomes evident when the concentration gets lower. Based on the intermediates, it can be proved that besides •OH, •H is also an important active free radical in the degradation.

the Photocatalytic degradation of phenol the supported nano-TiO_2/ZSM-5/silica gel (SNTZS) as a photocatalyst in a batch reactor was tried by Zainudin *et al.* **[89]** using. The synthesized photocatalyst composition was developed using nano-TiO_2 as the photoactive component and zeolite (ZSM-5) as the adsorbents, all supported on silica gel using colloidal silica gel binder. The optimum formulation of SNTZS catalyst was observed to be (nano-TiO_2:ZSM-5:silica gel:colloidal silica gel = 1:0.6:0.6:1) which giving about 90% degradation of 50 mg/L phenol solution in 180 min. The SNTZS exhibited higher photocatalytic activity than that of the commercial Degussa P25 which only gave 67% degradation. Its high photocatalytic activity was due to its large specific surface area (275.7 m^2/g), small particle size (8.1 nm), high crystalline quality of the synthesized catalyst and low electron–hole pairs recombination rate as ZSM-5 adsorbent was used.

Shaban Y.A. *et al.* **[90]** have investigated The photocatalytic degradation of phenol in seawater under UV and natural sunlight using visible light active carbon modified (CM)-n-TiO_2 nanoparticles, synthesized via a sol–gel method. Carbon modification of n-TiO_2 was performed using titanium butoxide, carbon-containing precursor, as a source of both carbon and titanium. For comparison, unmodified n-TiO_2 was also synthesized by hydrolysis and oxidation of titanium trichloride in the absence of any carbon source. This enhanced photoresponse of CM-n-TiO_2

is in agreement with the UV–Vis spectroscopic results that showed higher absorption of light in both UV and visible regions. The effects of catalyst dose, initial concentration of phenol, and pH were studied. The highest degradation rate was obtained at pH 3 and catalyst dose of 1.0 g /L.

A series of CeO_2-TiO_2 and CeO_2-TiO_2/SiO_2 composites with $TiCl_4$ and Ce $(NO_3)_3 \cdot 6H_2O$ as precursors were prepared by Chunjing H. *et al.* **[91]** via a facile co-precipitation method. When applied to the phenol photodegradation on a homemade batch reactor with an external cooling jacket, the CeO_2-TiO_2/SiO_2 catalysts exhibited significantly enhanced photodegradation efficiency in comparison with commercial Degussa P25 and CeO_2-TiO_2. The unique catalytic properties of CeO_2-TiO_2/SiO_2 were ascribed to improved electron–hole pairs separation efficiency and formation of more reactive oxygen species owing to the presence of $Ce^{3+/}Ce^{4+}$, as well as high dispersion of active component of CeO_2-TiO_2 as a result of the introduction of SiO_2.

Various compositions of cobalt and sulfur co-doped titania nano-photocatalyst were synthesized by Siddiqa, A. *et al.* **[92]** via sol–gel method. The synthesized materials consisted of quasispherical nanoparticles of anatase phase exhibiting a high surface area and homogeneous distribution of dopants. Cobalt and sulfur co-doped titania demonstrated remarkable structural and optical properties leading to an efficient photocatalytic activity for degradation of dyes and phenol under visible light irradiations. Moreover, the effect of dye concentration, catalyst dose and pH on photodegradation behavior of environmental pollutants and recyclability of the catalyst is also examined to optimize the activity of nano-photocatalyst and gain a better understanding of the process.

Adamu, H. *et al.***[93]** synthesized A simple one-pot of TiO_2-graphene oxide (GO)/ thermally reduced graphene oxide (TGO) composites were performed with different concentrations of GO/TGO (0.25, 0.5 and 1.0 wt%). The TiO2-0.25% TGO exhibited the highest photocatalytic activity for phenol degradation in aqueous solution and this was attributed to optimal adsorption efficiency of phenol along with prolonged lifetime of electron–hole pairs. Photocatalytic activity in the absence of dissolved oxygen (under nitrogen) was also performed and, in the case of TGO, confirmed the role of graphene as an electron sink and transporter for suppression of electron–hole pair recombination.

The activity of several supported ceria catalysts for the catalytic wet air oxidation of phenol using an autoclave reactor have investigated by Chen, I-Pin *et al.* **[94]** . Results indicated that the support and the Ce content are both important factors affecting phenol conversion, CeO_2/γ-Al_2O_3 was found to be the most active catalyst among the five tested. For the CeO_2/γ-Al_2O_3 catalyst, the optimal Ce content was about 20 wt.%. Using the optimal CeO2/γ-Al_2O_3 catalyst (loading 3.0 g/l), about 100% phenol conversion and 80% chemical oxygen demand (COD) removal reaction was achieved after 2 hours at 180 °C and 1.5 MPa O_2 partial pressure.

Chang, L. *et al.* **[95]**shown that the $CeO_2/\gamma\text{-}Al_2O_3$ catalyst is a feasible alternative to CeO_2 for the catalytic wet air oxidation (CWAO) of phenol because it remains an effective catalyst and yet is cheaper to prepare. In this study, we found that the optimal cerium content in the $CeO_2/\gamma\text{-}Al_2O_3$ catalyst was 20 wt.%, regardless of catalyst loading. Furthermore, at 180 °C, with a phenol concentration of 1000 mg/ L, and an O_2 partial pressure of 1.0 MPa or 1.5 MPa, the optimal catalyst loading was 3.0 g/L. The efficacy of CWAO of phenol improved with O_2 partial pressure, although the effects of O_2 pressure were more significant between 0.5 MPa and 1.5 MPa than between 1.5 MPa and 2.0 MPa. After 2 hours of reaction, approximately 100% phenol conversion and 80% total organic carbon (TOC) removal was recorded at 180 °C, 1000 mg /L of phenol and 3.0 g l−1 of catalyst. Higher phenol concentrations require both catalyst loading and O_2 partial pressure to be increased to maintain high performance. For example, for 2000 mg /L and 2500 mg/L phenol, nearly 100% phenol conversion and 90% TOC removal after 4 hours of reaction at 180 °C.

Nousir, S. *et al.* **[96]** carried out the Catalytic wet air oxidation (CWAO) of aqueous solution of phenol with pure oxygen at 160 °C in a stirred batch reactor on platinum supported oxide catalysts (Pt/CeO_2calcined at 650°C and 800 °C and $Pt/Ce_xZr_{1-x}O_2$ with x = 0.90, 0.75 and 0.50). The results demonstrate a poisoning of the catalysts during CWAO reaction due to the formation of different forms of carbon deposit on the materials: carbonates and polymeric carbon species.

Jingjing Xu **[97]** have prepared Ceria by a precipitation method, was used as a new photocatalyst under UV light irradiation. The photocatalytic degradation of phenol was investigated in the presence of a suspended mixture of ceria and activated carbon. A synergy effect was observed with an enhancement of the apparent rate constant by a factor of 5.6 times. The apparent quantum yield of the ceria–AC system was also increased 2.9 times. The activated carbon with strong adsorption activity provided sites for the adsorption of phenol. Then, the adsorbed phenol would migrate continuously to the surface of ceria particles. Some adsorbing on the catalyst when no traces of phenol were detected in the solution. This adsorbed phenol could be degraded by maintaining UV-irradiation.

García-Muñoz, P. *et al.* **[98]**have investigated an integrated process based on combination of adsorption, with a commercial activated carbon (AC), and heterogeneous photocatalysis, with a home-made titania catalyst (TiEt), has been studied in phenol and isoproturon removal. In this work, different physical mixtures of TiEt and AC catalysts were first studied in phenol photodegradation in order to optimize the TiEt/AC concentration ratio. In this sense, a higher degree of mineralization and an improvement of phenol photodegradation were reached with a 500/100 TiEt/AC mixture (500 mg/ L TiO_2: 100 mg /L AC). More than 55% of TOC conversion was achieved at 32 hours of irradiation time.

Activated carbons with different amounts of surface oxygenated groups were used by Messele, S. A. *et al.* **[99]** as adsorbents or supports for zero-valent iron (ZVI) catalyst and tested in phenol adsorption and catalytic wet peroxide oxidation, respectively. ZVI supported on activated carbon heat-treated at 900 °C yields the best phenol removal, reaching over 85% after 3 hours, under the conditions tested: 150 mg /L of initial phenol concentration, initial pH set at 3, 30 °C, and the stoichiometric amount of hydrogen peroxide for achieving complete mineralization.

the catalytic activity of platinum catalysts such as Pt/graphite, Pt/TiO_2, Pt/Al_2O_3, and Pt/active carbon was studied by Masende Z. P. G. *et al.* **[100]**using a slurry phase CSTR. Three model reactions, namely, phenol, maleic acid, and malonic acid oxidation were investigated in the temperature range from 120 to 170 °C and at a total reactor pressure of 1.7 MPa. Platinum on graphite was found to be most suitable for aqueous phase oxidation of phenol, maleic acid, and malonic acid. Complete conversion for both phenol oxidation as well as maleic acid oxidation to CO_2 was observed with Pt/graphite at stoichiometric oxygen excess close to 0% and at 150 °C. It was further found that in the presence of Pt/graphite catalyst and oxygen, malonic acid reaction proceeds via non-catalysed decarboxylation, and catalytic decarboxylation to CO_2 and acetic acid, and catalytic oxidation to CO_2 and H_2O. Acetic acid was found to be difficult to oxidise at temperatures below 200 °C.

In the present study the used catalysts were Zeolites (ZSM-5 and Mordinite) and the natural clay bentonite, the three used catalyst consist of aluminosilicates with different concentrations.

1.12 Metal-exchanged zeolites

Zeolites are inorganic microporous and microcrystalline materials capable of complexing small and medium-sized organic molecules.

Supporting with zeolites is found to be a better candidate as compared to other supporting materials due to advantages such as: to solid structure define channels and cavities of molecular dimension, super adsorption capability and special ion-exchange capability of zeolites **[101]**.

The use of zeolitic materials containing metal active species tetrahedrally coorddinated into zeolitic framework for catalytic abatement of phenol.

1.12.1 Zeolites

Zeolites ZSM-5 and mordenite are pentasil zeolites, consisting of units composed of 5 membered T-rings or O-linked tetrahedra. ZSM-5 has two types of interconnecting channels, a smaller one that is elliptical and linear, and a larger one that is close to circular, but zigzags through the aluminosilicate framework. Mordenite also has two interconnecting channels, although one is too small to accommodate organic molecules. Although zeolites have high surface areas (500-700 m^2/g), most of this area is internal .This is an

unusual property for solid materials and, fortunately, it allows the chemist to perform selective chemistry .
Whether zeolites are hydrophilic or hydrophobic can have a profound influence on their chemical reactivity. Organic molecules rely on H-bonding, electrostatics, and re-cation interactions for effective zeolite absorption and these interactions will clearly be influenced by the number of acidic sites present. As expected, the more Si is present, the more hydrophobic the zeolite and therefore the greater the ability these materials have to interact with hydrophobic organic molecules or to exclude hydrophilic molecules, such as water. Zeolite A and zeolites X/Y have a Si/A1 content at or close to 1 . And are highly hydrophilic absorbants. Pentasil zeolite ZSM-5, which can have very high Si content, has significant hydrophobic character and has poor affinity for water **[102]**. Zeolites have the capacity to accept electrons (via their metal ion centers) and, in the presence of a suitable donor, can generate radical cations. Like persistent carbenium ions, certain species are stable within the zeolite cavity for up to several months and can be monitored spectroscopically. For example, electron transfer occurs with conjugated aromatic systems, using NH_4Y, HY, and Na-ZSM-5 as acceptors **[103]**.

1.12.2 Supported metal zeolites

The removal in this study also will be done using supported noble metal catalyst.Among of the precious metals used for phenol removal was platinum (Pt) **[7]**.The doped catalysts were prepared by using hexachloroplatinic acid (H_2PtCl_6) as metal precursor and impregnation with hexadecyltrimethylammonium bromide (CTAB) as surfactant and added to the hydrogen form of zeolite (H-ZSM or H-Mordenite). These catalyst contained two loading of Pt(0.5wt% and 1 wt%) these catalysts named 0.5%Pt/H-ZSM-5 , 1%Pt/H-ZSM-5, 0.5%Pt/H-Mordenite and 1%Pt/H-Mordenite this was done with the aim of preparing high dispersed nano-Pt particles containing catalysts.

1.13 Bentonite

Is natural clay and an aluminosilicate material. Has a layered structure with the ability to swelling and have cations that can be exchanged. Bentonite have zeolitic properties, high surface area and used as a coagulant in water treatment **[104]**. By comparing the removal with the three aluminosilicates materials it was found that the removal with Zsm-5 is the best and by doping with a metal the removal increased.

1.14 UV/Vis spectroscopy

the ultraviolet (UV) region of the spectrum covers the range from 200 to 400 nm, and the visible region covers the range from 400 to 800 nm. The amount of energy available in this radiation, ranging from 143 kcal/mol (600 kJ/mol) to 36 kcal/mol (150 kJ/mol), is enough to cause an electronic transition in a molecule, that is, to excite an electron from an occupied MO to an antibonding MO.

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve. A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor. The wavelength of the light, in nanometers, is plotted along the x-axis, and the absorption band comes up from this axis, as was the case for NMR spectra. The wavelength range for most UV spectra begins at 200 nm because the O_2 of air and quartz glass absorb light with wavelengths shorter than this. Most absorption bands due to electronic transitions are broad and rather featureless like this one because each electronic energy level has numerous vibrational and rotational sublevels**[105]**. The amount of light absorbed by the sample is plotted along the y-axis as the absorbance (A), which is defined as

$$A = \log(I_0 / I) \qquad \textbf{(2)}$$

where I_0 is the intensity of the light striking the sample and I is the intensity of the light emerging from the sample. Absorbance is directly proportional to the concentration of the sample and the path length through the sample. The equation expressing this proportionality, known as the Lambert-Beer law, is

$$A = \varepsilon c l \qquad \textbf{(3)}$$

Where ε is the molar absorptivity or the molar extinction coefficient, in units of $M^{-1}\ cm^{-1}$, c is the concentration of the compound in moles per liter, and l is the path length in centimeters. For a particular compound, the wavelength at the maximum of the absorption band (λ_{max}) and the extinction coefficient at the maximum (**ε_{max}**) are characteristic constants for that compound and are often listed in reference books along with the melting point, boiling point, and other physical constants of the compound. The solvent in which the sample is dissolved is also reported because **λ_{max}** and **ε_{max}** vary slightly with the solvent **[105]**. From **Figure 4,** Phenol was measured at 270 in the UV spectrophotometer which is the wavelength of absorption maximum of most intensive band (**λ_{max}**). phenol had greater ratio of peaks intensity monitored at this value**[106]**.

1.15 Catalytic activity

The main parameters which determine the efficiency of the oxidation process are: temperature, the initial solution pH, initial phenol concentration, the catalyst concentrations, the wave length and intensity of UV radiations.

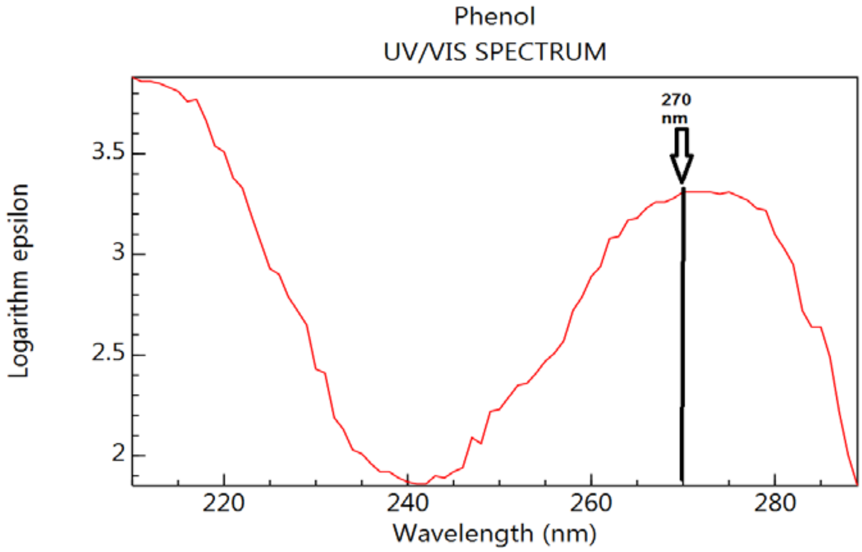


Figure 4. Phenol UV spectrum**[106].**

The effect of temperature was studied by Mohammad S. *et al.***[8]**using RuO_2/ZSM5 and RuO_2/AC for phenol removal in the presence of peroxymonosulphate. It ws seen that temperature showed quite significant impact on phenol oxidation process using either RuO_2/ZSM5 or RuO_2/AC. An increase in temperature of 10 °C would enhance the rate of phenol removal efficiency by about two times. the removal efficiency of phenol decreased with increasing initial phenol concentrations. Using RuO_2/AC, 100% removal of phenol achieved within 20 min at low concentrations (25-50 ppm).in case of 100 ppm the removal efficiency decreased to 83 % in 2 hours. A similar trend can also be seen using RuO_2/ZSM5 with.the effect of catalyst amount was studied and it was seen that high catalyst loading in solution would result in higher phenol removal. The Photocatalytic removal of phenol using Fe-TiO_2 by different illumination Sources studied by Shawabkeh *et al.* **[107]** . By study the effect of temperature on the removal of phenol.As the solution temperature increases the percent degradation of phenol is increased. This increase could be explained by the enhancement of the reaction rate took place between the phenol molecules and the hydroxyl radicals. Moreover, the enhancement of the degradation is probably due to the increasing collision frequency of phenol molecules. The effect pH values was studied by Shawabkeh *et al.* and found that the increase in solution pH will increase the percent of removal. The maximum removal value was 20.86% obtained at pH 10 while this value decreased to 4.2% at pH 2. The decrease in phenol removal with decreasing pH may be attributed to the decrease in hydroxyl ions that are needed to react with valence band hole to form hydroxyl radicals. In contrast, the adsorption of organics from aqueous solutions is increased with decreasing the pH as a result of neutralization of the surface of adsorbent with the excessive hydrogen ions in the solution which gives a controversially contradiction conclusion. However, this is not the case here because the hydrogen ions are consumed by reaction with conduction band electrons to liberate hydrogen gas. The effect of initial phenol concentrations was studied. it was seen that at low concentration (25-75 mg/L) a maximum degradation was achieved to reach a value of 18.5%, while a decrease in this capacity is occurred with further increasing in phenol concentration. This is due to the absorption of major illuminated light by phenol molecules which reduced the photocatalytic activity of the TiO_2 .Therefore, less phenol molecules will be degrades per a unit dose of TiO_2.

1.16 Reaction rout

As for the reaction route, A Santos *et al.* summarized it into six schemes, in which the intermediates are mostly acids, phenolic compounds; there are no alcohols. Andrzej Sobczyˇınski *et al.* based on their many years of research, also provided a reaction route, in which the intermediates include phenolic compounds, alcohols, aldehydes, but they did not detect them by phenol direct degradation. The key to speculate the reaction route is to detect the intermediates. There are at least 20 intermediates on the route from substrate to carbon dioxide during photodegradation of phenol **[108-110]**.

The most widely used method to detect them is extraction by organic solvent, after etherification or acetylation, followed by analysis by gas chromatography or gas chromatography/mass spectrometry (GC-MS)**[110,112],** but these methods have two weaknesses: (1) as the intermediates are mostly polar compounds, they can easily dissolve in water, the non- or low-polar solvents extract them from water hardly; while polar solvents are so easily dissolved in water that it is hard to part them from water. (2) Etherification only fits for derivatizing acids, while acetylation only for hydroxylated compounds. In addition to that, it is possible to detect intermediates by means of HPLC using retention time to analyze them qualitatively. However, this method needs not only many calibration standards but also a lot of time because there are many unknown compounds in the intermediates, and some compounds have the same retention time. Accordingly, this method is not perfect **[113,114]**.

To detect the intermediates produced by phenol is useful for disclosing the photo degradation mechanism; it is also helpful for studying the degradation of its derivatives like chlorophenols, chlorinated pesticides, phenoxy herbicides, etc.

Chapter 2

Materials and Methods

2.1. Materials

Phenol (phenol solution 80%, w/w, in water) was obtained from BDH Chemicals, England. Buffer solutions with pH 3:9 were purchased from Merk to adjust the pH of the solution. Zeolites namely (i)ZSM-5/Bentonite (Na-form) supplied by BDH as extrudates, (ii)Mordenite. All of the zeolites were in Na form. Bentonite, 1M NH_4Cl, Hexachloroplatinic acid (H_2PtCl_6) as metal precursor from Merck. hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$) CTAB as surfactant.

2.2 Apparatuses

The concentration of phenol was measured by UV-VIS spectrophotometer (UV-VIS- NIR- 3101 PC, Shimadzu) at 270 nm. The reaction was done in shaking water bath; the pH of solution was adjusted using a calibrated pH meter. The photocatalytic removal was done using UV-C lamp. Solutions were filtered using centrifuge. X-ray fluorescence was done with (PANanlytical, Epsilon 1) High-stability ceramic side window, 50 µm thin window (Be) for higher intensities and Max voltage of 50 kV, ideal for analyzing heavier elements Headquartered in Egham, Surrey, England. Scanning electron microscopy (SEM) was carried out using Jeol JSM 5300 Japan. The High Resolution Transmission electron microscopy (HRTEM) was carried out with a JEOL electron microscope (JEM-2100), operated at 200 kV, Japan. The X-Ray Diffraction Analysis (XRD) was carried out by (PANanlytical, X'PRT PRO) Using Cu-target with Ni-filtered radiation (λ = 1.542 A°), The diffraction angle

(2Θ) was ranged between 2° and °60. The chemisororption measurements were carried out using Micrometritics TPD/TPR 2900 analyser. The total amount of acidity were carried out using SETARAM Labsys TG-DSC16 equipment. UV-C(100-280 nm) , 25watt, 45cm, JAPAN . all apparatuses mentioned found in the Egyptian Petroleum Research Institute (EPRI).

2.3 Preparation of the Catalysts

The raw materials of zeolites were ZSM-5/Bentonite (Na-form) supplied by BDH as extrudates. NaM was bound with sodium montmorillonite (87.5/ 12.5 wt/wt) by preparing a homogeneous aqueous suspension of both materials, under continuous agitation, and heating for 2 hours. Next, the suspension was dried at 120ºC overnight. After grinding and sieving, particles with 0.75 mm average particle size were obtained. Finally, the bound material was air-calcined at 550ºC for 15 hours **[115]** .

2.3.1. Preparation of hydrogen-zeolite

Hydrogen-form of zeolite is prepared from the Na-form by exchanging Na+ ions with 1 M NH_4Cl. 10 g of zeolite was refluxed with 300 ml of 1 M NH_4Cl under agitation at 80 °C for 12 hours. The solid was filtered, washed with deionized water several times, and dried at 120˚C overnight. The ammonium form obtained was calcined at 500˚C for 3hours in the presence of current of air (40 ml/ minute). High calcination temperatures helped to create the H-form (hydrogen form) of zeolites by decomposing the NH_4-form and removed the organic impurities. Thus, calcinations at the above stated temperatures were enough to convert all the zeolites into H-form **[85]** .

2.3.2 Preparation of Pt/H-ZSM-5

Pt-containing catalysts were prepared by using hexachloroplatinic acid (H_2PtCl_6) as metal precursor and impregnation with hexadecyltrimethylammonium bromide CTAB ($C_{19}H_{42}BrN$) as surfactants **[116]**. The catalysts contained two loadings of Pt (0.5 wt% and 1wt %).This was done with the aim of preparing high dispersed nano-Pt particles containing catalysts. These nano catalysts prepared using CTAB as follow;

The molar ratio of CTAB/H_2PtCl_6 is 2 according to the stiochometric equation:

$$H_2PtCl_6 \rightarrow 2H^+ + (\mathrm{PtCl})^{-2} \qquad \textbf{(3)}$$

$$2\,C_{19}H_{42}BrN \rightarrow 2\,C_{19}H_{42}N^{+1} + 2\,Br^{-1} \qquad \textbf{(4)}$$

The required volume of the platinum complex solution that needed to reach the aimed final platinum content (0.5 and 1.0 wt % Pt) was added drop-wise to a suspended solution of 2 g of zeolite in 10 ml of deionized water under stirring. The mixture was stirred for 1 hours at room temperature. Drying, calcination and reduction processes were carried as mentioned before.

2.4 Catalyst characterization

Catalysts used named H-ZSM-5, H-Mordenite, Bentonite, 0.5%Pt/H-ZSM-5, 1%Pt/H-ZSM-5 and 1%Pt/ H-Mordenite .

Chemical analysis was carried out to evaluate total silica, alumina and alkali metals by X-ray fluorescence and the ignition loss (I.L.) was obtained by heating to 1000 °C till constant weight.

Scanning electron microscopy (SEM) is a technique used to investigate the morphology of the crystals. after coating with thin film of gold to be conductive. All samples were mounted on stubs and gold-coated prior to analysis, to make them electrically conductive. The magnification was about 2500X. The morphology, location and size distribution of Pt particles have been investigated by High Resolution Transmission electron microscopy HRTEM. The sample for this analysis were first prepared in a suspension with 30% of ethanol, and the mixture then ultrasonicated for 5 min until the suspension was homogeneous. Afterwards, one drop of this mixture was placed over a copper grid previously covered with collodion and coal for use in the HRTEM.

The structural parameters were determined by X-Ray Diffraction Analysis (XRD). Using Cu-target with Ni-filtered radiation (l = 1.542 A°). The diffraction angle (2q) was ranged between 2^o and 60^o.

The specific surface area (BET) for the parent and prepared impregnated samples were determined from N_2 adsorption-desorption isotherms measured at liquid nitrogen temperature (-196^{o}C). All samples were degassed at 350^{o}C for 2h in nitrogen atmosphere prior to adsorption.

the acidic character of Pt-containing catalysts as well as H-ZSM-5 and H-mordenite were characterized using pyridine adsorption technique. Acidic sites were investigated by pyridine adsorption and the desorption of pyridine is monitored by TGA. First, Platinum crucible containing 50 mg of the sample was placed in a shallow porcelain plate and inserted into a glass reactor adapted to a tubular furnace. The sample was dehydrated in dried N_2 (100 ml min^{-1}) at 120^{o}C for 2hours, cooled to 70^{o}C, and then gaseous pyridine diluted in N_2 was allowed to pass through the sample for 1.5hours. The temperature was held at 70^{o}C under N_2 for one hour to remove the physically adsorbed pyridine. After that, the sample was analyzed by TG.

The chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow of 50 ml min-1 and pulses of H_2 (99.9995% purity). In order to calculate the metal dispersion, an adsorption stoichiometry of metal/H = 1 was assumed. Dispersion measurements with H_2 pulses were carried out at 60 ^{o}C to avoid the spill over phenomenon. Previously, the sample was pre-treated by heating at 15 ^{o}C min^{-1} in argon flow up to 250 ^{o}C and kept constant at this temperature for 20 min. Then, the sample was reduced in situ. Next, the hydrogen was removed by flowing nitrogen for 30 min, the temperature being 10 ^{o}C higher than the reduction temperature. Finally, the sample was cooled to the experiment temperature in an argon gas flow. The dispersion measurements with H_2 pulses had an error of ±5% **[117]**.

2.5 Phenol analysis

Phenol was used as a model for phenolic compounds. A stock solution of phenol (1000 ppm) was prepared by dissolving 1 gm of phenol in 1000 ml of deionized water and stored in dark brown tightly closed bottle. Preparation of working solution (100 ppm). Preparation of standard calibration curve for phenol measurements up to 100 ppm (1, 5, 10, 25, 50 and100) was done using serial dilution method. Adjust the UV spectrophotometer at 270 nm **[118]**. Measuring the different phenol concentrations absorbance from low to high. **Figure 5.** show the calibration curve in which the measured absorbance versus its concentration. From this curve we can measure the concentration of any absorbance of phenol. and the removal efficiency of phenol was estimated by applying the following equation:

$$\text{Removal \%} = ((A^\circ - A)) / (A^\circ) \times 100 \qquad (5)$$

Where A^o and A are blank (before reaction) and sample absorbance, respectively. Based on the Beer–Lambert's law A^o and A are proportional to C^o and C which C^o and C are the concentration of blank and sample at (t) time **[118]**.

2.6 Catalytic activity of the catalysts

The experiment of removal of phenol from aqueous solutions was done by suspending an optimized amount (1gm) of (H-Mordenite, Bentonite, H-ZSM-5, 0.5%Pt/ZSM-5 1%Pt/H-ZSM-5 or 1%Pt/H-Mordenite) in different reactors to 100 ml of solution containing 100 ppm of phenol .and placed in shaking water bath at 25 ºC and 150 rpm, the reaction was run for 6 hours. Prior to analysis, 5 mL of the suspension was withdrawn from the reactor and centrifuged for 10 min and the absorbance was measured in 270 nm by using a calibrated UV spectrophotometer **[118]**. The removal efficiency of phenol was estimated by applying equation **(5)**.then the time at which the best removal occurs was known (time profile).

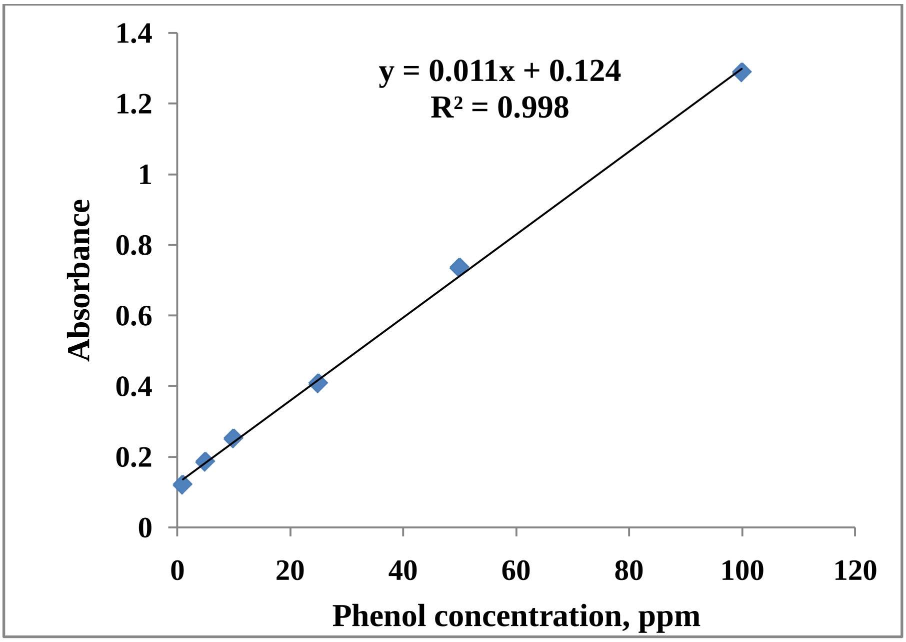


Figure 5. calibration curve for phenol

2.7 Effects of removal parameters

The effect of various removal parameters was studied as follow:

- Temperature effect was studied by suspending 0.1gm of catalyst either H-ZSM5, H-mordenite, bentonite, 0.5%Pt/H-ZSM5, 1%Pt/H-ZSM5 or 1%Pt/H-Mordenite was added to 100 of solution containing 100 ppm of phenol. Placed in shaking water bath adjusted at 30 ºC, 150 rpm and applying the optimum time for each catalyst (time profile). 5 ml of the suspension was withdrawn, centrifuged and measured for its phenol content in the UV spectrophotometer at 270 nm and applying equation **(5)** to obtain the removal percent. This procedure was done at 40 ºC and 50 ºC to investigate the optimum temperature at which the best removal occurs was estimated for each catalyst.

- The effect of pH was done by suspending 0.1 gm of catalyst to 100 of solution containing 100 ppm of phenol , the initial pH was measured and adjusted at pH = 3 using drops of buffer solution. Placed in the shaking water bath at 25 ºC and 150 rpm. This experiment was done at pH 5,7 and 9 using buffer solution. Applying the time profile for each catalyst. 5 ml of the suspension was withdrawn, centrifuged and measured for its phenol content in the uv spectrophotometer at 270 nm and applying equation **(5)** to obtain the removal percent. The optimum pH at which the best removal occurs was investigated.
- The optimum conditions of time, temperature and pH was applied to solutions containing different initial phenol concentrations (25, 50, 100, 150 and 200 ppm) .this was done by adding 0.1 gm of catalyst to 100 ml of solutions containing different initial phenol concentrations, adjusting the optimum pH for each catalyst and placed in shaking water bath adjusted at the optimum temperature for each catalyst. 5 ml of the suspension was withdrawn, centrifuged and measured for its phenol content in the UV

spectrophotometer at 270 nm and applying equation **(5)** to obtain the removal percent.

- The effect of increasing the amount of catalyst (catalyst dose) was done by varying the amount of catalyst (0.2, 0.3, 0.4 and 0.5). These different amounts of catalyst were added to 100 ml of solution containing 100 ppm of phenol. The optimum conditions (time, temperature and pH) for each catalyst were applied, placed in shaking water bath. 5 ml of the suspension was withdrawn, centrifuged and measured for its phenol content in the UV spectrophotometer adjusted at 270 nm and applying equation **(5)** to obtain the removal percent. The optimum dose of catalyst was investigated.

- The effect of irradiating with UV-C(100-280nm) was done by suspending the optimum catalyst dose to 100 ml of solution containing 100 ppm of phenol , the optimum conditions were applied (time profile, temperature and pH) for each catalyst. Photocatalytic experiments were carried out in a quartz reactor (made from glass in which quartz content is no less than 95%, penetration is 69%). a UV-C (100-280 nm) was positioned above the shaking water bath **.**The photocatalytic removal of phenol was done by using A UV source of 25 W mercury vapor lamp UV-C . This lamp emits ultraviolet light with two peaks in the UV-C band at 253.7 and 185 nm due to mercury (Hg) within the lamp. Eighty five to 90% of the UV produced by these lamps is at 253.7 nm, where only five to ten percent is at 185 nm. Photocatalytic experiments were carried out in a cylindrical photoreactor with a lid, it was made from glass in which quartz content is no less than 95%, penetration is 69%. The fused quartz glass tube passes the 253.7 nm radiation but blocks the 185 nm wavelength. Such tubes have two or three times the UV-C power of a regular fluorescent lamp tube **Fig.(6)**. These low-pressure lamps have a typical efficiency of approximately thirty to forty percent, meaning that for every 100 watts of electricity consumed by the lamp, they will produce approximately 30-40 watts of total UV output. These "germicidal" lamps are used extensively for disinfection of surfaces in laboratories and food processing industries, and for disinfecting water supplies.

Figure 6. UV-C lamp

Chapter 3

Results and Discussions

RESULTS and DISCUSSIONS

3.1 Analysis and characterization of the prepared catalysts

The chemical, morphological and structural characterizations of the prepared catalysts have been studied by various techniques.

3.1.1 Chemical analysis

Chemical analysis was carried out to evaluate total silica, alumina and alkali metals by x-ray fluorescence and the ignition loss was obtained by heating to 1000^{o}C till constant weight. The results of chemical analysis of zeolites (ZSM5 – Mordenite) and Bentonite are presented in **Table 4.** It is clear that the silica/alumina ratio (SiO_2/Al_2O_3 = ~ 6.37) for Mordenite in conformity with the published value **[119]**.The high siliceous ZSM5 of SiO_2/Al_2O_3 = 75.26 possesses the MFI structure which is in consistent with the finding of **[120].** Some of the elements; e.g., Ti, Si, V, Mo and etc. in the zeolite are detected and determined quantitatively. The low content of Na_2O in the H-forms of the both zeolites indicates the high exchangeability of Na-Mordenite and Na-ZSM5 with ammonium chloride solution. The ignition loss revealed low values of ZSM5 zeolite (Na and H-forms).This is due to the presence of high silica content at the expense of low alumina content. It is known that Na cations are linked with Al atoms in the framework of the zeolites**.** Also in this Table the chemical composition of Bentonite **[121].**

3.1.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a technique used to investigate the morphology of the crystals. The results of scanning electron microscopy for the samples are represented in **Figure 7**.The SEM micrographs reveal the shapes and sizes of all the samples.

The SEM micrographs reveal the shapes and sizes of all the samples. Cubic units can be seen in the ZSM5 zeolite (H-ZSM5, 0.5Pt/H-ZSM5$_{CTAB}$, 1Pt/H-ZSM5$_{CTAB}$), while spherical aggregates in the H-Mordenite. The H-ZSM5 and H-Mordenite appears as corn flake-like crystals with a fluffy appearance revealing its extremely fine plate-like structure **[122]**.A comparison of these pictures indicates no visible change in the crystal form and mean diameter. However, the morphology for different samples exhibits a unique crinkly, ridged, less condensed texture that partly accounts for the reduced basal spacing of montmorillonite. Pt crystallites are noticeable in the loaded zeolite sample Pt/H-ZSM -5$_{CTAB}$, and Pt/H-Mordenite $_{CTAB}$.

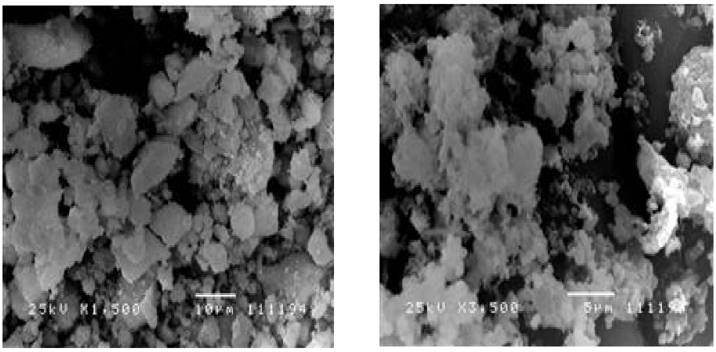
3.1.3. High Resolution Transmission electron microscopy (HRTEM)

The morphology, location and size distribution of Pt particles have been investigated by HRTEM. The HRTEM micrographs of different Pt-zeolite catalysts are shown in **Figure 8**.

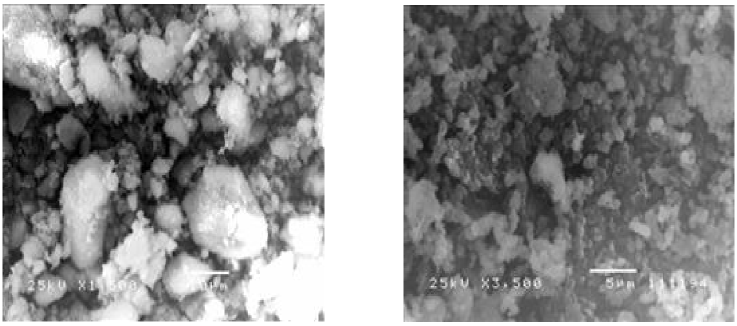
Table 4.Chemical Analysis of zeolites and Bentonite

Components, Wt%	***Na-Mord.***	***H-Mord.***	***Na-ZSM5***	***H-ZSM5***	***Bentonite***
SiO_2	66.760	76.934	91.615	92.044	58.78
Al_2O_3	10.480	12.829	1.233	1.223	19.24
Na_2O	7.670	0.511	0.349	0.140	2.73
CaO	0.351	---	0.069	0.083	4.21
Fe_2O_3	0.169	0.499	0.139	0.179	3.58
MgO	0.119	0.234	---	---	2.13
ZrO_2	0.150	---	---	---	---
Cl^-	0.099	0.139	---	---	---
K_2O	0.082	0.087	---	---	1.35
Cr_2O_3	0.022	---	---	---	---
PbO	0.098	---	---	---	---
P_2O_5	---	0.025	0.033	0.026	---
SO_3	---	0.042	---	---	---
CuO	---	---	---	---	---
ZnO	---	---	0.012	0.017	---
SrO	---	---	---	---	---
TiO_2	---	---	0.047	0.082	0.37
SiO2/Al2O3 molar ratio	6.37	5.99	74.30	75.26	3.05
I.L	14.000	8.700	6.503	6.206	7.48

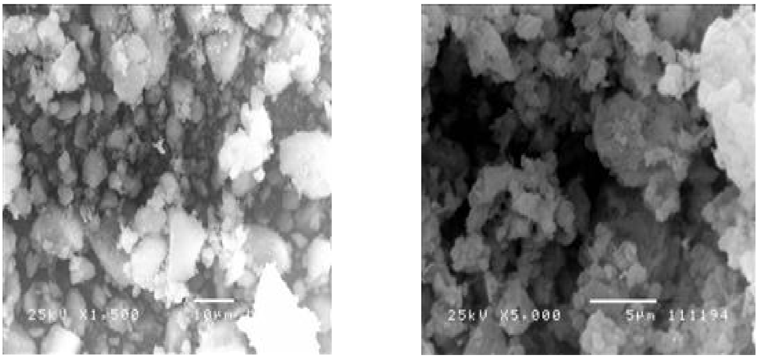
Ignition loss (I.L), as determined by burning one gram sample at 1000°C till constant weight.



H-ZSM5 H- Mordenite



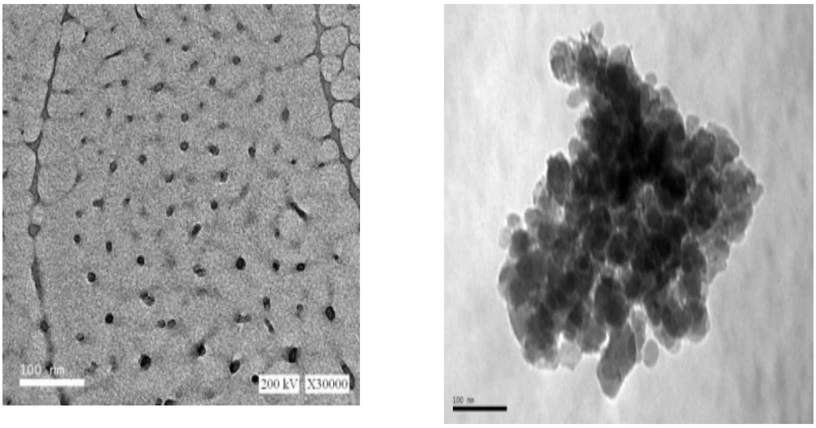
0.5Pt/H-ZSM5$_{CTAB}$ 0.5Pt/H-Mordenite$_{CTAB}$



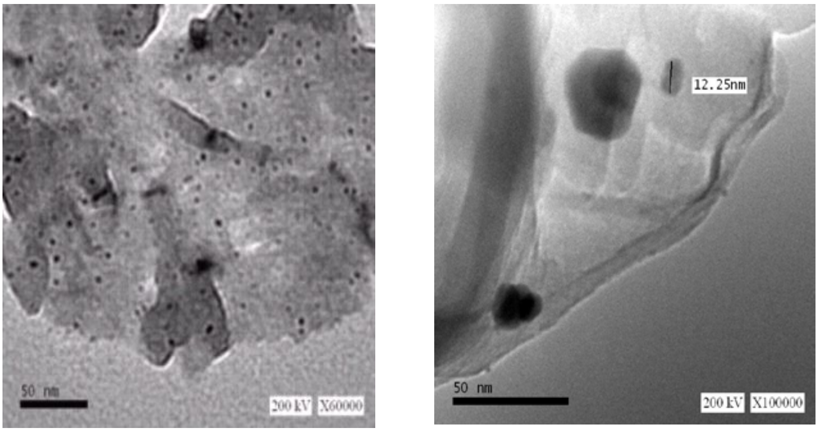
1Pt/H-ZSM5$_{CTAB}$ 1Pt/H-Mordenite$_{CTAB}$

Figure 7. SEM photos of the H-ZSM5, H-Mordenite and the loadings of H-ZSM5 and H-Mordenite

According to different contrast in the HRTEM micrographs we observed coffin-shaped zeolite crystallites, laminated structure of montmorillonite and Pt particles.



0.5Pt/H-ZSM5$_{CTAB}$ 1Pt/H-ZSM5$_{CTAB}$



1Pt/H-Mordenite$_{CTAB}$ 0.5Pt/H-Mordenite$_{CTAB}$

Fig. 8. Bright field HRTEM image of platinum nano particles formed on the surface of ZSM5

The Pt particles were located both on the montmorillonite and the zeolite crystallite surfaces. The images are composed of black points corresponding to the metal particles, which are over lighter and bigger zeolite particles, where, depending on the contrast, crystallographic planes become evident. HRTEM pictures of the platinum catalysts with a content of 1 wt. % confirmed the higher metallic dispersion of the platinum catalysts.

Micrograph of sample 0.5Pt/H-ZSM5$_{CTAB}$ indicates that Pt is well-dispersed on the surface of zeolite particles with the size of 1.3-2.6 nm.

3.1.4. X-ray diffraction analysis (XRD)

H-ZSM5 as well as H-Mordenite were analyzed by XRD. Also The parent zeolites as well as the Pt-containing catalysts were analyzed by XRD. The diffraction patterns are shown in **Figure 9.**The diffractograms exhibited the diffraction lines of MFI structure characteristics of ZSM5 as compared with the JCPDS, 055-0067 card. The patterns of Pt-containing catalysts are almost similar to those of H-ZSM5. This is due to good dispersion of Pt on the surface of the both supports.

3.1.5. Nitrogen Adsorption Measurements

The textural properties for the parent and prepared impregnated samples were determined from Nitrogen adsorption-desorption isotherms measured at liquid nitrogen temperature (-196^{o}C). The specific surface area was

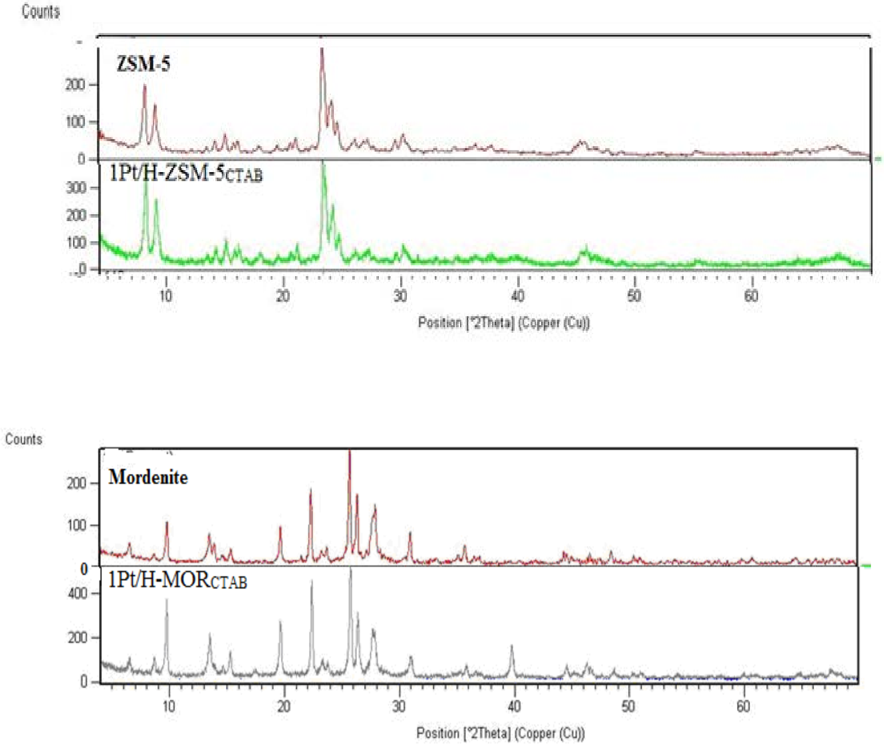


Figure 9. X-ray diffraction analysis pattern of used H-Mordenite and H- ZSM5 and their loadings

evaluated by the BET equation in its normal range of applicability **[123]** **.** The values of specific BET surface area, together with the total pore volumes and average pores radius after application of BET equation are summarized in **Table 5.** For Pt/ZSM-5 catalysts, the values of surface area (S_{BET}) and pore volume are very close to those of parent H/ZSM-5. This could be attributed to the low concentrations of Pt loadings. With respect Pt/ZSM-5 prepared using CTAB, surface area and pore volume decrease as compared with H-ZSM-5. This may be explained in terms of dispersion of Pt species on the surface and partial pore filling by Pt particles. The values of S_{BET} and Vm decrease by increasing Pt loading from 0.5% to 1.0% **[124]**. For mordenite catalysts, Pt loadings have insignificant effect on the surface textural characteristics. This could be related to distribution of the Pt particles on the surface of mordenite which has high surface area (321 m^2/g).

3.1.6. Total Acidity measurements

Acidity is one of the most important characteristics of zeolites which make them very useful in acid catalysis. The catalytic properties, such as activity and selectivity, depend not only on the number of the acid sites but also on the acid strength of the intervening sites. In the present work, we characterized the acidic character Pt-containing catalysts as well as H-ZSM5 and H-Mordenite using pyridine adsorption technique. Both Brønsted and Lewis acid sites are occur in zeolites. Brønsted acid sites are almost generated by the procedure represented by **Equation (6)**, where aqueous ion exchange tack place with an ammonium salt followed by thermal decomposition of the ammonium ions inside the zeolite.

$$\mathbf{NH_4^+ + Na^+ Z^- \rightarrow Na^+ + NH_4^+ Z^- \rightarrow^{300–400oC} NH3\uparrow + H^+ Z^-} \qquad \mathbf{(6)}$$

Where, Z: negatively charged framework

The chemical nature of the Brønsted acid sites in zeolite materials are viz. bridging hydroxyl groups formed by the proton and a framework oxygen in an AlO_4 tetrahedron **[125].**

Table 5. Textural properties for catalysts*.

Sample	S_{BET}, m^2/g	V_m, cc/g	r, Å
H-ZSM5	**274.875**	**0.079**	**22.264**
H-Mordenite	**321.830**	**0.092**	**11.963**
0.5Pt/H-ZSM5 $_{CTAB}$	**266.996**	**0.077**	**25.506**
0.5Pt/H-MOR$_{CTAB}$	**334.549**	**0.096**	**11.359**
1Pt/H-ZSM5$_{CTAB}$	**238.386**	**0.068**	**26.335**
1Pt/H- MOR$_{CTAB}$	**353.084**	**0.093**	**12.644**

*** S_{BET}**, surface area V_m, the monolayer capacity is the volume of gas required to cover the whole surface of the solid with a unimolecular layer in cm^3/g.

Upon severe heat treatment (>500°C), the Brønsted acid sites are degraded (‘dehydroxylation’), water is split off with the concomitant formation of Lewis acid sites. Their precise chemical nature is less clear. For some time, they were looked upon as tricoordinated aluminum and/or tricoordinated, positively charged silicon in the framework. however, was able to demonstrate that silicon in dehydroxylated zeolites remains tetracoordinated and much of the aluminum is converted to octahedral rather than trigonal coordination. This led **Ku¨hl [126]** to conclude that $[(AlO)^{+}\ ]^{n+}{}_{n}$ units removed from the zeolite framework act as true Lewis sites.

Lago and co-worker **[127]** showed that the catalytic activity stems from the Brønsted rather than the Lewis acid sites. It is doubtful whether the Lewis sites play a role at all in acid-catalyzed reactions. It has been claimed that, under certain circumstances, Lewis acid sites might enhance the strength of nearby Brønsted sites, thereby exerting an indirect pro-influence on the catalytic activity.

The acidity in a zeolite is obviously related to the framework aluminum content **[125]**, this due to the higher electro-negativity of silicon compared to aluminum, the strongest Brønsted acid sites in zeolites will occur on completely isolated AlO_4^- tetrahedral.

Pt dispersion decreases the total acidity of the parent zeolites **[128]**. As shown in **Table 6.** By increasing Pt loading, the amount of acidity decreases. Moreover, the catalyst prepared using CTAB show the best acidic character 666.23 for 0.5Pt/H-ZSM5$_{CTAB}$ and 800.24 for 1Pt/H-MOR$_{CTAB}$.

Table 6 . Total acidity of Pt loaded H-ZSM5 catalysts and Pt loaded H-Mordenite catalysts

Catalyst	**Total acidity, µmole/g**
H-ZSM5	**967.65**
0.5%Pt/H-ZSM5$_{CTAB}$	**666.23**
1%Pt/H-ZSM5$_{CTAB}$	**587.85**
H-Mordenite	**1508.19**
0.5%Pt/H-MOR$_{CTAB}$	**912.75**
1%Pt/H-MOR $_{CTAB}$	**800.24**

3.1.7. Pulse Titration Measurements

The dispersion of metal particles over the support is an important parameter to be controlled since it determines the quantity of metal particles available on the support surface to participate in a reaction. In this context, an H_2-pulse chemisorption technique is used to study the effect of different surfactant (viz., CTAB) on the Pt dispersion on H-ZSM5. Results are presented in **Table 7**. We can show that, the Pt dispersion values of Pt/H-ZSM5 have a range from 20.11% up to 89.13%, which decreases with an increase in Pt concentration. The using of CTAB in preparation of Pt/H-ZSM5 gives the best dispersion values.

Generally, high dispersion values have been observed for the catalysts based on the two supports.

Table 7. Pt dispersion values for H-ZSM5 catalysts

Catalyst	**Dispersion %**
0.5%Pt/H-ZSM5$_{\mathbf{CTAB}}$	**89.13**
0.5%Pt/H-MOR$_{\mathbf{CTAB}}$	**98.00**
1%Pt/H-ZSM5$_{\mathbf{CTAB}}$	**20.11**
1%Pt/H-MOR$_{\mathbf{CTAB}}$	**31.95**

3.2. Preliminary study of phenol removal

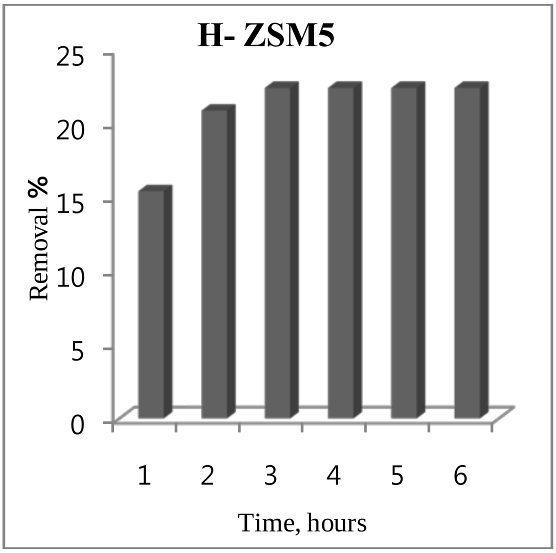
Prior to analysis, aliquots of treated samples were regularly (every hour) withdrawn from the reactor and centrifuged for 10 min. The supernatant was then immediately analyzed for its phenol content. The absorbance was measured in 270 nm by using calibrated UV spectrophotometer and by applying equation **(3)**.0.5Pt/H-Mordenite will be neglected, because no phenol removal occurs.

Effect of time on phenol removal efficiency using H-ZSM5 was shown on **Table 8** and **Figure 10**. These data show that increasing the time increases linearly the removal percent from 15.37% within 1 hours to 22.38% within 3 hours.

Table 8. Time profile using H-ZSM5

Time, Hours	Removal %
1	15.37
2	20.84
3	22.38
4	22.38
5	22.38
6	22.38

Figure 10. Time profile using H-ZSM5



Phenol removal efficiency using H-Mordenite was shown on **Table 9** and **Figure 11.** These data show that increasing the time increases linearly the removal efficiency of 35.88% was observed in 1 hour. this percentage increased to 43.66% within 3 hours.

Removal efficiency using Bentonite was shown on **Table 10** and **Figure 12**. These data show that increasing the time increases the removal percent from 14.85% within 1 hour to 16.39 within 2 hours, and then no more removal occurs after this time run.

Effect of time on phenol removal efficiency using 0.5%Pt/H-ZSM5 was shown on **Table 11** and **Figure 13.** These data show that increasing the time increases the removal percent from 89.11% within 1 hour to 90.77 within 2 hours . no more removal occurs after 2 hours run.

Table 9. Time profile using H-Mordenite

Time, hours	Removal %
1	35.88
2	38.7
3	43.66
4	43.66
5	43.66
6	43.66

Figure 11. Time profile using H-Mordenite

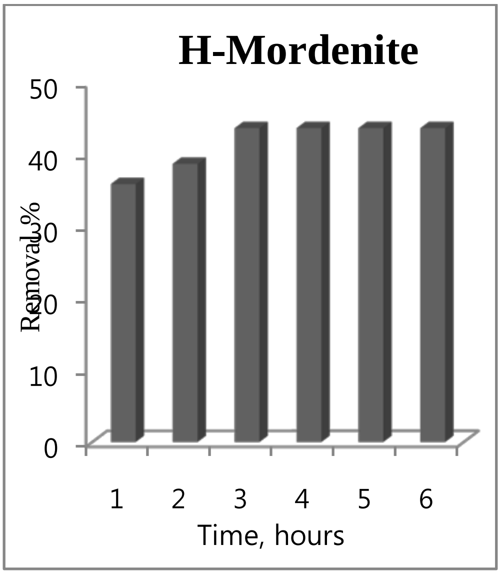


Table10. Time profile using Bentonite

Time, hours	Removal %
1	14.85
2	16.39
3	16.39
4	16.39
5	16.39
6	16.39

Figure 12. Time profile using Bentonite

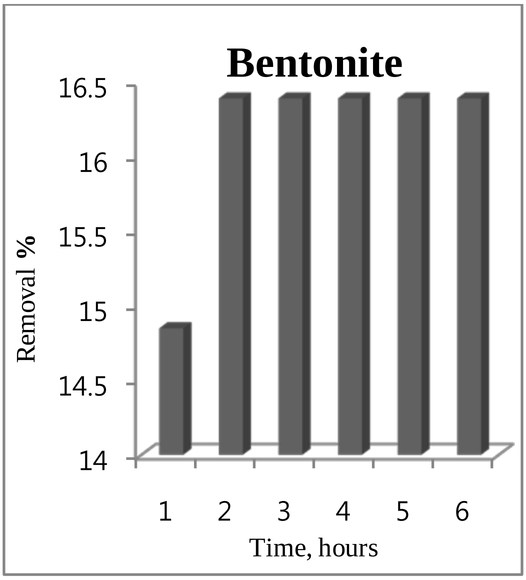
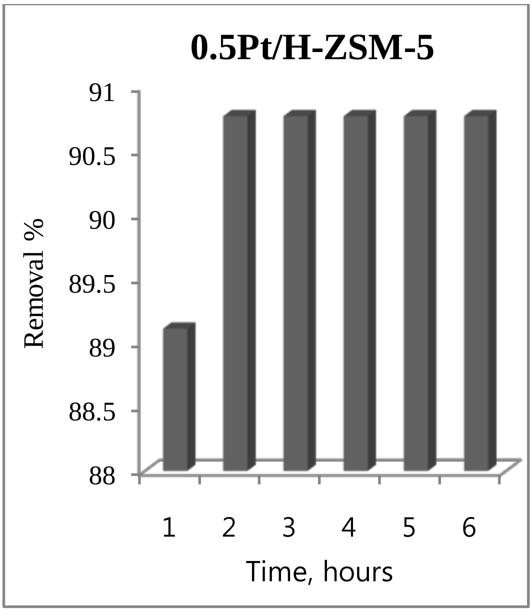


Table 11. Time profile using 0.5Pt/H-ZSM5

Time hours	Removal %
1	89.11
2	90.77
3	90.77
4	90.77
5	90.77
6	90.77

Figure 13. Time profile using 0.5Pt/H-ZSM5



Effect of time on phenol removal efficiency using 1%Pt/H-ZSM5 was shown on **Table 12** and **Figure 14**. These data show that increasing the time increases the removal percent from 86.22% within 1 hour to 92.29 within 5 hours. No more removal occurs after 5 hours run.

Effect of time on phenol removal efficiency using 1%Pt/H-Mordenite was shown on **Table 13** and **Figure 15**. These data show that increasing the time increases the removal percent from 20.22% within 1 hour to 39.4% within 3 hours. No more removal occurs after 3 hours run.

Figure 16 shows a comparison between the time profiles for phenol removal using H-ZSM5, H-Mordenite and Bentonite. As can be seen that the percent of removal was 22.4% after 3 hours for H-ZSM5, 43.6% after 3 hour for H-Mordenite,16% after 2 hours for Bentonite.

Table 12. Time profile using 1Pt/H-ZSM5

Time, hours	Removal %
1	86.22
2	87.08
3	87.85
4	89.64
5	92.29
6	92.29

Figure 14. Time profile using 1Pt/H-ZSM5

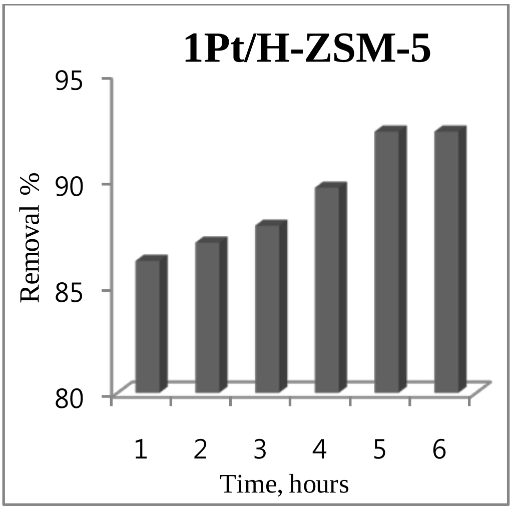


Table 13. Time profile using 1Pt/H-Mordenite

Time, hours	Removal %
1	20.22
2	29.6
3	39.4
4	39.4
5	39.4
6	39.4

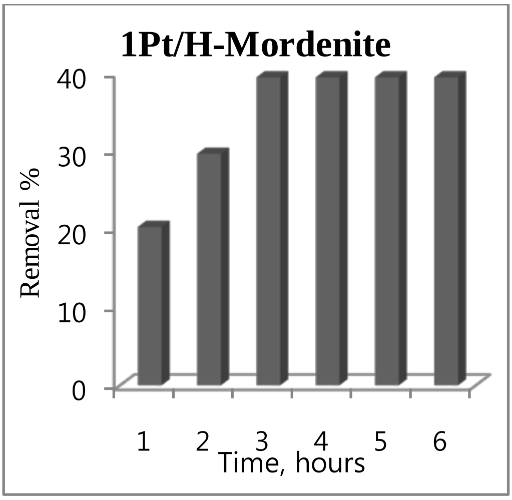


Figure 15. Time profile using 1Pt/H-Mordenite

Figure 17 shows that in case of using 0.5Pt/H-ZSM5, the removal was 90.8% after 2 hours and 92.3% after 5 hours for 1 Pt/ H-ZSM5 compared with the parent H-ZSM5.

Figure 18 shows the phenol removal efficiency using H-Mordenite compared with 1Pt/H-Mordenite. H-Mordenite removes 43.6% within 3 hours. While 1Pt/H-Mordenite removes 43.9% within 3 hours. Hence, no significant increase in the removal was observed in case of loading by Pt, because that the surface area for 1Pt/H-Mordenite is close to the surface area of the parent H-Mordenite. The two samples can remove phenol despite of low efficiency. The poorest removal for H-Mordenite is possibly due to its hydrophilic nature and lower SiO_2/Al_2O_3. The ring dimension is small (0.26 × 0.57 nm), this is also a reason for low removal since phenol molecular size is higher (0.6 nm) **[85]**.

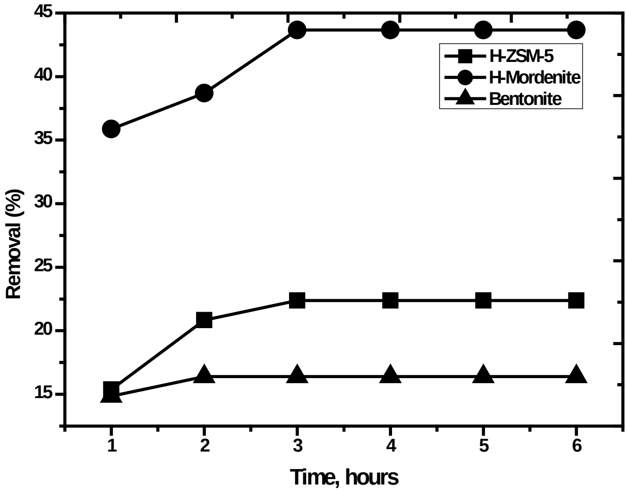


Figure 16. Time profile for H-ZSM-5, H-Mordenite and Bentonite

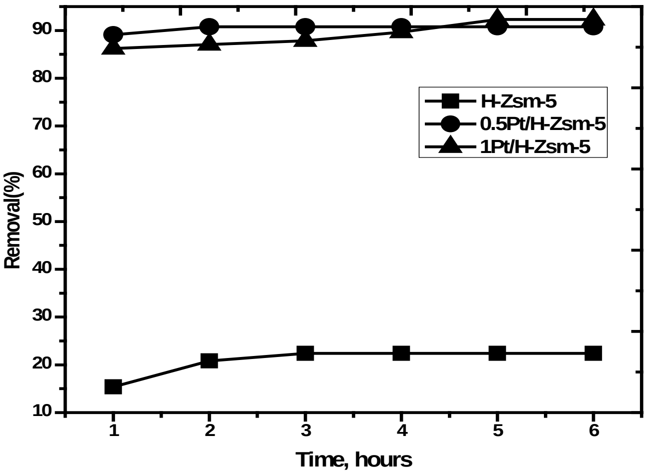


Figure 17. Time profile for H-ZSM-5, 0.5Pt/H-ZSM-5 and 1Pt/ H-ZSM-5

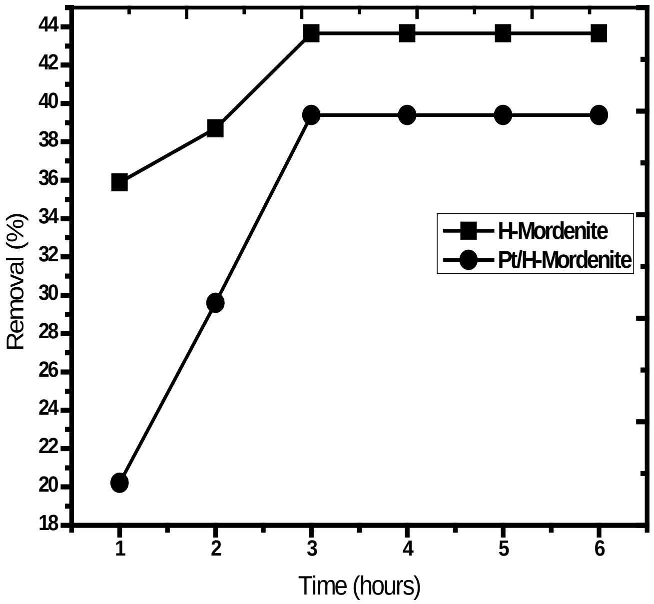


Figure 18. Time profile for H-Mordenite and 1Pt/ H-Mordenite

3.3. Effects of reaction parameters on phenol removal

In this study the reaction parameters are temperature, initial pH, initial phenol concentration, catalyst dose and UV irradiation.

3.3.1. Effect of temperature

As can be seen, temperature showed significant impact on phenol oxidation process at different temperatures 30ºC, 40ºC and 50ºC. An increase in temperature increases the removal efficiency .This increase could be explained by the enhancement of the reaction rate took place between the hydroxyl radicals $OH^{\cdot}$ and phenol molecules. Moreover, the increase in removal may be due to the increasing collision frequency of phenol molecules **[129]**.

Effect of varying temperature on phenol removal efficiency using H-ZSM5 was shown on **Table 14** and **Figure 19**. These data show that increasing the temperature increases linearly the removal percent from 23% at 30 ºC to 25% at 50 ºC.

Effect of varying temperature on phenol removal efficiency using H-Mordenite was shown on **Table 15** and **Figure 20**. These data show that increasing the temperature has quite significant increase. The removal percent increases from 23% at 30 °C to 25% at 50 °C.

Table 14 . Effect of temperature using H-ZSM5

Temp. ºC	Removal %
30	23.4
40	23.66
50	24.51

Figure 19. Effect of temperature using H-ZSM5

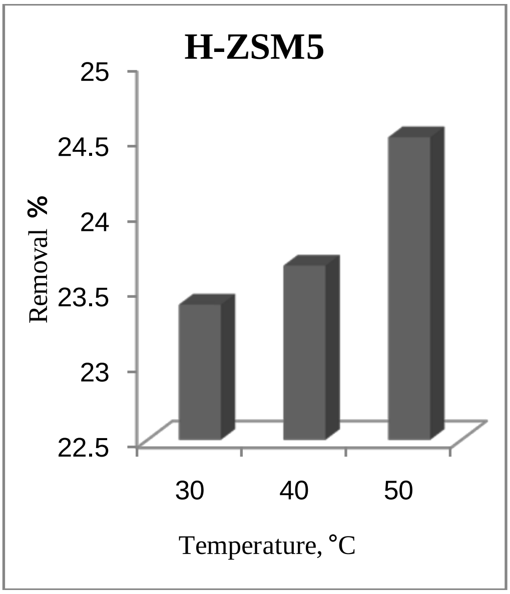


Table 15 . Effect of temperature using H-Mordenite

Temp. ºC	Removal %
30	11
40	11.2
50	11.3

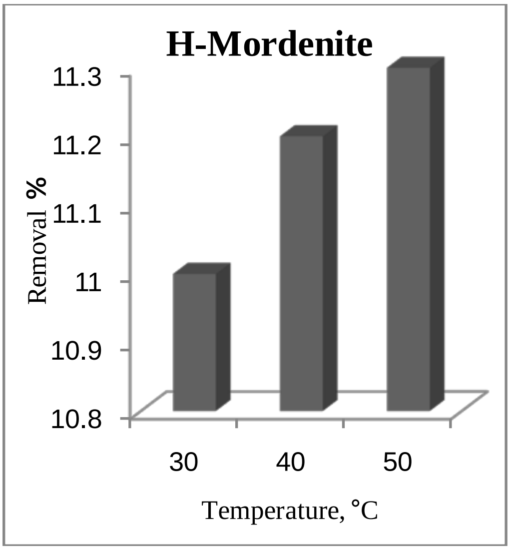


Figure 20 . Effect of temperature using H-Mordenite

Effect of varying temperature on phenol removal efficiency using Bentonite was shown on **Table 16** and **Figure 21**. These data show that increasing the temperature increases linearly the removal percent from 2.8% at 30º C to 11.18% at 50 ºC .

Effect of varying temperature on phenol removal efficiency using0.5%Pt/ H-ZSM5 was shown on **Table 17** and **Figure 22**.These data show that increasing the temperature increases linearly the removal percent from 28.44% at 30 ºC to 29.56% at 50º C.

Effect of varying temperature on phenol removal efficiency using 1Pt/H-ZSM5 was shown on **Table 18** and **Figure 23.** These data show that increasing the temperature increases linearly the removal percent from 21.01% at 30 ºC to 26.91% at 50 ºC .

Table 16 . Effect of temperature using Bentonite

Temp. °C	Removal %
30	2.8
40	9.7
50	11.18

Figure 21. Effect of temperature using Bentonite

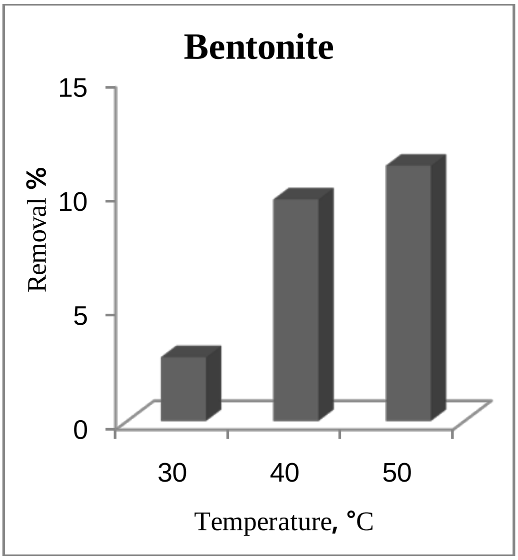


Table 17 . Effect of temperature using 0.5Pt/H-ZSM5

Temp. °C	Removal %
30	28.44
40	29.21
50	29.56

Figure 22 . Effect of temperature using 0.5Pt/H-ZSM5

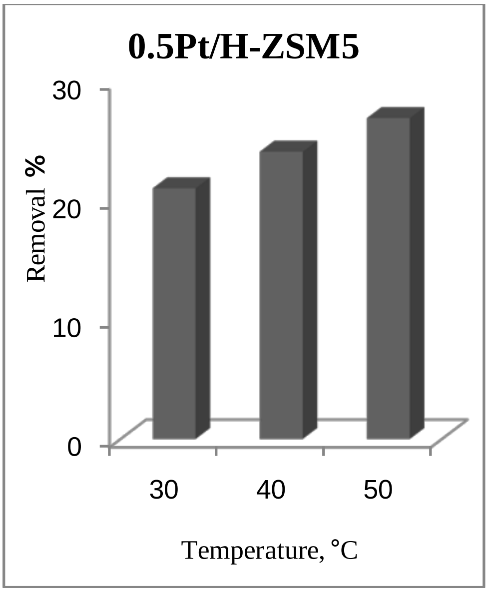
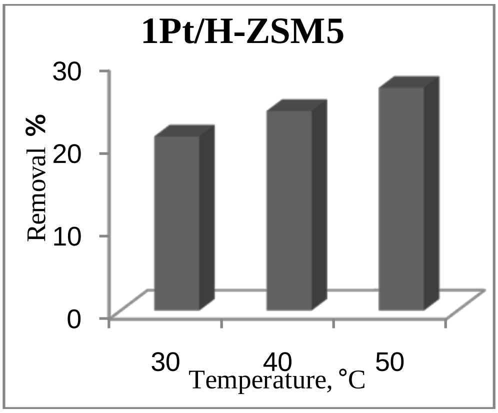


Table 18 . Effect of temperature using 1Pt/H-ZSM5

Temp. ºC	Removal %
30	21.01
40	24.09
50	26.91

Figure 23 . Effect of temperature using 1Pt/H-ZSM5



Effect of varying temperature on phenol removal efficiency using 1Pt/H-Mordenite was shown on **Table 19** and **Figure 24.**These data show that increasing the temperature increases linearly the removal percent from 12.3% at 30 ºC to 15.1% at 50 ºC .

Table 19. Effect of temperature using 1Pt/H- Mordenite

Temp. ºC	Removal %
30	12.3
40	13.4
50	15.1

Figure 24. Effect of temperature using 1Pt/H-Mordenite

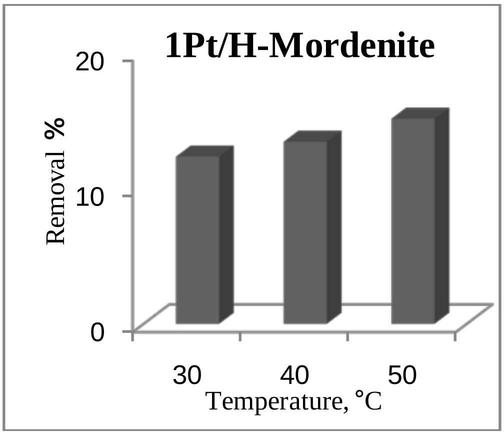


Figure 25 shows a comparison between the effects of reaction temperature on phenol removal using H-ZSM5, H-Mordenite and Bentonite**.** As can be seen that the highest removal percent for these catalyst was at 50 °C. The highest removal occur for H-ZSM5, H- Mordenite and Bentonite is 24.5%, 11%, 11.2% respectively.

Figure 26 shows a comparison between the effects of reaction temperature on phenol removal using the supported platinum catalysts (0.5%Pt/ZSM5 and 1%Pt/ZSM5). As can be seen that the highest removal was 29.6% and 27% respectively at 50 °C.

Figure 27 shows a comparison between the effects of reaction temperature on phenol removal using H-Mordenite or 1Pt/H-Mordenite. Temperature showed quite significant impact on phenol removal process using either H-Mordenite or 1Pt/H-Mordenite. The highest removal occurs at 50 °C.

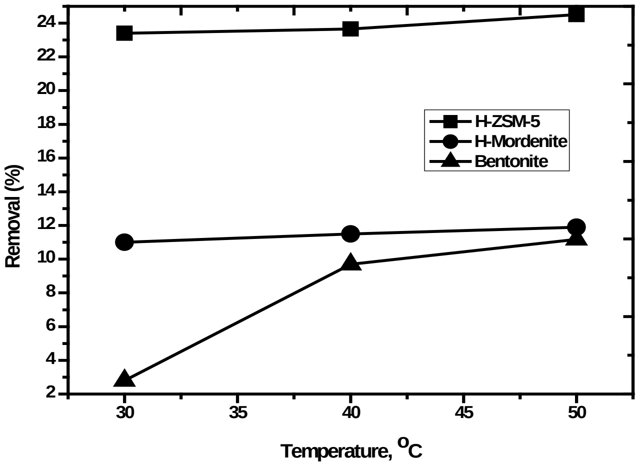


Figure 25. Effect of temperature on removal using H-ZSM-5, H-Mordenite and Bentonite

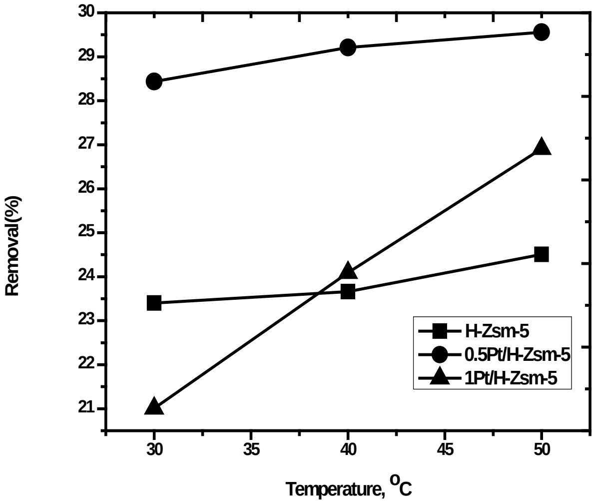


Figure 26. Effect of temperature on phenol removal using H-ZSM-5, 0.5Pt/H-ZSM-5 and 1Pt/ H-ZSM-5

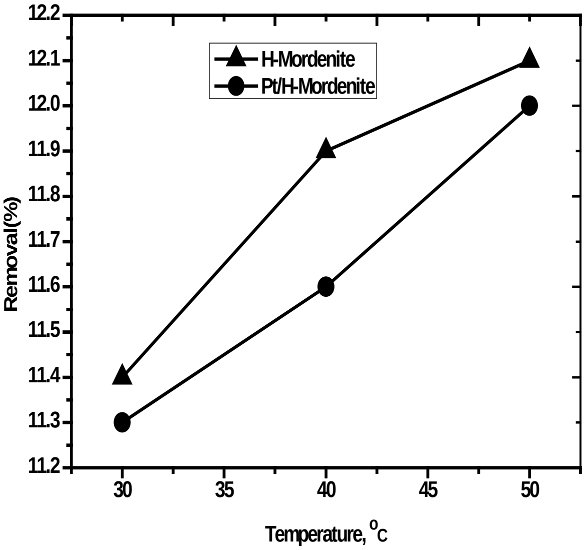


Figure 27. Effect of temperature on phenol removal using H-Mordenite and 1Pt/ H-Mordenite

3.3.2. Effect of initial pH value

This study investigates the adsorption of phenol at varied initial pH environments. In order to determine the optimum pH conditions for the removal of phenol solutions.

Table 20 and **Figure 28** show the effect of varying pH on phenol removal efficiency using H-ZSM5.From these data it was notable that the removal efficiency increases at pH 7.

The results of the effect of pH value on the removal efficiency of phenol using H-Mordenite was obtained in **Table 21** and **Figure 29**. The obtained results show that the removal of phenol is dependent on the pH value. The removal efficiency increases at pH 7.

Table 22 and **Figure 30** show the effect of varying pH on phenol removal efficiency using Bentonite. It is clearly seen that the removal efficiency increases at pH 3.

Table 20 . Effect of pH value using H-ZSM5

pH	Removal %
3	21.68
5	13.15
7	33.57
9	25.71

Figure 28 . Effect of pH value using H-ZSM5

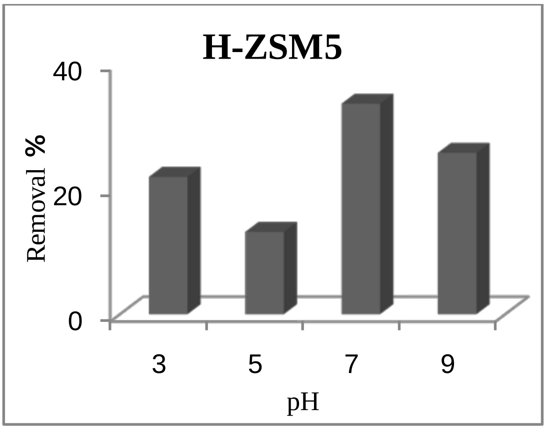


Table 21. Effect of pH value using H- Mordenite

pH	Removal %
3	11.6
5	10.07
7	12
9	9.88

Figure 29. Effect of pH value using H-Mordenite

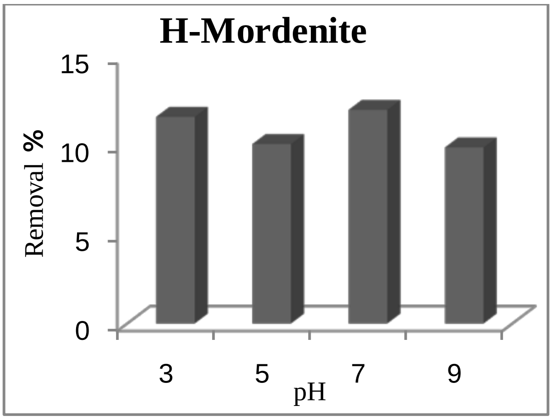


Table 22. Effect of pH value using Bentonite

pH	Removal %
3	36.31
5	19.64
7	20.84
9	17.16

Figure 30. Effect of pH value using Bentonite

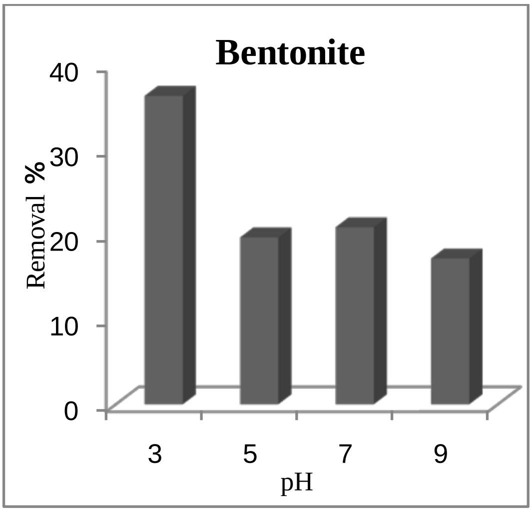


Table 23 and **Figure 31** show the effect of varying pH on phenol removal efficiency using 0.5Pt/H-ZSM5.it is clearly seen that the removal of phenol is dependent on the

pH value. The maximum removal was maintained when the pH of 7 is reached.

Table 24 and **Figure 32** show the effect of varying pH on phenol removal efficiency using 1Pt/H-ZSM5.it is clearly seen that the removal of phenol is dependent on the pH value. The removal of phenol was improved under acidic rather than basic conditions. The maximum removal was maintained when the pH of 7 is reached.

The effect of varying pH on phenol removal efficiency using 1Pt/H-Mordenite was shown in **Table 25** and **Figure 33.** It is clearly seen that the removal of phenol is dependent on the pH value. The removal of phenol was improved under basic rather than acidic conditions. The maximum removal was maintained when the pH of 9 is reached.

Table 23. Effect of pH value using 0.5Pt/H-ZSM5

pH	Removal %
3	32.98
5	35.88
7	36.82
9	34.6

Figure 31. Effect of pH value using 0.5Pt/H-ZSM5

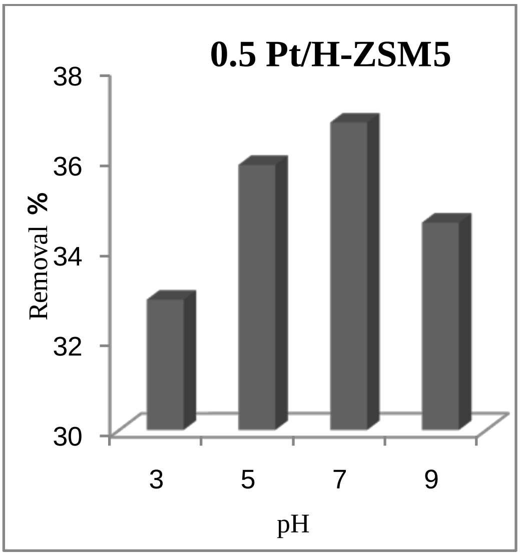


Table 24. Effect of pH value using 1Pt/H-ZSM5

pH	Removal %
3	35.37
5	36.56
7	32.29
9	35.79

Figure 32. Effect of pH value using 1Pt/H-ZSM5

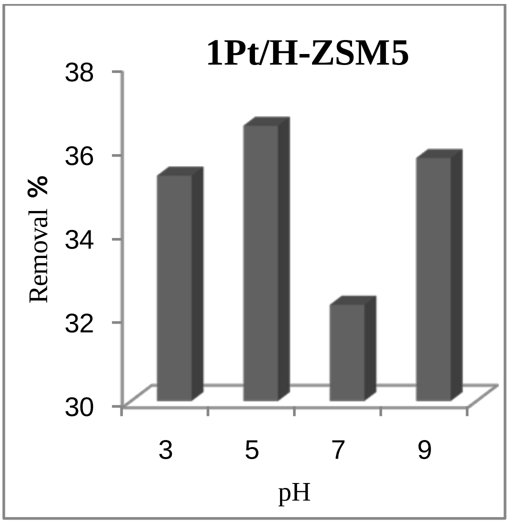
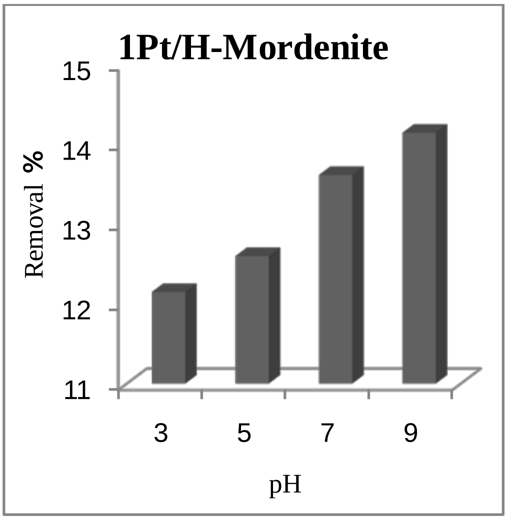


Table 25. Effect of pH value using 1Pt/H- Mordenite

pH	Removal %
3	12.15
5	12.6
7	13.61
9	14.14

Figure 33. Effect of pH value using 1Pt/H-Mordenite



3.3.3. Effect of initial phenol concentration

The catalytic removal of phenol was studied over a wide range of initial concentrations from 25 to 200 mg/L. The optimum conditions of time, temperature and pH for every catalyst were applied to remove various initial concentrations of phenol.

Table 26 and **Figure 34** show the effect of varying initial phenol concentration on phenol removal efficiency using H-ZSM5.it was seen that At low concentration (25ppm) a maximum removal was achieved to reach a value of 68.82%, while a decrease in this capacity to18.1% is occurred with further increasing in phenol concentration to 200 ppm.

Table 26. Effect of Initial phenol conc. using H-ZSM5

Initial Phenol Conc.	Removal %
25	68.82
50	40.82
100	34.68
150	23
200	18.1

Figure 34. Effect of Initial phenol conc. using H-ZSM5

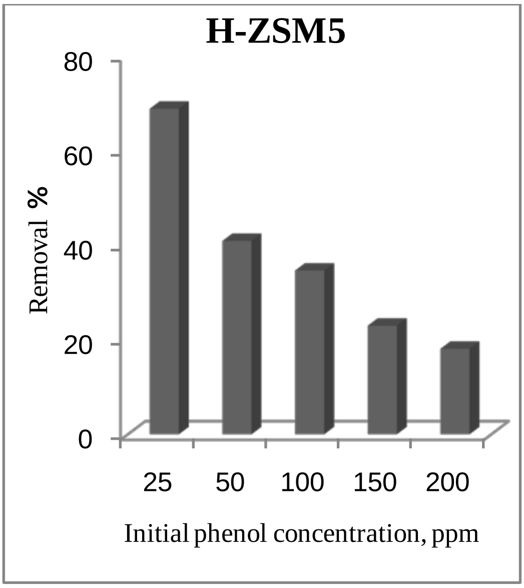


Table 27 and **Figure 35** show the effect of varying initial phenol concentrations on phenol removal efficiency using H-Mordenite.it was seen that At low concentrations (25ppm) a maximum removal was achieved to reach a value of 38.74%, while a decrease in this capacity to 9.6% is occurred with further increasing in phenol concentration to 200 ppm.

Table 28 and **Figure 36** show the effect of varying initial phenol concentrations on phenol removal efficiency using Bentonite. From these data it was seen that the removal efficiency decreases from 44.21 to 12.6 by increasing the initial concentrations form 25 ppm to 200 ppm.

Table 27. Effect of Initial phenol conc. using H-Mordenite

Initial Phenol Conc.	Removal %
25	38.74
50	20.84
100	16.48
150	12.6
200	9.6

Figure 35. Effect of Initial phenol conc. using H-Mordenite

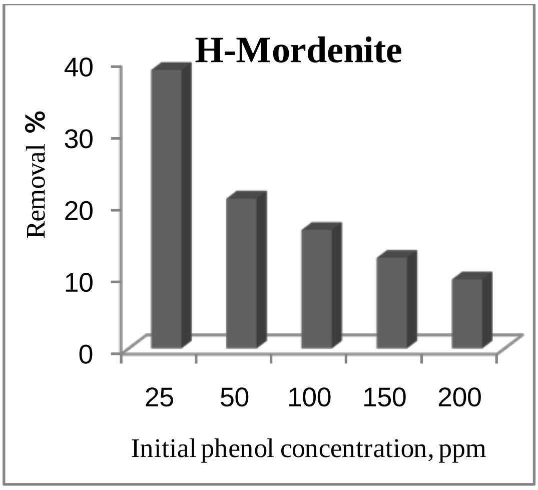


Table 29 and **Figure 37** show the effect of varying initial phenol concentrations on phenol removal efficiency

using 0.5Pt/H-ZSM5.it was seen that At low concentrations (25ppm) a maximum removal was achieved to reach a value of 82.5%, while a decrease in this capacity to 17.9% is occurred with further increasing in phenol concentration to 200 ppm. The effect of varying initial phenol concentrations on phenol removal efficiency by using 1 Pt/ H-ZSM-5 was shown in **Table 30** and **Figure 38**. As can be seen that 1 Pt/ H-ZSM-5 show complete removal of phenol in case of initial concentration of 25 ppm. This removal efficiency decreases to 11.3% for 200 ppm of phenol initial concentration.

Table 28. Effect of Initial phenol conc. using Bentonite

Initial Phenol Conc.	Removal %
25	44.21
50	28.85
100	23.83
150	13.4
200	12.6

Figure 36. Effect of Initial phenol conc. using Bentonite

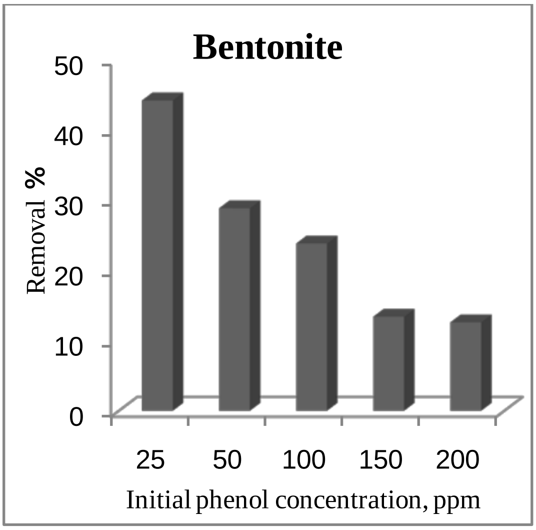


Table 31 and **Figure 39** show the effect of varying initial phenol concentrations on phenol removal efficiency using 1Pt/H-Mordenite. It was seen that At low concentrations (25ppm) a maximum removal was achieved

to reach a value of 38.4%, while a decrease in this capacity to 10.1% is occurred with further increasing in phenol concentration to 200 ppm.

Table 29. Effect of Initial phenol conc. using 0.5Pt/H-ZSM5

Initial Phenol Conc.	Removal %
25	82.5
50	57.74
100	45.11
150	22.7
200	17.9

Figure 37. Effect of Initial phenol conc. using 0.5Pt/H-ZSM5

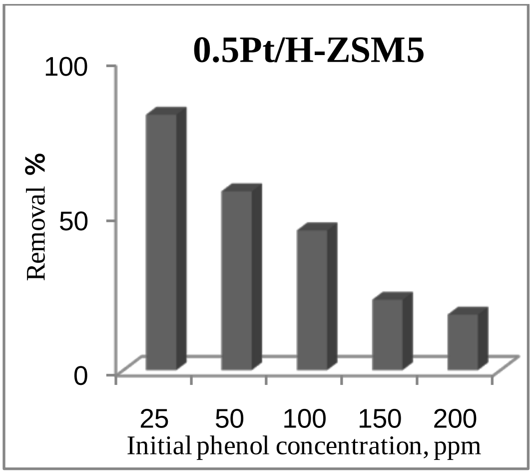


Table 30. Effect of Initial phenol conc. using 1Pt/H-ZSM5

Initial Phenol Conc.	Removal %
25	100
50	42.87
100	39.64
150	19.7
200	11.3

Figure 38. Effect of Initial phenol conc. using 1Pt/H-ZSM5

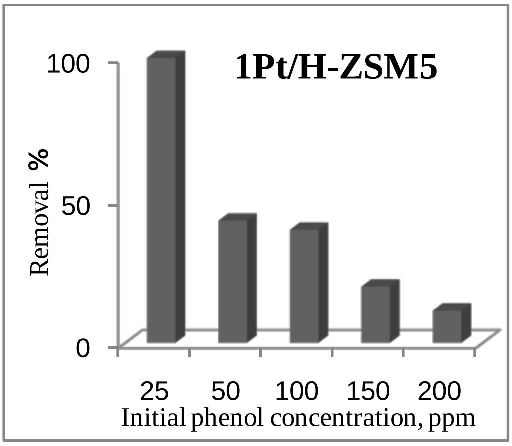
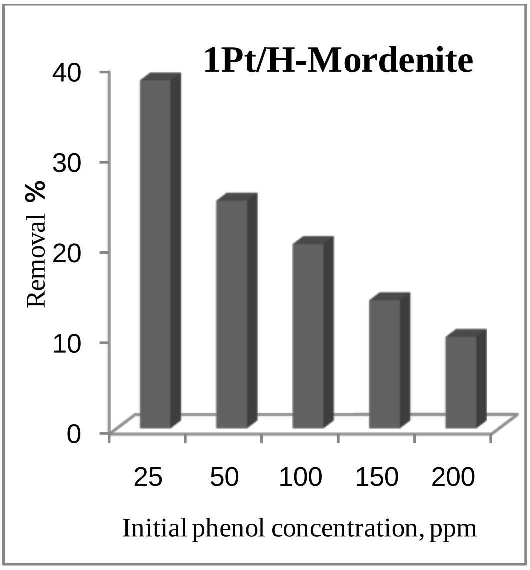


Table 31. Effect of initial phenol conc. using 1Pt/H- Mordenite

Initial Phenol Conc.	Removal %
25	38.4
50	25.1
100	20.3
150	14.15
200	10.1

Figure 39. Effect of initial phenol conc. using 1Pt/H-Mordenite



Figures 40-42 show that the removal efficiency of phenol decreased with increasing phenol concentration for all catalysts. This can be explained in the term of the saturation of the limited number of active sites of the catalyst. The active sites for catalytic reaction remain the same at fixed catalyst dosage **[123]**.

3.3.4. Effect of catalyst dose

By varying the amount of catalyst (0.2, 0.3, 0.4 and 0.5 gm) to 100 ml of solution containing 100 ppm of phenol and applying the optimum conditions for each catalyst.

The effect of using different amounts of H-ZSM5 was shown in **Table 32** and **Figure 43**.The removal efficiency increases from 42.63% using 0.2 g of H-ZSM5 to

51% by using 0.5 g of H-ZSM5.

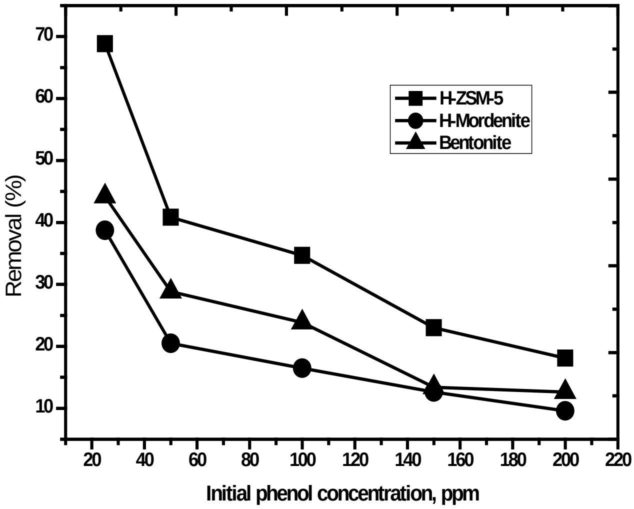


Figure 40. Effect of varying phenol initial concentrations on phenol removal using H-ZSM-5, H-Mordenite and Bentonite.

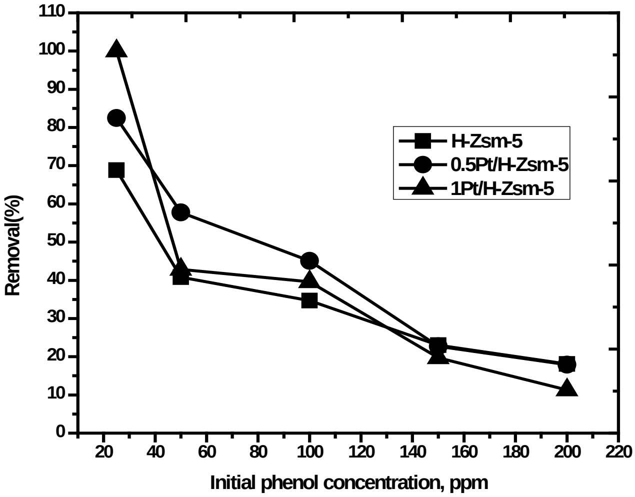


Figure 41. Effect of varying phenol initial concentrations on phenol removal using H-ZSM-5, 0.5Pt/H-ZSM-5 and 1Pt/ H-ZSM-5.

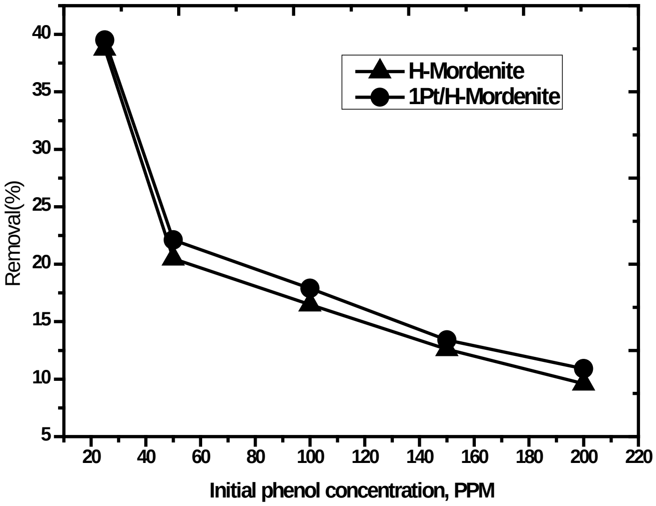


Figure 42. Effect of varying phenol initial concentrations on phenol removal using H-Mordenite and 1Pt/ H-Mordenite

The results of using different amounts of H-Mordenite on phenol removal was shown in **Table 33** and **Figure 44**. These results show increasing efficiency of phenol removal by increasing the catalyst amount in solution. The removal increases from 28.79% using 0.2 g of catalyst to 37.42 using 0.5 g of catalyst.

By using different amounts of Bentonite, the results of removal efficiency of phenol was obtained in **Table 34** and **Figure 45**. From these results, it was seen that the removal efficiency is quite affected by increasing the amount of Bentonite. By using 0.2 g of Bentonite the removal was 25%. This percentage increases to 29% by using 0.5 g.

Table 32. Effect of catalyst dose using H-ZSM5

Catalyst Dose, g	Removal %
0.2	42.36
0.3	44.17
0.4	46.22
0.5	51

Figure 43. Effect of catalyst dose using H-ZSM5

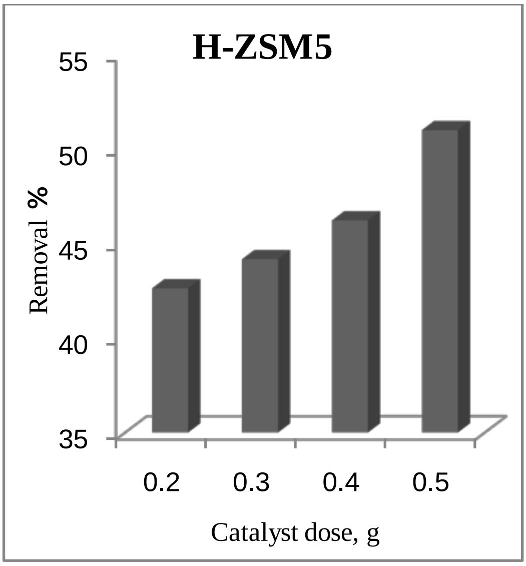
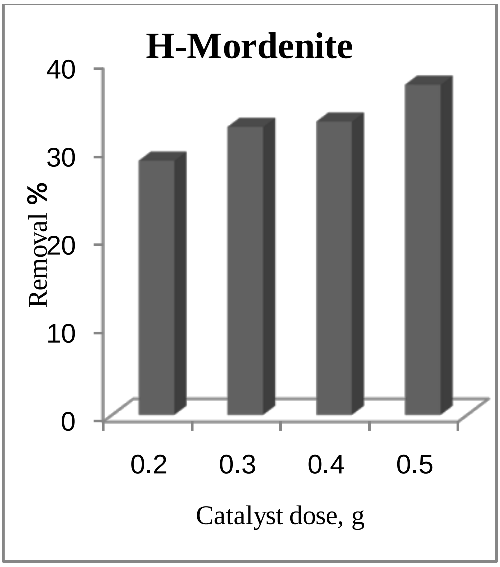


Table 33. Effect of Catalyst dose using H-Mordenite

Catalyst Dose, g	Removal %
0.2	28.79
0.3	32.63
0.4	33.23
0.5	37.42

Figure 44. Effect of catalyst dose using H- Mordenite



The results of the removal efficiency of phenol using different amounts of 0.5 Pt/H-ZSM5 was investigated in **Table 35** and **Figure 45**. From these results, it was shown that high catalyst dose in solution would result in higher phenol removal efficiency. The removal efficiency of phenol was lower at 0.2g -0.3g of catalyst. At 0.4g - 0.5g the removal efficiency increases from 55.11% to 60.5% respectively.

The effect of using different amounts of 1Pt/H-ZSM5 for the removal of 100 ppm of phenol solution was obtained in **Table 36** and **Figure 46**. It was seen that the removal efficiency increased significantly by increasing the amount at 0.2-0.5g of1Pt/H-ZSM5. The removal efficiency was 69.2% at 0.5g compared with 42.55% at 0.2g.

Table 34. Effect of Catalyst dose using Bentonite

Catalyst Dose, g	Removal %
0.2	25
0.3	26.14
0.4	26.48
0.5	29

Figure 45. Effect of catalyst dose using Bentonite

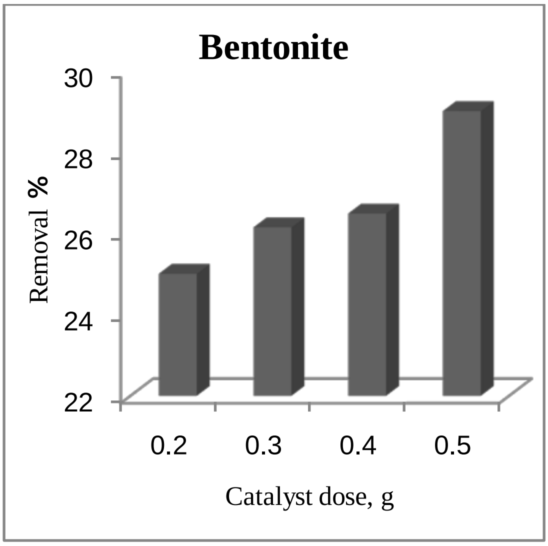


Table 35 . Effect of catalyst dose using 0.5Pt/H-ZSM5

Catalyst Dose, g	Removal %
0.2	45.97
0.3	47.16
0.4	55.11
0.5	60.5

Figure 46. Effect of catalyst dose using0.5Pt/ H-ZSM5

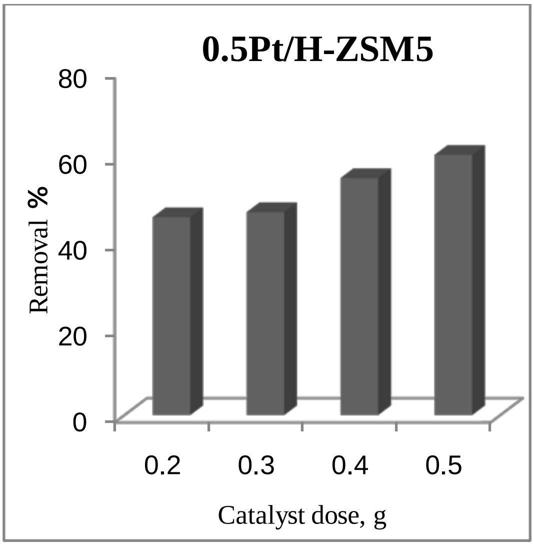
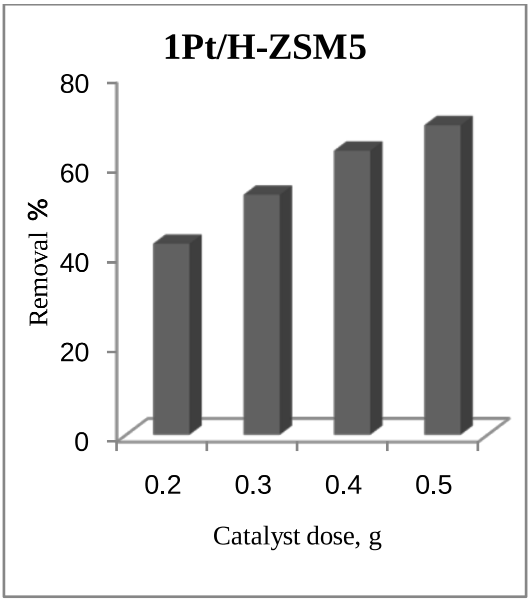


Table 36. Effect of Catalyst dose using 1Pt/H-ZSM5

Catalyst Dose, g	Removal %
0.2	42.55
0.3	53.49
0.4	63.23
0.5	69.29

Figure 47. Effect of catalyst dose using 1Pt/ H-ZSM5

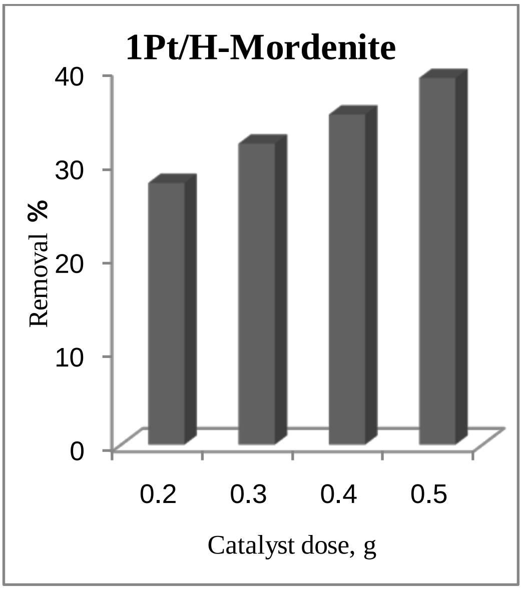


In case of using 1Pt/H-Mordenite the removal efficiency results was investigated in **Table 37** and **Figure 48**.These results show that using 0.2g could remove 27.9% of phenol from solution. by increasing the amount of 1Pt/H-Mordenite to 0.5g ,the removal increases to 39.1%.

Table 37. Effect of catalyst dose using 1Pt/H-Mordenite

Catalyst Dose, g	Removal %
0.2	27.29
0.3	32.1
0.4	35.21
0.5	39.1

Figure 48. Effect of catalyst dose using 1Pt/ H-Mordenite



Figures 49-51 show the effect of catalyst loading on phenol removal. It was seen that higher catalyst loading in solution would result in higher phenol reduction, because increasing the amount of catalyst will increase the adsorption and also the available active sites to initiate the oxidation **[6]**. It was concluded that the optimum loading for all catalysts were 0.5 gm. **Figure 49** shows that the percent of removal by using 0.5 g of H-ZSM5 was 51%. For 0.5 g

of H-Mordenite was 37.5%. For 0.5 g of Bentonite was 29 %.

Figure 50 shows that the removal efficiency was 60.5% and 69.29 % by using 0.5 g of 0.5%Pt/H-ZSM5 and 1%Pt/H-ZSM5 respectively, compared with the parent H-ZSM5.

Figure 51 shows that the highest removal of phenol using 1%Pt/H-Mordenite was 39.1% compared with the parent H-Mordenite. There is insignificant increase in case of loading with platinum. Because that the surface area for 1%Pt/H-Mordenite is close to the surface area of the parent H-Mordenite **[79]**.

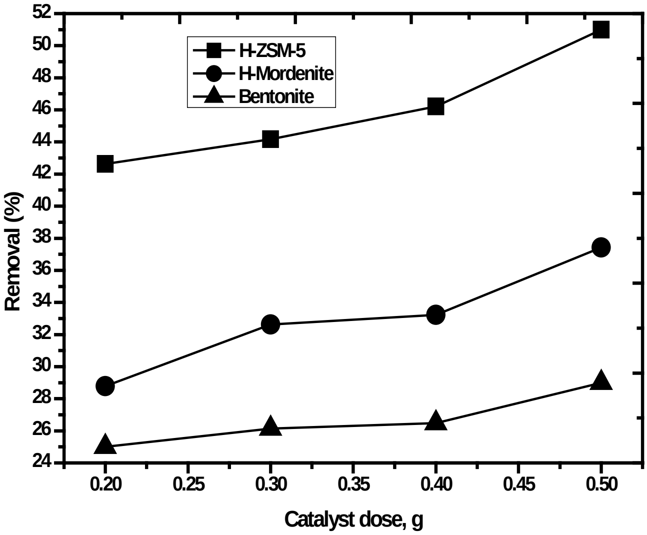


Figure 49. Effect of varying catalyst dose on phenol removal using H-ZSM-5, H-Mordenite and Bentonite.

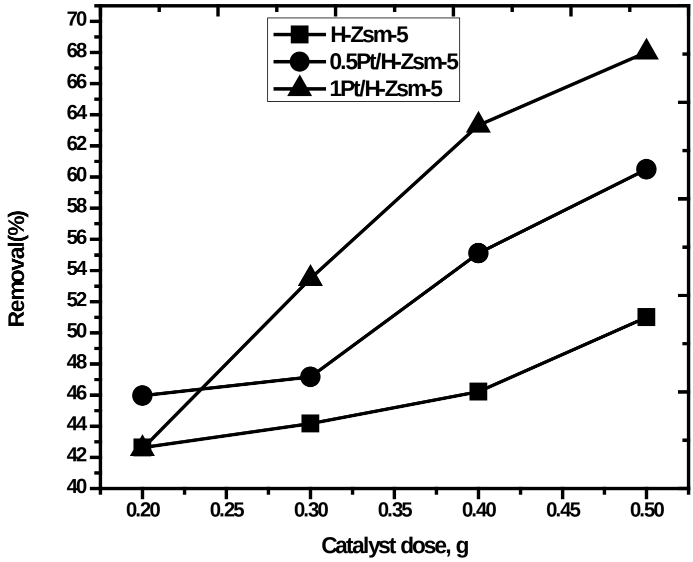


Figure 50. Effect of varying catalyst dose on phenol removal using H-ZSM-5, 0.5Pt/H-ZSM-5 and 1Pt/ H-ZSM-5.

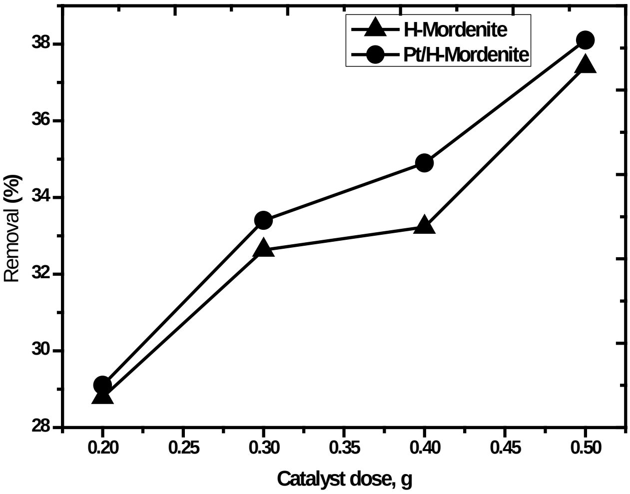


Figure 51. Effect of varying catalyst dose on phenol removal using H-Mordenite and 1Pt/ H-Mordenite

3.3.5 Effect of UV irradiation

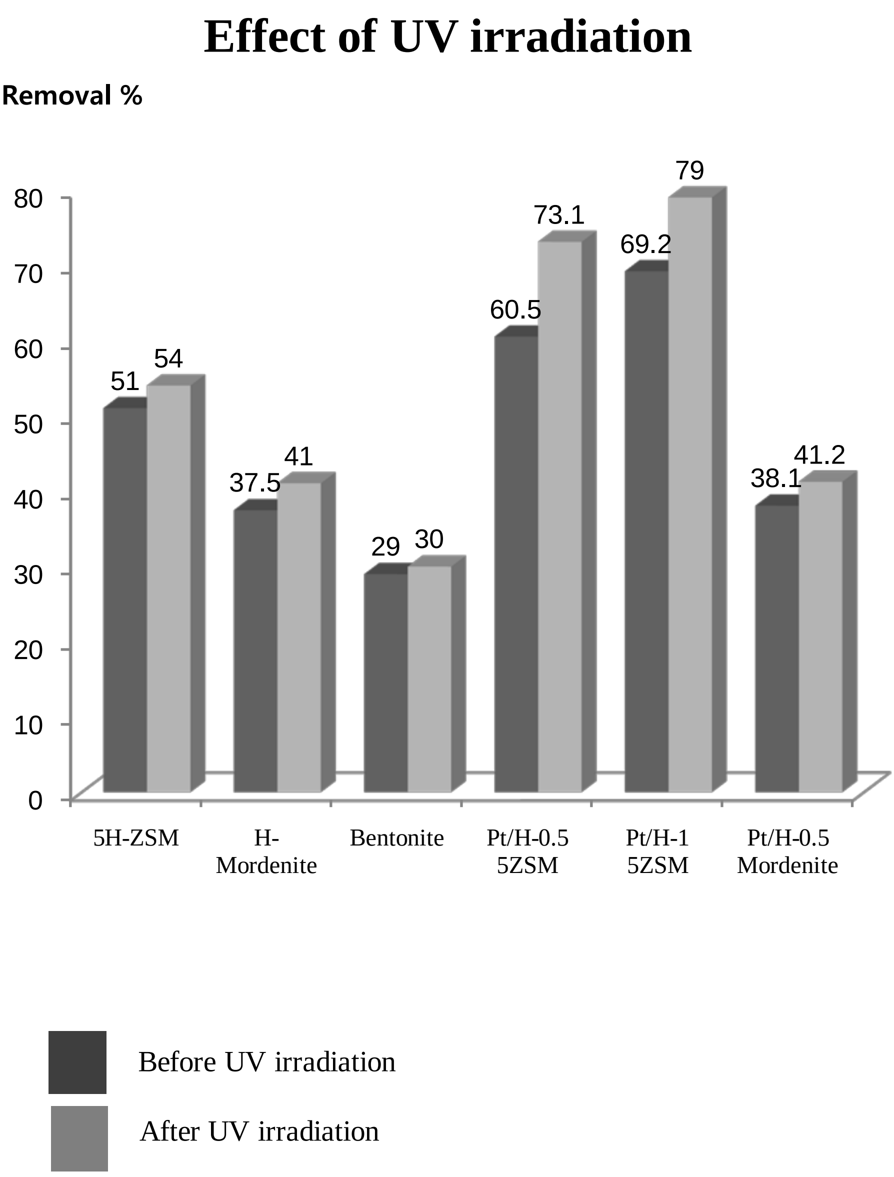
The photocatalytic removal of phenol from aqueous solutions using H-ZSM5, H-Mordenite , Bentonite, 0.5%Pt/ZSM5, 1%Pt/ZSM5 and 1%Pt/H-Mordenite was studied by applying the optimum conditions for each catalyst from the previous experiments. A Hg lamb (UV-C) was positioned above the shaker to supply irradiation process in a quartz reactor. By applying the optimum conditions for each catalyst (Time, Temperature, pH and catalyst dose). **Figure 52** shows that the percent of removal increased to 54%, 41% and 30% for HZSM5, H-Mordenite and Bentonite respectively. In case of using 0.5%Pt/ZSM5 and 1%Pt/ZSM5 the removal was 73.1%and 79% respectively. In case of using 1%Pt/H-Mordenite the percent of removal increased to 41.2%.

UV-C(100–280nm) can remove low concentrations of phenol. This wavelength is in the region of maximum germicidal effectiveness and is highly effective in phenol removal by generating $OH^{\cdot}$ radicals in the solution($OH^{\cdot}$ radicals are formed when this radiation strips the hydrogen atoms from water molecules).

Under the ultraviolet radiation gives rise to electron–hole pairs on the surface, which react with water molecules to give •OH. During the process, H+ or H• is scavenged by oxygen to form HO_2• radicals, which finally convert to •OH radicals. Therefore, the principal reaction Leading to organics decomposition would be the one with •OH radicals. But based on the intermediates detected in this experiment, it can be concluded that •H also takes part in the photo degradation. The reaction route can be described as follows, •H may be produced through three routes: **(1)** water molecules react with holes in the electron–hole pairs to produce •OH and H+, H+ combines with the electron from the electron–hole pairs; **(2)** during the process of •OH attacking the aromatic ring, carbon–hydrogen bond break up, hydrogen is substituted for •OH, and •H is produced; **(3)** as catalysts exists or not, the main intermediates detected are the same and UV only provides energy to break covalent bonds, •H may also be produced by the break of oxygen–hydrogen bond in water molecules and phenol molecules; or carbon–hydrogen in phenol molecular. The energy of this wavelength (472 kJ/mol) is higher than the bond energy of O-H (462.8 kJ/mol), C-O (357.7 kJ/mol), C-H (413.0 kJ/mol), so these bonds probably break upon UV irradiation **[12]**.

From the previous results of investigating the effects of reaction parameters conditions on phenol removal efficiency, we can conclude the optimum conditions of using H-ZSM5, H-Mordenite , Bentonite, 0.5%Pt/ZSM5, 1%Pt/ZSM5 and 1%Pt/H-Mordenite for removal of solution containing 100 ppm of phenol. These conditions are summarized in **Table 38**. From these data, the two doped H-ZSM5 have the high efficiency for phenol removal from solutions By using GC–MS, It was expected that the main intermediates of phenol removal under ultraviolet illumination are the same, whether catalysts presents or not. See **Figure 3**.

Figure 52. Comparison of phenol removal before and after UV irradiation.



They include 2-hydroxy-propaldehyde, hydroxy-acetic acid, 3-hydroxy-propyl acid, glycerol, catechol, (E)-2 butenedioic acid, resorcinol, hydroquinone and 1,2,3 benzenetriol. The formation of glycerol, hydroxyaldehyde and hydroxyl acid showed that besides •OH, •H is also an important active free radical in the removal **[12]**.

Table 38. Catalysts experimental conditions and the corresponding phenol removal efficiency are reported for a qualitative comparison.

Catalysts	**Phenol removal %**	**Conditions**				
		Time, hours	**Temp. , °C**	**pH**	**Catalyst Dose, g**	**UV**
H-ZSM5	54%	3 h	50 °C	7	0.5 g	UV-C
H-Mordenite	41%	3 h	50 °C	7	0.5 g	UV-C
Bentonite	30%	2 h	50 °C	3	0.5 g	UV-C
0.5% Pt/ZSM5	73.1%	2 h	50 °C	7	0.5 g	UV-C
1% Pt/ZSM5	79%	5 h	50 °C	5	0.5 g	UV-C
1% Pt/H-Mordenite	41.2%	3 h	50 °C	9	0.5 g	UV-C

From **Table 38,** it can be noticed that, although Pt/H-Mordenite catalysts have higher surface area, higher acidity and higher Pt dispersion, but the Pt/H-ZSM5 was more selective than Pt/H-Mordenite. This could be explained in terms of pore structure of the studied zeolites. Mordenite has one-dimensional pore structure with side-pockets whereas ZSM5 consists of three dimensional channels. It has been reported that only one third to two-third of the acid sites from mordenite are accessible to alkanes. **Carvill, et al. [130]** have argued that in one-dimensional zeolites, the catalyst activity was controlled by the accessibility to the active sites, because the effect of “single file diffusion”. The three-dimensional structure of ZSM5 zeolite allowed easy access to a greater number of active sites compared to that of one-dimensional zeolites.

Conclusions and Summary

CONCLUSIONS

Water pollution from industrial sources constitutes a major environmental pressure. The development of new methods for wastewater treatment is one of challenge facing scientists.

In this study the feasibility of using AOPs for wastewater treatment was assessed.

- CWAO is a type of AOPs in which a catalyst is used to avoid the high pressure and temperature needed for oxidation process in the conventional WAO.
- the catalysts used for AOPs of phenol in this work are heterogeneous in which the catalyst and the medium are in different phase
- The used materials are aluminosilicates catalyst these catalysts contain silicone and aluminum in different ratio these catalysts are zeolites (H-ZSM -5, H-Mordenite), the natural clay bentonite.
- Zeolites also can be used as supporting materials .in this study ZSM -5 doped with two different concentrations of platinum are used. H-Mordenite doped with 1% platinum.
- The doped H-ZSM-5 prepared using wet impregnation method of either H-ZSM-5 or H-Mordenite and the source of platinum.
- The source of platinum is hexachoroplatinic acid.

- The chemical, morphological and structural characterizations of the prepared catalysts have been studied by various techniques.

- Phenol was chosen as a studying object because it is considered as intermediate product in the oxidation pathway of higher molecular weight phenolic compounds.

- The catalytic activity of catalysts (H-ZSM-5, H-Mordenite, Bentonite, 0.5%Pt/ H-ZSM-5, 1%Pt/ H-ZSM-5 and 1%Pt/ H-Mordenite) were tested to remove phenol. The removal of phenol was done using the previous catalysts at the standard conditions (25 °C, 125 rpm).

- It was seen that doped H-ZSM-5 is highly active in removing phenol. But the doped H-Mordenite has no significant increase in the removal compared with the parent H-Mordenite, because that the surface area for 1Pt/H-Mordenite is close to the surface area of the parent H-Mordenite.

- By studying the effect of removal parameters (temperature, pH, different initial phenol concentrations and catalyst dose) for each catalyst. We get the optimum conditions for each catalyst at which best removal occurs.

- By changing the temperature of the removal experiment (30,40 and 50 C) , it was noticed that the removal increased for each catalysts expect H-Mordenite the effect is quite significant.

- The varied pH (3, 5, 7 and 9) would have an effect on the removal of phenol.

- These optimum conditions of temperature and pH when applied to different phenol concentrations, it was seen that by increasing phenol concentration the removal would decreased. This can be explained in the term of the saturation of the limited number of active sites of the catalyst. The active sites for catalytic reaction remain the same at fixed catalyst dosage

- It was seen that the increase in catalyst amount would increase the removal percent for each catalyst. It was seen that higher catalyst loading in solution would result in higher phenol reduction, because increasing the amount of catalyst will increase the adsorption and also the available active sites to initiate the oxidation.

- Irradiation with UV-C (100-280nm) would increase the percent of removal for all catalysts, because this wavelength is in the region of maximum germicidal effectiveness and is highly effective in phenol removal by generating $OH^{\cdot}$ radicals in the solution ($OH^{\cdot}$ **r**adicals are formed when this radiation strips the hydrogen atoms from water molecules). The energy of this wavelength (472 kJ/mol) is higher than the bond energy of O-H (462.8 kJ/mol), C-O (357.7 kJ/mol), C-H (413.0 kJ/mol), so these bonds probably break upon UV irradiation

- The optimum conditions for the removal of phenol by using the previous catalysts were investigated.

- The conditions at which the best removal of phenol using ZSM-5(51%) occurs by using 0.5gm of catalyst, pH 7, 50 Cº, 100ppm of phenol and increased to 53.4% by irradiation with UV-C after 3 hours. Also the removal with Mordenite at the same conditions but the temperature is not effective. The removal increased from 37.5% to 41% by irradiation with UV. The removal with Bentonite was 29% under conditions of 0.5 gm, pH 3, 50 ºC and 100 ppm of phenol. The removal under UV-C irradiation increased to 30%.

- The removal with 0.5%Pt/ZSM-5 at the same conditions increased from 60.5% to 73.1% by irradiation with UV-C.
- The removal with 1%Pt/ZSM-5 occurs at the same conditions but at pH of 5 and the removal under UV-C irradiation increased from 68.1% to 77%.

- It was concluded that the Pt/H-ZSM-5 catalysts was more selective than Pt/H-Mordenite although Pt/H-Mordenite catalysts have higher surface area, higher acidity and higher Pt dispersion, This could be explained in terms of pore structure of the studied zeolites. Mordenite has one-dimensional pore structure with side-pockets whereas ZSM-5 consists of three dimensional channels. It has been reported that only one third to two-third of the acid sites from mordenite are accessible to alkanes.

SUMMARY

The present thesis comprises three chapters:

Chapter 1

- Includes an introduction to water pollution and the sources of pollution in the environment
- Also, includes an introduction to pollution of water with phenolic compounds
- Give a brief notes to the industrial sources of phenol .
- Phenol properties and its effect on health.
- The conventional methods of phenol removal and the methods recently used.
- Using AOPs to remove phenol is a very promising method.
- Also a brief description of the used catalysts in this study.

Chapter 2

Describes the materials, reagents, instruments and methods applied for the preparation of the catalysts used during this study. Also the calibration curve for phenol used to obtain the concentration of phenol.

Chapter 3

Represents the results and discussion of the present study which were divided into three parts:

Part(1)characterization of the prepared catalysts used for remaval of phenol using SEM, HRTEM, XRD, nitrogen adsorption desorption, pulse titration measurements and the total amount of acidity.

Part(2)

Contains a preliminary study of phenol removal to obtain the time profile for each catalyst. These results of this part summarized as follow:

The percent of removal were 22.4% after 3 hours for H-ZSM-5 , 40% after 3hour for H-Mordenite and 16% after 2 hour for Bentonite. for 0.5Pt/H-ZSM-5 the removal was 90.8% after 2 hour and 92.3% after 5 hour for 1 Pt/ H-ZSM-5 compared with the parent H-ZSM-5. In case of using Pt/H-Mordenite the removal was 43.9% within 3 h

Part (3): the effect of reaction parameters on phenol removal .

The results of this part are summarized as follow:

- The effect of temperature it was seen that the increase in temperature would increase the removal of phenol. The best removal for all catalysts used is 50°C. On otherhand, the temperature has quite significant impact on phenol removal process using either H-Mordenite or 1%Pt/H-Mordenite.

- pH has a basic effect on the removal percent ,where the varied pH has varied phenol removal percent.

- Phenol concentrations affect the removal percent in a reversible effect in which the increase in phenol concentration would decrease the removal percent.
- The amount of catalyst used would increase the removal percent for all catalysts.
- UV-C(100-280 nm) irradiation would affect the removal percent of phenol and increase the removal percent.
- The optimum conditions for catalysts at which high removal effeciency occurs were investigated.

References

REFERENCES

1- The Environmental Quality Sector (EQS), (EEAA). "National profile for the management of chemicals in Egypt." 1999.

2- Mobarak, A. "The Challenges of Sustainable Industrial Development in Egypt: A Country Paper for the World Summit on Sustainable Development (WSSD)." United Nations Industrial Development Organization (UNIDO) (2001).

3- Abdel-shafy, H. I. and Aly, R. O., *CEJOEM*, (2002), 8 (1), 3-21.

4- European Pollutant Emission Register review report, JUNE (2004), 4, 79. http://www.env-edu.gr/Documents/EPER.pdf .

5- The International Programme on Chemical Safety (I PCS) No 161, (1994).

6- Caribbean Environment Programme (CEP), United Nations Environment Programme (UNEP), CEP Technical Report #40, (1998), 2, 9.

7- Liotta, L. F.; Gruttadauria, M.; Di Carlo, G.; Perrini, G.; Librando, V. *J., Hazard. Mater*. (2009)162, 588-606.

8- Mohammad, S.; Shukla, P. R.;Tade',M. O.; Wang, S., *J. Hazard. Mater.*, (2012), 183-190.

9- Jia, J.; Zhang, S.; Wang, P.; Wang, H., *J. Hazard. Mater.*, (2012), 29, 205.

10- Park, Y.; Ayoko, G. A.; Kurdi, R.; Horvath, E.; kristof, J.; Frost, R. L., *J. Colloid Interf. Sci*. (2013), 406, 196-208.

11- EPA National Library Network. [Online] Available :http://water.epa.gov/scitech/methods/cwa/pollutants.cfm , 1st JULY (2014), 29.

12- Carey, F.A., Organic Chemistry 4th Ed., Chapter 24, McGraw Hill Editions, University of Virginia, (2001).

13- Fortuny, A.; Bengoa, C.; Font, J. and Fabregat, A., *J. Hazard. Mater.*, (1999), 181, B64.

14- Guo, Z.; Ma, R.; Li, G. *Chem. Eng. J.* (2006), 119, 55–59.

15- Amore, J.E.; Hautala, E., *J. Appl. Toxicol.* , (1983), 3, 272–290.

16- Smith, M. B.; March, Jerry, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (6th ed.), New York: Wiley-Interscience, 2007.

17- Becker, H.; Berger, W.; Domschke, G.; Fanghänel, E. Organikum - Organisch Chemisches Praktikum. Wiley-VCH Verlag GmbH20, 1999, ISBN: 3527297197.

18- World Health Organization, WHO (2008), http://www.who.int/en/ .

19- Ley sobre vertidos industriales al sistema integral de saneamiento, Servicio de coordinacion legislativa y relaciones institucionales, Law 10/1993, October 26th, Spain.

20- Jordan, W.; Van Barneveld, H.; Gerlich, O.; Kleine-Boymann, M.; J.Ullrich, Phenol in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag, (2002).

21- Schmidt, R.J., *Appl. Catal. A: Gen.*, (2005), 280, 89–103.

22- Franck, H.G. and Stadelhofer, J. W. Industrial Aromatic Chemistry, Springer Verlag, Berlin, (1989), 148–157.

23- Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. *J. Hazard. Mater.* (2008), 160, 265–288.

24- Jordan, W.; van Barneveld, H.; Gerlich, O.; Kleine-Boymann, M. and Ullrich, J., Phenol in: Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag,(2002).

25- Wittcoff, H.A. and Reuben, B.G. Industrial Organic Chemicals, Wiley, (1996), 236–255.

26- Canadian Environmental Protection Act, Priority Substances List Assessment Report: Phenol, 24th JUNE (2013), www.ec.gc.ca .

27- Lifton, R.J., The Nazi Doctors, Basic Books, (1986), 254–268.

28- Pinto, R.T.P.; Lintomen, L.; Luz Jr. L.F.L. and Wolf-Maciel, M.R., Strategies for recovering phenol from wastewater: thermodynamic evaluation and environmental concerns, Fluid Phase Equilibrium. (2005), 228‑229, 447‑457.

29- Dabrowski, A.; Podkoscielny, P. ; Hubicki, Z. and Barczak, M. , *Chemosphere* (2005), 58 ,1049‑1070.

30- Ghizellaoui, S. and Meniai, A.H., *Desalination* ,(2005), 185, 457‑472.

31- Sunil, J.K. and Dr. Jayant P. K., *International Journal of Scientific and Research Publications*, (2013), 3(4), 1-5.

32- Miodrag Stanisavljević., Lidija Neldic. “Removal Of Phenol From Industrial Wastewaters By horseradish (Cochlearia Armoracia L) Peroxidase” Working and Living Environmental Protection , (2004), 2(4), 345 – 349.

33- Vasudevan, P. T. and Lee, L. O., *Biotechnology*, (1996), 60(1), 73-82.

34- Nicell, J.A.; Saadi, K.W. and Buchanan I.D., *Bioresource Technology*, (1995), 54(1), 5–16.

35- Abdelwahab O.; Amin N.K. and El-Ashtoukhy ES, *J. Hazard Mater.*, (2009), 163(2-3), 711-716.

36- Zazouli, M. A. and Taghavi, M., *Journal of Water Resource and Protection,* (2012), 4, 980-983.

37- Rao, N. N.; Singh, J. R.; Mishra, R. and Nandi, T., *J. for Scientific and Industrial Research* (2009), 68, 823-829.

38- Xu, J. Q.; Duan, W. H.; Zhou, X. Z. and Zhou, J. Z., *J. Hazard. Mater.*, (2006), 131(1–3), 98–102.

39- Ilisz, I.; László, Z. and Dombi, A., *Appl. Catal. A: General*, (1999), 180(1–2), 25–33.

40- Akbal, F. and Nur Onar, A., (2003), 83 (3), 295-302.

41- Barrios-Martinez, B. M. A. and Roche, P. M. N., *Biochem. Eng. J.* (2006), 30,174–183.

42- Bevilaqua, J.V.; Cammarota, M. C.; Freire, D. M. G. and Sant’Anna Jr., G. L., *Braz. J. Chem. Eng.* (2002), 19(2), 151-158.

43- Movahedyan, H.; Khorsandi, H.; Salehi, R. and M. Nikaeen, *J. Environ. Health. Sci. Eng.*, (2009), 6(2), 115-120.

44- Jiang, L. and Mao, X., *Int. J. Electrochem. Sci.*, (2012), 7, 4078 – 4088.

45- Rubalcaba, A.; Sua´ rez-Ojeda, M.E.; ber, F. Stu¨ ; Fortuny, A.; Bengoa, C.; Metcalfe, I.; Font, J.; Carrera, J. and Fabregat, A., *Water Sci.Technol.*, (2007), 55 (12) , 221–227 .

46- Esplugas, S.; Giménez,J.; Contreras, S.; Pascual, E. and Rodŕıguez, M., *Water Res.*, (2002), 36(4), 1034–1042.

47- Siedlecka, E. M.; Stepnowski, P., *Pol. J. Environ. Stud.*, (2005), 14(6), 823-828.

48- Matatov-Meytal, Y. and Sheintuch, M., *Ind. Eng. Chem. Res.*, (1998), 36, 309.

49- Debellefontaine, H.; Foussard J.N., *Waste management*, (2000), 20, 15.

50- Pintar, A., *Catal. Today*, (2003), 77, 451.

51- Hancock F.E., *Catal. Today*, (1999), 53, 3.

52- Stuber, F.; Font, J.; Fortuny, A.; Bengoa, C.; Eftaxias, A. and Fabregat, A., *Top. Catal.*, (2005), 33, 1.

53- Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E. and Rodriguez, M., *Water Res.*, (2002), 36, 1034.

54- Pera-Titus, M.; Garcia-Molina , V.; Banos, M. A.; Gimenz, J. and Esplugas, S., *Appl. Catal. B: Environmental*, (2004), 47, 219-256.

55- Stohs, S.J. and Bagchi, D., *Free Radical Biol. Med.*, (1995), 18 ,321.

56- Bigda, R.J., *Chem. Eng. Prog.*, (1995), 91, 62.

57- Bautista, P.; Mohedano, A.F.; Casas, J.A.; Zazo, J.A. and Rodriguez, J.J., *J. Chem. Technol. Biotechnol.*, (2008), 83, 1323.

58- Okawa K.; Suzuki, K.; Takeshita, T. and Nakano, K., *J. Hazard. Mater.*, (2005), B127, 68.

59- Aguiar, A.; Ferraz, A., *Chemosphere*, (2007), 66, 947.

60- Pignatello, J.J.; Oliveros, E. and MacKay, A., *Environ. Sci. Technol.*, (2006), 36, 1.

61- Hocevar, S.; Batista, J., and Levec, J., *J. Catal.*, (1999), 184, 39.

62- Arena, F.; Giovenco, R.; Torre, T.; Venuto, A. and Parmaliana A., *Appl, catal. B*, (2003), 45 ,51.

63- Wu, Q.; Hu, X. and Yue, P., *Chem. Eng. Sci.*, (2003),58 , 923.

64- Levec, J. and Pintar, A., *Catal. Today*, (2007), 124, 172.

65- Garcia-Molina, V.; Lopez-Arias, M.; Florczyk, M.; Chamarro, E. and Espulgas, S., *Water Res.*, (2005), 39, 795.

66- Debellefontaine, H.; Chakchouk, M.; Foussard, J.N.; Tissot, D. and Striolo, P., *Environ. Pollution*, (1996), 92, 155.

67- Luck, F., *Catal. Today*, (1999), 53, 81.

68- Caudo, S.; Centi, G.; Genovese, Ch. And Perathoner, S., *Top. Catal.*, (2006), 40, 207.

69- Fajerwerg, K. and Debellefontaine, H., *Appl. Catal. B: Environ.*, (1996), 10, L229.

70- Luo, M.; Bowden, D. and Brimblecombe, P., *Appl. Catal. B: Environ.*, (2009), 85, 201.

71- Ramirez, J.H.; Costa, C.A.; Madeira, L.M.; Mata, G.; Vicente, M.A.; Rojas, M.L.; Lopez, A.J. and Martin, R.M., *Appl. Catal. E: Environ.*, (2007), 71, 44.

72- Zazo, J. A.; Casas, J. A.; Mohedano, A.F. and Rodriguez. J.J., *Applied Catalysis B: Environ.*, (2006), 65, 261.

73- Dantas, T.L.P.; Mendoca, V.P.; Jose, H.J.; Rodrigues, A.E. and Moreira, R.F.P.M., *Chem. Eng. J.*, (2006), 118, 78.

74- Arana, J., Pulido; E., Rodriguez, V.M.; Pena, A., Dona, J. M.; Gonzales, O. and Perez, J., *J. Hazard. Mater.*, (2007), 146, 520.

75- Priya, M. H. and Madras, G., *Ind. Eng. Chem. Res.*, (2006), 45, 482.

76- Roostaei N. and Tezel FH., *J Environ Manage.*, (2004), 70(2), 157-64.

77- Caetano, M.; Valderrama, C.; Farran, A. and Cortina, J. L., *Journal of Colloid and Interface Science*, (2009), 338(2), 402–409,15 .

78- Qadeer, R. and Rehan, A. H., *Turk J Chem.*,(2002), 26, 357 -361 ,.

79- Maarof, H. I. and Hameed, B. H., “Adsorption Isotherms for Phenol Onto Activated Carbon” AJChE, VOl.4, No. 1, 70-76.

80- Uddin, M. T.; Islam, M. S. and Abedin , M. Z., *ARPN J. Eng. Appl. Sci.*, (2007), 2, 2.

81- Mixa, A. and Staud, C., *Int. J. Chem. Eng.*, (2008), Article ID 319392, 12 pages.

82- Gupta, C.; Pradhan, N. C. and Adhikari, B., *Bull. Mater. Sci.*, (2002), 25(6), 533–536.

83- Diaconu, I.; Nechifor, G.; Nechifor, A. C.; Ruse, E. and Totu, E. E., *U.P.B. Sci. Bull., Series B*, (2009), 71, 4.

84- Maduna Valkaj, K.; Katovic, A. and Zrnčević, S., *J. Hazard. Mater.*, (2007), 144, 3, 663-667.

85- Amin, N.A.S.; Akhtar, J. and Rai, H. K. *Chem. Eng. J.*, (2010), 158, 520–527.

86- Mohammad, S.; Shukla, P. R.;Tade',M. O. and Wang, S. *J. Hazard. Mater.*, (2012), 183-190.

87- Yan, Y.; Jiang, S. and Zhang, H., *Sep. and Purif. Technol.*, (2014), 133, 365–374.

88- Yan, Y.; Jiang, S. and Zhang, H., *R. Soc. Chem. Adv.*, (2015),

89- Zainudin, N. F.; Abdullah, A. Z. and Mohamed, A. R., *J. Hazard. Mater.*, (2010), 174, 1, 299–306.

90- Shaban, Y. A.; El Sayed, M. A.; El Maradny, A. A.; Al Farawati, R. Kh. and Al Zobidi, M. I. *Chemosphere*, (2013), 91, 307–313.

91- Hao, C.; Li, J.; Zhang, Z.; Ji, Y.; Zhan, H.; Xiao, F.; Wang, D. and Liu, B., *Appl. Surf. Sci.*, (2015), 331, 17–26.

92- Siddiqa, A.; Masih, D.; Anjum, D. and Siddiq, M., *J. Environ. Sci.*, (2015), 37, 100–109.

93- Adamu, H.; Dubey, P. and Anderson, J. A., *Chem. Eng. J.*, (2016), 284, 380-388.

94- Chen, I. P.; Lin, S. S.; Wang, C. H.; Chang, L. and Chang, J. S., *Appl. Catal. B: Environmental*, (2004), 50, 1, 49–58,

95- Chang, L.; Chen, I. P.; Lin, S. S., *Chemosphere*, (2005), 58, 4, 485–492.

96- Nousir, S.; Keav, S.; Barbier, J. Jr.; Bensitel, M.; Brahmi, R. and Duprez, D., *Appl. Catal. B: Environmental*, (2008), 84, 3, 723–731, 97- Xu, J., *Powder Technol.* , (2011), 210, 1, 1–5,

98- García-Muñoz, P.; Carbajo, J.; Faraldos, M. and Bahamonde, A., *J. Photochem. Photobiol. A*, (2014), 287, 8–18.

99- Messele, S. A. O. S. G. P.; Soares, J.J.M.; Órfão, C.; Bengoa, F.; Stüber, A.; Fortuny, A. and Fabregat, J. Font, *Catal. Today* (2015), 240, 73–79,

100- Masende, Z. P. G.; Kuster, B. F. M.; Ptasinski, K. J.; Janssen, F. J. J. G.; Katima, J. H. Y. and Schouten, J. C., *Top. Catal.* (2005), 33(1), 87-99 .

101- Nezamzadeh-Ejhieh, A. and Ghanbari-Mobarakeh ,Z. J., *Ind. Eng. Chem.*, (2014).

102- Sen, S. E.; Smith, S. M. and Sullivan, K. A. *Tetrahedron* (1999), 55, 12657-12698.

103- Ramamurthv, V.; Caspar, J.V. and Corbin, D.R.J. *Am. Chem. Soc.*, (1991), 113, 594-600.

104- Naswir, M.; Arita, S. Marsi, and Salni, *Journal of Clean Energy Technologies*, (2013), (1)4.

105- Joseph M. Hornback Organic chemistry. 2nd Edition Brooks Cole, (2006), Ch 15, 609-612,633.

106- Martynoff, M., Note de laboratoire: Spectres d'absorption de quelques p-quinones, Bull. Soc. Chim. Fr., (1949), 16, 258-261.

107- Shawabkeh, R. A.; Omar, A. K. and Gasan, I. B., *Inter. J. Chem.* (Toronto, ON, Can.), (2010), 2(2).

108- Santos, A.; Yustos, P. and Quintanilla, A., *Appl. Catal. B: Environ.*, (2002), 39, 97–113.

109- Sobczy´nski, A.; Duczmal, L. and Zmudzi´nski, W. *Mol. Catal. A: Chem.*, (2004), 213, 225–230.

110- Fabrizio, R. ; Marco, C.; Davide, N.; Riccardo, G.; Luca, V.; Luca, T.; Paolo, B.; Alberto, M.; Renato, B. I.; Michele, B. and Herbert, M., *Chemosphere*, (1996), 332, 159–2173.

111- Pichat, P.; Guillard, C.; Maillard, C.; Amalric, L.; D'Oliveira and J.-C. TiO_2 photocatalytic destruction of water aromatic pollutants: intermediates; properties; degrability correlation; effects of inorganic ions and TiO2 surface area; comparison with H_2O_2 Processes, J, in: D.F. Ollis, H. Al- Ekabi (Eds.), Photocatlytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, (1993), 207–223.

112- Xiusheng, M.; Shaogang, C.; Xiaobai, X. and Keyuan, H., *Environ. Chem.*, (1995), 14, 436–441.

113- Alnaizy, R. and Akgerman, A., *Adv. Environ. Res.*,(2000), 4, 233–244.

114- Drenzek, N.J.; Nyman, M.C.; Clesceri, N.L.; Block, R.C. and Stenken, J.A., *Chemosphere*, 54, (2004), 387–395.

115- Morales, R.; Melo, L.; Llanos, A. and Zaera, F., *J. Molec. Catal.*, (2005), 228, 227-232 .

116- Diaz, Y.; Melo, L.; Mediavill, M.; Albornoz, A. and Brito, J. L., *J. Molec. Catal.* , (2005), 227, 7-15.

117- De Lucas, A.; Sanchez, P.; Dorado, F.; Ramos, M. J. and Valverde, J. L., *Appl. Catal. A*, (2005), 215-225.

118- Xie, J.; Meng, W.; Wu, D.; Zhang, Z. and Kong, H., *J. Hazard. Mater.*, (2012), 231- 232, 57-63.

119- Davis, B. Molecular Sieves Principles of Synthesis and Identification, Van Nostrand Reinhold, New York, USA, (1989), 422.

120- Bibby, D.M.; Aldridge, L.A. and Milestone, N.B. ,*J. Catal,* (1981), 72, 373.

121- G¨ulten AKC_AY, M. Kadir YURDAKOC, *J. Chem.,* (1999) , 23, 105 - 113.

122- Denis L.G.; Claudio A.; Vanda P.L. and Romulo S.A. , *J. Hazard. Mater.*, (2008), 155, 230.

123- Brunauer, S.; Emmett, P.H. and Teller, E., *J. Am. Chem. Soc.*, (1938), 60, 309.

124- Sowmiya M., Sharma A., Parsodkar S., Mishra B.G. and Dubey A., *Appl. Catal. A*, (2007), 333, 272.

125- Jens Weitkamp, *Solid State Ionics*, (2000), 131, 175–188.

126- Ku¨hl, G.H., *J. Phys. Chem. Solids* (1977), 38, 1259.

127- Lago, R.M.; Haag, W.O.; Mikovsky, R.J.; Olson, D.H.; Hellring, S. D. and Schmitt, K.D. , in Y. Murakami, A. Iijima, J.W. Ward (Eds.), ″New Developments in Zeolite Science and Technology: Studies in Surface Science and Technology ″, Kodansha/ Elsevier, Tokyo/Amsterdam, (1986), Vol. 28, 677.

128- Jiménez, C.; Romeroa, F. J.; Roldán, R.; Marinas, J. M. and Gómezb, J. P., *Appl. Catal. A*, (2003), 249, 175–185.

129- Shaban, Y. A.; El Sayed, M. A.; El Maradny, A. A.; Al Farawati, R. Kh. and Al-Zobidi, M. I., *Chemosphere*, (2013), 91, 307–313.

130- Carvill, B.T.; Lerner, B.A.; Adelman, B.J.; Tomczak, D.C. and Sachtler, W.M.H., *J. Catal.*, (1993), 144, 1–8.

Arabic summary

الملخص العربي

دراسة عن ازالة بعض المركبات الفينولية من مياه الصرف الصناعي

تنقسم الرسالة الي ثلاثة فصول:

<u>الفصل الاول</u>:

ويتضمن المقدمة وفيها استعراض لمشكلة تلوث المياه وأسباب التلوث وايضا استعراض لمشكلة التلوث عن طريق المركبات العضوية وخصوصا المركبات الفينولية وفي هذه الدراسة تم اختيار الفينول كمثال للمركبات الفينولية لانه يعتبرمركب وسيط للمركبات الفينولية الاخري فى عملية الاكسدة مثل الكلوروفينول والنيتروفينول.

كما تناولت المقدمة خصائص الفينول والمصادر التي ينتج منها مثل صناعة المبيدات ومحطات تكرير البترول كما تضمنت تأثيره علي الصحة العامة.كما تناولت المقدمة طرق الازالة المستخدمة قديما وحديثا.

ومن طرق الازالة المستخدمة حديثا وهي عن طريق الاكسدة الي ثاني أكسيد الكربون والمياه.

وايضا في عملية الاكسدة تم الاستعانة بعامل حفاز لتقليل الظروف الخاصة بدرجة الحرارة والضغط المستخدمة في طرق الاكسدة التقليدية.

كما تم استعراض نبذة عن العوامل الحفازة التي سيتم استخدامها في الدراسة وهي ثلاثة مركبات تحتوي علي الالومنيوم والسليكون بنسب مختلفة وهي الزيوليت والموردينيت والبنتونيت وتم استعراض خصائص تلك المركبات.

وأخيرا يتضمن الفصل الاول أهداف الدراسة والتي تتلخص في:

- تحضير عدد من العوامل الحفازة ثنائية التأثير عن طريق تحميل عنصر

البلاتين بتركيزين مختلفين علي الزيوليت.

- توصيف تللك العوامل بطرق التوصيف المختلفة.

- تطبيق عملية الازالة للفينول مع دراسة العوامل المؤثرة علي عملية الازالة من درجة حرارة ودرجة الحموضة وتطبيق تللك الظروف علي تركيزات مختلفة من الفينول وايضا استخدام كميات مختلفة من العوامل الحفازة وأخيرا دراسة تأثير الأشعة فوق البنفسجية الفئة C (١٠٠- ٢٨٠نانوميتر).

- وفي النهاية يتم اختيار انسب الظروف لكل عامل حفاز.

الفصل الثاني

يتضمن الفصل الثاني المواد والمحاليل المستخدمة في تحضير العوامل الحفازة.

وايضا تضمنت الأجهزة المستخدمة في عمليات الازالة للفينول وأيضا الاجهزة المستخدمة في توصيف العوامل الحفازة.

وأخيرا الطرق المسخدمة في تحضير العوامل الحفازة وايضا البرنامج الإحصائي الخاص لحساب نسبة الإزالة.

الفصل الثالث

ويمثل عرض النتائج ومناقشة نتائج الدراسة الحالية والتي تتلخص في الاتي:

- عمليات التوصيف الخاصة بالعوامل الحفازة التي تم تحضيرها والتحليل الكيميائي للزيوليت والموردينيت والبنتونيت.

- تم عمل تجربة لإزالة الفينول لدراسة عنصر الوقت الخاص بكل عامل حفاز وتم عمل رسم بياني يوضح الوقت اللازم لحدوث اعلي نسبة إزالة.

- تم عمل دراسة للعوامل المؤثرة علي إزالة الفينول واستنتاج الظروف المناسبة لحدوث اعلي نسبة إزالة .

- دراسة درجة الحرارة أظهرت وجود تأثير لدرجة الحرارة تأثيرا طرديا علي الإزالة والوصول لأعلي نسبة إزالة عند درجة حرارة ٥٠° مئوية لكل العوامل

الحفازة ماعدا الموردينيت حيث يوجد تأثيرطفيف لدرجة الحرارة.

- تم ايضا دراسة تأثير درجة الحموضة علي عملية الإزالة ووجود تباين في درجة الحموضة للعوامل المستخدمة للحصول علي أعلي نسبة إزالة.

- دراسة تأثير إستخدام تركيزات مختلفة من الفينول ووجود تأثير عكسي بينه وبين نسبة الإزالة.

- وأخيرا دراسة زيادة كمية العامل الحفاز ووجود تأثير طردي علي نسبة الإزالة لكل العوامل الحفازة المستخدمة في الدراسة.

- وفي النهاية تطبيق استخدام الأشعة فوق البنفسجية الفئة C (١٠٠- ٢٨٠ نانوميتر) ووجد ان لها تأثير لها حيث انها تساعد علي ارتفاع نسبة الإزالة. ثم عمل جدول يوضح الظروف المناسبة لكل عامل حفاز ووجد ان العوامل الحفازة المكونة من الزيوليت (ZSM5) وعنصر البلاتين(0.5%- 1%) هي الانسب لازالة الفينول لانها ثلاثية الابعاد بعكس الموردينيت .

جامعة قناة السويس

كلية العلوم بالإسماعيلية

موافقة مجلس الكلية

وافق مجلس كلية العلوم –جامعة قناة السويس بتاريخ / /٢٠١٦ ، كما وافق نائب رئيس الجامعة بتاريخ / / ٢٠١٦ علي منح درجة الماجستير في العلوم (كيمياء عضوية) للطالب /**أحمد حسين فتحي محمد عبد الفتاح** (من الخارج) تحت عنوان:

دراسة عن إزالة بعض المركبات الفينولية من مياه الصرف الصناعي

لجنة الحكم والمناقشة:

١ - أ.د/ محيي الدين عبد الفتاح عبد العاطي ....

أستاذ الكيمياء العضوية-رئيس قسم الكيمياء – كلية العلوم-

جامعة قناة السويس بالاسماعيلية

٢ - أ.د/ إبراهيم السيد محيي الدين ....

أستاذ الكيمياء العضوية- رئيس قسم الكيمياء – كلية العلوم-

جامعة بورسعيد - بورسعيد

٣- عن لجنة الاشراف

أ.د/ جيهان عبد الرازق حسنين ....

أستاذ الكيمياء العضوية- قسم الكيمياء – كلية العلوم-

جامعة قناة السويس بالاسماعيلية

وكيل لشئون الكلية للدراسات العليا والبحوث **عميد الكلية**

أ.د **أ.د**

عنوان الرسالة

دراسة عن إزالة بعض المركبات الفينولية من مياه الصرف الصناعي

اسم الطالب/ أحمد حسين فتحي محمد عبد الفتاح

اسم الدرجة العلمية/ رسالة الماجستير في العلوم (كيمياء عضوية)

تاريخ المناقشة/ ٢٧/ ٣ / ٢٠١٦

لجنة المناقشة **التوقيع**

١- أ.د/ محيي الدين عبد الفتاح عبد العاطي ....

أستاذ الكيمياء العضوية-رئيس قسم الكيمياء –
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٢- أ.د/ إبراهيم السيد محيي الدين ....

أستاذ الكيمياء العضوية- رئيس قسم الكيمياء

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٣- أ.د/ جيهان عبد الرازق حسنين ....

أستاذ الكيمياء العضوية- قسم الكيمياء –

كلية العلوم- جامعة قناة السويس بالاسماعيلية

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دراسة عن إزالة بعض المركبات الفينولية من مياه الصرف الصناعي

اسم الطالب/ **أحمد حسين فتحي محمد عبد الفتاح**

لجنة الإشراف **التوقيع**

١- أ.د /جيهان عبد الرازق حسنين ....

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– كلية العلوم- جامعة قناة السويس بالاسماعيلية

٢- د./ داليا رضوان عبد الحافظ ....

باحث بقسم التكرير- معهد بحوث البترول

-القاهرة

جامعة قناة السويس
كلية العلوم بالإسماعيلية
قسم الكيمياء

دراسة عن إزالة بعض المركبات الفينولية من مياه الصرف الصناعي

رسالة مقدمة من

أحمد حسين فتحي محمد عبد الفتاح

بكالوريوس العلوم (٢٠٠٤)

كجزء من متطلبات الحصول علي درجة الماجيستيرفي العلوم

في

الكيمياء (الكيمياءالعضوية)

الي

قسم الكيمياء

جامعة قناة السويس

٢٠١٦