REMOVAL OF NITROGEN CONTAINING ORGANIC COMPOUNDS USING CATALYTIC WET AIR OXIDATION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2005

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this dissertation entitled **"REMOVAL OF NITROGEN CONTAINING ORGANIC COMPOUNDS USING CATALYTIC WET AIR OXIDATION"**, in the partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in **"Industrial Pollution Abatement"**, submitted in the department of **CHEMICAL ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY, ROORKEE**, is an authentic record of my own work carried out during the period from July 2004 to June 2005 under the guidance of **Dr. Shri Chand,** Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree of this institute or any other institute.

Dated: June, 28, 2005
Place: IIT Roorkee.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENTS

I take the opportunity to pay my regards and a deep sense of gratitude to **Dr. Shri Chand**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, for his keen interest, constant guidance and encouragement throughout the course of this work. His experience and deep insight of the subject helped this work always on a smooth and steady path. Useful criticism and personal help extended in hour of need had been immensely useful. It is with great pleasure and deep sense of indebtedness I wish to express my sincere thanks to him.

Thanks are due to **Dr. B. Mohanty**, Professor and Head, Department of Chemical Engineering, for providing all the required facilities during the dissertation.

I am indebted to Dr. I.D. Mall, Associate Professor, Department of Chemical Engineering, whose enthusiastic association helped me a lot, especially in providing Pollution lab facilities for the successful completion of this dissertation work.

I wish to acknowledge my thanks to Dr. I. M. Mishra, Professor, Department of Chemical Engineering and Dr. B. Prasad, Assistant Professor, Department of Chemical Engineering for their valuable suggestion and support during my dissertation work.

I am also thankful to Mr. A. Prasad, Lab Assistant, Mass Transfer Research Lab, Department of Chemical Engineering for his help provided during my work.

I am greatly indebted to my friends whose enthusiastic support, encouragement and help, made me come up with this report.

It is very hard to express my feeling in proper words for my parents who apart from providing me the best available education have encouraged me in all my endeavors. I owe much of my academic success to them.

Though it is not possible to mention everyone, none can be forgotten for their direct/ indirect help.

Date: 28/06/05

(RAJA RAMAN CHAUDHARY)

ABSTRACT

Wastewater treatment and re-use of industrial process water is a critical issue for the suitable development of human activities. The need for effective water recycling has reinforced the research on tailored low cost pollution abatement since the existing solutions are no longer universal. The nitrogen-containing organic waste produced in industries is usually characterized by high concentration and high temperature, and is not treatable by biological methods directly. In particular, the Catalytic Wet Air Oxidation (CWAO) process is one of the most promising technologies for the remediation of moderately concentrated and toxic pollutants with the use of a stable and active catalyst.

The experimental runs were conducted in a stainless steel high pressure reactor. In this study, a hydrophobic Cu-Co/C (Copper 5% wt.-Cobalt 5%wt. supported on carbon) catalyst (heterogeneous) and $CuSO_4$ (homogeneous catalyst) were first used in a batch reactor to remove nitrogen containing organic compound from wastewater. For this purpose, the catalytic activity and stability of copper and cobalt based catalyst supported by activated carbon was tested for the catalytic wet air oxidation of the target compound, pyridine at mild conditions of temperature and pressure. Copper and cobalt, are relatively inexpensive catalytic material and have shown stability to yield higher conversion efficiencies. Kinetic modelling of the results is also undertaken using the classical gradient based method. Detailed kinetic analysis of CWAO is shown.

It was found that higher temperature and higher oxygen partial pressure enhanced the removal of pyridine. In our study the initial pH of the sample was optimised which was 4 for both the catalyst. Apart from that the catalyst concentration also plays important role in getting higher conversion efficiencies. Both the catalysts were studied at various reaction conditions and found that $CuSO_4$ is more active as compared to Cu-Co/C. The highest reactivity of 75.1 was observed using 5mg/l concentration of $CuSO_4$ catalyst at 160 °C, 9 bar total pressure after 2 hour reaction time. The kinetics of the reaction shows a first order reaction with respect to substrate concentration.

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NOMENCLATURES

BOD : Biochemical oxygen demand
COD : Chemical oxygen demand
E (P) Act : Environmental protection act
EIA : Environment impact assessment
PAC : Poly aluminum chloride
ppt : Precipitation
TC : Total carbon
TOC : Total organic compound
TSS : Total suspended solid
TDS : Total dissolved solids
TS : Total solids
WAO : Wet air oxidation
WO : Wet oxidation
CWAO : Catalytic wet air oxidation.

SYMBOLS

C_o : Initial concentration.
P_T : Total Pressure in the reactor.
T : Temperature (°C)
T : Time (hours)

CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

A significant challenge confronting engineers and scientists in developing countries is the search for appropriate solutions to the collection, treatment and disposal or reuse of domestic and industrial waste. There is increasing environmental concern worldwide regarding the disposal of wastewater containing non-biodegradable organic compounds. Since most pollutants do not respect national boundaries, a worldwide effort to monitor their movement and to develop tools to prevent them from polluting environmental components or to remediate consequent pollution is desirable.

The problems of water quality in developing countries are in most cases caused by expanding industries, agricultural activities, and rapid urbanization. India is one of the developing countries, which faces water pollution due to growing industrial activities. Generally, there are very few wastewater treatment facilities. The most widely used treatment systems in India include stabilization ponds, and natural and constructed wetlands, most of all using biological processes. The effluents from chemical and related industries contain organic compounds, which cannot be treated by conventional biological oxidation. The process industries that have a significant wastewater effluent include refining, chemicals, petrochemicals, pharmaceuticals, agrochemicals, and pulp and paper industries. The organic pollutants e.g. nitrogen containing compounds such as Pyridine and Aniline, are toxic and cause considerable damage and threat to the ecosystem in water bodies and to the human health.

Industrial activities have been fast expanding for the past decades in India. In India, most industries commenced during the colonial and post-independence period and were established without adequate environmental consideration. These industries include, among others, petrochemical, chemical, and pharmaceutical industries, which use both natural and synthetic organic chemicals. Water pollution is caused by both synthesis and the application of industrial products in such areas as: nutrition, transportation, accommodation and energy exploitation. Although not always acknowledged, chemical activity is indispensable to sustaining life; also it is needed to achieve and maintain a high standard of living. Examples of products needed in modern life include medicaments, cleaning and disinfecting products, cosmetics, stabilizers, artificial fertilizers, pesticides, fuel, batteries, polymers (thermoplastics, thermosetting resins, elastomers, fibres), paint and dyes. These product classes inevitably result into pollution during their production, use and disposal (Patnaik, 1999 [61])

Improper discharge of wastewater containing toxic organic compounds such as pyridine, aniline, phenol and its derivatives presents a major threat to the environment and must be prevented because of the extreme toxicity to aquatic life even at concentration levels of the order of 1.0 ppm (Wang, 1992 [74]; Lee et al., 1992 [44]). These reasons call for the development of more feasible, effective and efficient effluent treatment technologies, which accomplish the destruction of these wastes into non-toxic or biodegradable end products.

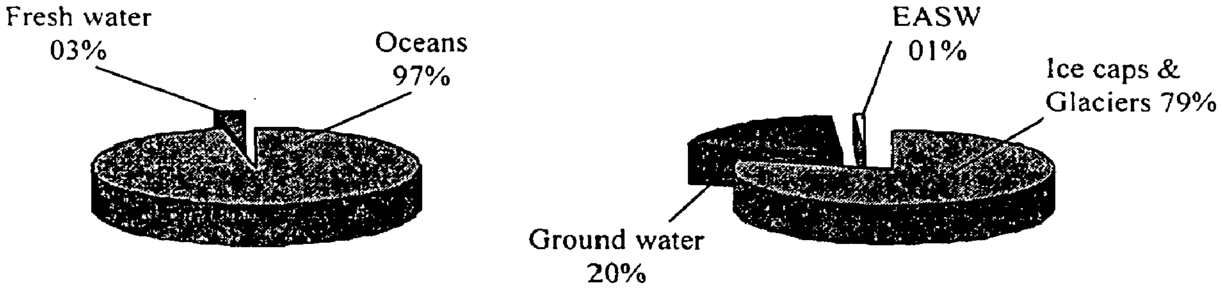
While water quality appears to be degraded with industrial growth, agricultural expansion and rapid urbanization in developing countries like India, it is unfortunate that little information is available to evaluate the extent to which chemical contamination has impacted the health of people and of freshwater ecosystems. According to the World Meteorological Organization (WMO, 1997 [77]), the total surface water withdrawal in India during the year 1994 was 1.2 km^3, of which the percent withdrawals by sector were: agriculture (89%), domestic (9%) and industry (2%). For water pollution control, it has become necessary, in recent years, to remove nitrogenous components from wastewater, particularly organic compounds, which is responsible for toxic water pollution in rivers and lakes. The technologies used for the treatment of such wastes should preferably achieve the destruction of the hazardous waste components to give innocuous end products

Owing to the worldwide emphasis on the industrial and other wastewater problem. Biological processes, air stripping and breakpoint chlorination methods are well developed and have been applied to remove nitrogen from some industrial or domestic wastewaters. Supercritical water oxidation and catalytic wet oxidation are still under development. Wet oxidation has been successfully operated in treating toxic organic compounds and sewage sludge. However, ammonia is usually one of the end products in the wet oxidation process and it is difficult to oxidize it further.

This introductory chapter presents the context of the research and the objectives for undertaking catalytic wet oxidation studies using copper-cobalt catalysts. This chapter provides an overview of the water pollution problems and challenges related to water pollution in India and other developing countries.

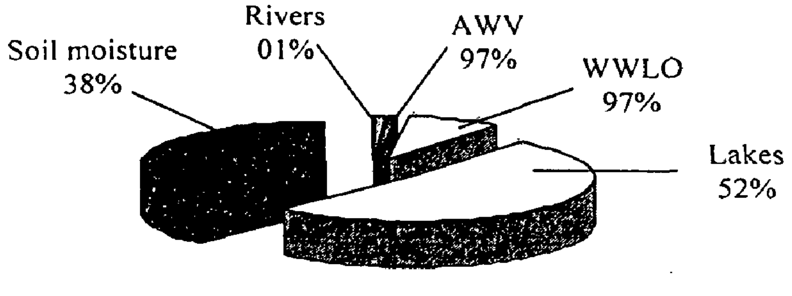
1.0 GENERAL

Water is the most precious natural resource that exists on our planet as over 70% of the Earth's surface is covered by water. The oceans contain 97% of the earth's water, while the remaining 3% is classified as fresh water. Seventy-nine percent of this surface fresh water is stored as ice and glaciers and 20% as groundwater. The remaining freshwater, which is about 1% of the world's total, is contained in lakes, rivers, soil moisture etc., as shown in Fig. 1.1. It can be seen that the water available for humankind use is very small as such it needs to be protected from all forms of contamination.



Total Water

Fresh Water



Easily Assessable Surface Water

Fig. 1.1 Distribution of World's Water
EASW: easily assessable surface water, AWV: atmospheric water vapors,
WWLO: water within living organisms

Surface water is the resource for the provision of drinking water, irrigation water for agricultural activities, and process water for industrial activities. Since water means new potential, new hope for a better tomorrow and new life, human settlement and development has concentrated around water resources. As such the most densely populated and commercially developed areas are the shorelines of oceans, lakes and rivers.

Although on the one hand this fact is recognized, on the other hand it is disregarded by polluting rivers, lakes and oceans, since the same water bodies are used as depository of wastes. During use, water becomes contaminated with various kinds of substances. In many regions, particularly in parts of the developing world, poverty combined with rapid population growth is leading to widespread degradation of water resources. At the same time, rapid urbanization and industrialization in many developing countries are creating high levels of water pollution associated with harmful industrial effluents and sewage discharges. Agricultural activities have created problems in water receiving bodies due to run-off, which bring with them pesticides and fertilizers (Shiklomanov, 1997 [68]). Since only a little amount of water is available for human needs, it is therefore important to preserve water resources in order to enhance both current and future potential.

In order to manage environmental pollution at global level, the United Nations Environmental Program (UNEP, 1972) [73] in was designed to be the "environmental conscience of the United Nations". In response to this, towards the end of the 20th Century, environmental legislation in most, if not all countries has been enacted to safeguard environmental integrity. Legislation has put in place stringent regulations regarding environmental and health quality standards, especially on the utilisation of water resources. However, even with these stringent measures pollution of water resources is still a major problem. In order to combat water pollution, it is important to understand the sources of and problems related to polluting agents.

1.1 MAJOR SOURCES OF WATER POLLUTION

Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of unwanted material to the water. When it is unfit for its intended use, water is considered polluted. The source of water pollution may be a point or a non-point source. Point sources of water pollution occur when harmful or toxic substances are emitted directly into a water body at a single point of discharge. The oil spill from the Refineries, Fertilizer, Leather and other Chemical Industries well illustrates a point source. A non-point source delivers pollutants via a wide area. An example of this type of water pollution is when pesticides or fertilizers are washed from agricultural fields by rain, run-off into a water body such as lake or river. While pollution arising from non-point sources accounts for the majority of contaminants in streams and lakes, it is much more difficult to control. Table 1.1 shows a summary of major pollution sources and their effects. The level of nutrients such as nitrates and phosphorus in the freshwater ecosystems and toxicity due to pesticides is still a problem in the world.

Table 1.1 Common water pollutants and their effects

POLLUTANT	PRIMARY SOURCE	EFFECTS
Organic matter	Industrial wastewater and domestic sewage	Depletes oxygen from the water column as it decomposes, stressing or suffocating aquatic life.
Excess nutrients (nitrates, phosphorous)	Run-off from agricultural lands and urban areas	Over-stimulates growth of algae (a process called eutrophication), which then decomposes, robbing the water oxygen and harming aquatic life. High levels of nitrates in drinking water lead to illness in humans
Heavy metals	Industries and mining sites	Persists in freshwater environment, like river sediments and wetlands, for long periods. Accumulates in the tissue of fish and shellfish. Toxic to both aquatic organisms and humans who eat them

Microbial contaminants (e.g. cryptosporidium, cholera and other bacteria, amoebae, etc.)	Domestic sewage, cattle, natural sources	Spreads infectious diseases through contaminated water supplies, causing millions of cases of diarrhoea diseases and intestinal parasites, and providing one of the principal causes of childhood mortality in the developing world
Toxic organic compounds (oil, pesticides, some plastics, industrial chemicals)	Wide variety of sources, from industrial sites, to automobiles, to farmers and domestic gardeners	Displays a range of toxic effects in aquatic fauna and humans, from mild immune suppression, to acute poisoning, or reproductive failure
Dissolved salts (salinization)	Leached from alkaline soils by over-irrigation, or drawn into coastal aquifers from over-drafting of groundwater	Leads to salt build-up in soils, which kills crops or cuts yields. Renders freshwater supplies undrinkable
Acid precipitation or acid run-off	Deposition of sulphate particles, mostly from coal combustion. Acid run-off from mine tailings and sites	Acidifies lakes and streams, which harms or kills aquatic organisms and leaches heavy metals such as aluminum from soils into water bodies
Silt and suspended particles	Soil erosion and construction activities on watersheds	Reduces water quality for drinking and recreation and degrades aquatic habitats by smothering them with silt, disrupting spawning, and interfering with feeding

Thermal pollution	Fragmentation of rivers by dams and reservoirs, slowing water and allowing it to warm. Industrial uses such as cooling towers	Affects oxygen levels and decomposition rate of organic matter in water column. May shift the species composition of a river or lake

In most cases, the major causes of these contaminants are the industrial processes, increased use of pesticides, manure and industrial fertilizer in agriculture. In the USA, for example, agriculture is the greatest source of pollution degrading the quality of surface waters like rivers and lakes as shown in Table 1.2 (Carpenter et al., 1998) [09]. Similarly, despite some positive trends in Europe, the overall state of many European rivers with respect to nutrient concentrations remains poor (European Economy Agency, 1998) [18]. Dissolved nutrients act as fertilizers, stimulating algal blooms and eutrophication of many inland waters. Dissolved nitrates in drinking water can also harm human health.

While most industrialized countries have greatly reduced the effects of these pollutants from point sources such as factories and sewage treatment plants, in most developing countries like India the traditional pollution sources like sewage are still a major problem particularly near urban centers. An estimated 90 percent of wastewater in developing countries is still discharged directly into rivers and streams without any waste processing treatment (Mato., 2002 [54]; WMO, 1997 [77]). Other pollutants like pesticides and fertilizers pollute the water receiving body in both urban centers and agricultural areas.

Table 1.2 Nitrogen and phosphorous discharge into U.S. surface waters from point and non-point sources (in thousands of metric tons per annum) (Carpenter et al., 1998) [09]

SOURCE	NITROGEN	PHOSPHORUS
Non-point sources		
Crop lands	3,204	615
Pastures	292	95
Rangelands	778	242

Forests	1,035	495
Other rural lands	659	170
Other non-point sources	695	68
Total non-point discharges	**6,663**	**1,658**
Total point sources	1,495	330
Total discharge (point + non-point)	8,158	2,015
Non-point as a percentage of total	**82%**	**84%**

Agricultural activities in India pollute waters through the application of pesticides, herbicides and fertilizers. The use of pesticides and fertilizers in India has been increasing over the last 10-15 years and it is likely to continue increasing in the future. A large amount of expired pesticides are improperly stored in some parts of the country, thus causing a threat to the aquatic environment. Another significant water pollutant comes from various industrial manufacturing processes such as pyridine manufacturing.

1.2 SOURCES OF SOME NITROGEN COMPOUNDS IN WASTEWATER

Before presenting the most relevant results on the treatment of waters contaminated by nitrogen-containing compounds, it seems necessary to remember the origin of the pollution by nitrogen. Some nitrogenous compounds are produced naturally like amine acids, proteins or humic substances. Also, human metabolism produces urea and ammonia. However, most of the products come from industrial activity and in particular from chemical, petrochemical and food industries. In the case of aniline and its colourful derivatives, manufacturer and user of dyes, such as textile industrial processes, are more particularly concerned. It is indeed estimated that 15% of the world production of dyes are lost during their fabrication or their use; this corresponds to a world-wide throwing out of 128 tones per day. Sewage treatment units and agriculture are also responsible for the presence in the environment of a large range of nitrogenous compounds. Among the family of organic compounds there are many nitrogen containing organic compounds in which nitrogen is contained in one or other forms the most concerned ones are aniline, nitrobenzene, acrylonitrile and pyridine, of these pyridine is contaminating the water and aqueous environment during it manufacturing itself and thus need special treatment for its removal.

1.3 WET AIR OXIDATION

1.3.1 Why Wet Air Oxidation?

the various treatment processes available are chemical treatment physical treatment (adsorption, reverse osmosis etc), biological treatment, wet air oxidation etc, more often a combination of two or more method is used to get better results of treatment.

Chemical treatment is used for pH adjustment, coagulation of colloidal impurities (using alum, PAC, $FeSO_4$ etc), precipitation of dissolved pollutants (metal removal as hydroxides, carbonates etc), reduction and sludge conditioning. However chemical treatment is usually costly if large volumes are to be treated particularly if the waste is organic in nature. In this view chemical treatment is usually used a pretreatment for pH adjustment color removal and removal of toxic compounds so that the other treatment method such as biological treatment can be used.

Biological treatment is a method suitable for nearly all the applications. However it is necessary for the resulting sludge to be disposed of by either land filling of burning with a corresponding expenditure of energy following elaborate thickening and dewatering procedures. In spite of this it is the most popular treatment method. It is popular to the extent that the wastewaters those are not suitable for bio-treatment due to toxicity or high organic loads are treated by other means to make the final effluent suitable for bio-treatment. The disadvantages of biological treatment are that it requires a large area of land which is costly and may not be always available. Further biological treatment processes react unfavorably to shock loads.

Adsorption method for treatment of various pollutants is used by use of activated carbon, organic residues and some synthetic resins. This method is also favorable particularly for high molecular weight organics having low solubility in water. Carbon treatment is an attractive method if the spend carbon can be regenerated by bio-treatment, solvent extraction and WAO etc.

Reverse osmosis is a membrane process used for desalination of brackish water and removing dissolved solids from certain industrial wastewaters. A concentrated and much smaller waste stream are produced presumably making disposal simpler. However the technique is not frequently used primarily due to high membrane replacement costs.

Wet air oxidation is a well established technique for treating wastewater particularly the toxics and highly organic wastes. Wet sir oxidation involves the liquid phase oxidation of organic or oxidizable inorganic components at elevated temperatures (125 – 320 °C) and at high pressure in the range of 0.5 MPa to 20 MPa or more using gaseous source of oxygen. Enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. The elevated pressures are required to keep water in liquid state. Water also acts as a moderant by providing a medium for heat transfer and removing excess heat by evaporation. WAO has been demonstrated to oxidize organics compounds to CO_2 and other innocuous end products.

1.3.2 Theory of Wet Air Oxidation

Basically four types of oxidation processes can be used to treat aqueous wastes polluted with organic matter.

1. Activated Sludge Processes (Rahmani. H., 1993 [63]), which are suitable neither for toxic waters nor for chemical oxygen demand (COD) above about 10 gm/l -l (10 000 ppm). This process requires long residence times for the decomposition of COD components. It also produces large amounts of sludge.

2. Incineration, which is appropriate for effluents having a COD greater than about 100gm/l -1 (100 000 ppm), but is handicapped by energy cost, corrosion problems and the ecological perception of a process which can disseminate products of incomplete combustion and dust in the atmosphere.

3. Chemical Oxidation at ambient temperature using strong oxidisers (Ernst et al., 1980 [19]; Dorr, M. 1989 [16]) like chlorine or ozone, suitable for very low concentrations. These processes, however, have various drawbacks such as production of chloramines, operation costs, etc.

4. Wet Oxidation in the liquid phase at high temperature. In this case, it is necessary to consider various possibilities. The first one is wet oxidation by hydrogen peroxide with ferrous salts at temperatures around 100°C (Debellefontaine et al., 1996 [14]). This is reliable and adaptable, but its operation cost, mainly bound to the oxidiser. The second one is oxidation in the supercritical state (Webley, et al., 1991 [75]). This is very efficient, but extremely drastic conditions for temperature and pressure limit the development of the process. Wet air oxidation is the third possibility. This process uses a clean oxidiser and is suitable for removal of nitrogen loads and toxic wastes and particularly organic nitrogen and ammonia can be treated, and energy recovery is feasible. A recent paper (Chak-chouk et al., 1995) [11] reports the testing of WAO as a possible route to eliminate organic nitrogen ranging from 10 to 100 mg/l (10,000-100,000 ppm). It is an enclosed process, having a very limited interaction with the environment.

Wet oxidation is an attractive destruction method for the treatment of waste streams which are too dilute to incinerate and too concentrated for biological treatment. Wet oxidation can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures.

The original development work done on WAO took place some fifty years ago. More than 60 years ago, Zimmerman [80], was looking for an alternative method to treat special black liquor form paper mills. Because of their very high silica content, the usual evaporation and combustion method (kraft process) was unsuitable. Zimmerman [80] did extensive testing of wet air oxidation technology and its application to treating spent pulp mill liquor. Zimmerman [80] found he could burn pulp mill liquor and described a method using air at high pressure leading to the combustion of organic compounds dissolved or suspended in liquid water at a relatively low temperature as long as oxygen was present.

The basic idea of the WAO process (Zimmermann, 1960 [80]) is to enhance contact between molecular oxygen and the organic matter to be oxidised. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by high pressure, which also increases the concentration of dissolved oxygen (Himmelblau, 1960 [29]) and thus the oxidation rate.

The process can treat any kind of waste produced by various branches of industrial activity or sludge produced by the conventional treatment processes (physical, chemical, biological, etc.) (Harada, et al. 1994 [27]). WAO is one of the few processes that do not turn pollution from one form to another, but actually eliminate it. Usually, at about 250°C, practically all compounds, except acetic and propionic acids, can be completely transformed. Under such conditions, the final product is not only carbon dioxide but various carboxylic acids, mainly acetic acid according to Foussard et al. (1989) [21]. Acetic acid needs the most extreme conditions (320°C) to oxidise to carbon dioxide.

1.3.3 WAO Reaction Concepts

The type of oxidant for a given organic compound may influence both the reaction mechanism and pathway. The most reported oxidizers for oxidation of dilute aqueous solutions of organic compounds are: hydrogen peroxide, the hydroperoxyl radical, the hydroxyl radical, the ozone radical ion, ozone and atomic oxygen.

The majority of work using ozone to oxidize phenol has been carried out at ambient temperatures, since ozone is a powerful oxidant even at low temperatures. In wet oxidation reactions, the two commonly used oxidants have been oxygen (either molecular oxygen or in air) and hydrogen peroxide. Other oxidizers are widely used in advanced oxidation processes (AOP's) due to the fact that these processes aim at in-situ production of the oxidizers.

In wet oxidation, water with dissolved oxygen is used to oxidize the target compound. The main reactions are described in eq. (1.1) to (1.8). Hydroxyl radicals are produced from the dissociation and oxidation of water according to eq. (1.1) and (1.2). Hydroperoxyl radicals are formed from the oxidation of water (eq. 1.2) and the target compound RH (eq. 1.6). Hydroxyl radicals are also produced from hydrogen peroxide (eq. 1.4) and from the reaction of atomic oxygen with the target compound (eq. 1.8). Hydrogen peroxide is produced by the recombination of hydroperoxyl radicals (eq. 1.3) or by the reaction of hydroperoxyl radicals with the target compound (Eq. 1.7). Atomic oxygen is produced from the dissociation of oxygen (Eq. 1.5). Although the hydroperoxyl radical is less reactive than the hydroxyl radical, it plays an important role because of its relative abundance.

$H_2O \rightarrow OH + H$ .... (1.1)

$H_2O + O_2 \rightarrow OH + HO_2$ .... (1.2)

$2HO_2 \rightarrow H_2O_2 + O_2$ .... (1.3)

$H_2O_2 \rightarrow 2OH$ .... (1.4)

$O_2 \rightarrow 2O$ .... (1.5)

$RH + O_2 \rightarrow R + HO_2$ .... (1.6)

$RH + HO_2 \rightarrow R + H_2O_2$ .... (1.7)

$RH + O \rightarrow R + OH$ .... (1.8)

During catalytic wet oxidation (CWO), oxygen may participate in reaction either as an adsorbed species on the catalyst surface or as a part of the lattice oxygen present in metal oxides (Matatov-Meytal et al. 1998) [55]. Both free radical (homolytic) and ionic (heterolytic) oxidation reaction mechanisms have been proposed for the oxidation of aromatic compounds, resulting in a ring-opening reaction.

This shows that the WAO process is very efficient but only under severe temperature conditions. A free radical chain reaction mechanism accounts for the wet oxidation of organic compounds. The global equation rate is presented in eq (1.9). In most cases, a first-order reaction with respect to the organics is observed (Lixiong et al., 1991 [46]). Usually, the partial order with respect to oxygen ranges from 0 to 0.5 (Lixiong et al., 1993 [47]), but Joglekar et al. (1991) [26] have reported values close to 1, typical of an oxygen-transfer limitation or of an auto-catalytic effect of phenolic compounds.

$$Rate = k_o.\exp(-E_a / RT).[C]^{\alpha}.[dissolved\, O_2]^{\beta} \qquad \text{..................} (1.9)$$

where,

k_o = pre-exponential factor ($(g\, litre^{-1})^{(1-\alpha-\beta)} \min^{-1}$)

E_a = activation energy (J/mol)

R = ideal gas constant (8.314 J/mol-K)
T= temperature (K)
[C] = concentration of the organic reactant (g/litre)
[dissolved 0_2] = concentration of the oxidant (g.litre)
α = partial order of the reaction with respect to the organic reactant; and
β = partial order of the reaction with respect to the oxidant.

Typical conditions for wet oxidation range from 180°C and 2 MPa to 315°C and 15 MPa. Residence times may range from 15 to 120 min and the COD removal may typically be about 75 to 90%.

1.3.4 Catalytic Wet Air Oxidation

Wet air oxidation of nitrogen containing organic compounds in water using noble/non noble metal catalysts seems to be a promising and an environmental friendly method to improve water quality. The process uses air/oxygen as the oxidant, which is contacted with the organic compound over a catalyst at elevated temperatures and pressures. The WAO process is capable of converting nitrogen organic contaminants ultimately to carbon dioxide and water and other compounds such as nitrogen into its inert forms. However, one of the major drawbacks of noble metal catalysts, such as platinum, is deactivation during liquid phase oxidation. Furthermore, catalytic wet oxidation technology is, at present, one of the costliest processes of pollution control.

Various types of catalysts have been tested in order to lower the temperature and pressure constraints and to increase the oxidation rate. Chowdury et al. (1975) [12] have demonstrated the catalytic effect of Fe 2^+ and Cu 2^+ salts and peroxides. More promising results have been obtained by continuously injecting hydrogen peroxide with ferrous salts in a batch reactor (Debellefontaine et al., 1992 [13]). The addition of about 10 ppm of Removal of nitrogenous compounds from aqueous wastes ferrous iron with less than 15% (of the amount for a stoichiometric oxidation) of hydrogen peroxide can turn the high-pressure WAO process into a medium pressure one.

Organic nitrogen compounds are easily transformed into ammonia, which is very stable in WAO conditions. Fig. 2 shows a basic flow diagram of a WO plant, which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat- exchanger as well as a reactor with a relief valve and a downstream separator. The waste is retained in the reactor for a sufficient period of time to achieve the desired chemical oxidation (30-120 min). The simplest reactor design is usually a co-current vertical bubble column with a height- to-diameter ratio in the range of 5-20. Some design aspects of WO reactors have been reported. About 100 plants are in operation today, mostly to treat waste streams from petrochemical, chemical and pharmaceutical industries as well as residual sludges from waste water treatment. These plants aim either at a complete oxidative decomposition of pollutants or at a partial oxidation into low-molecular weight compounds which can then be treated further by biological processes.

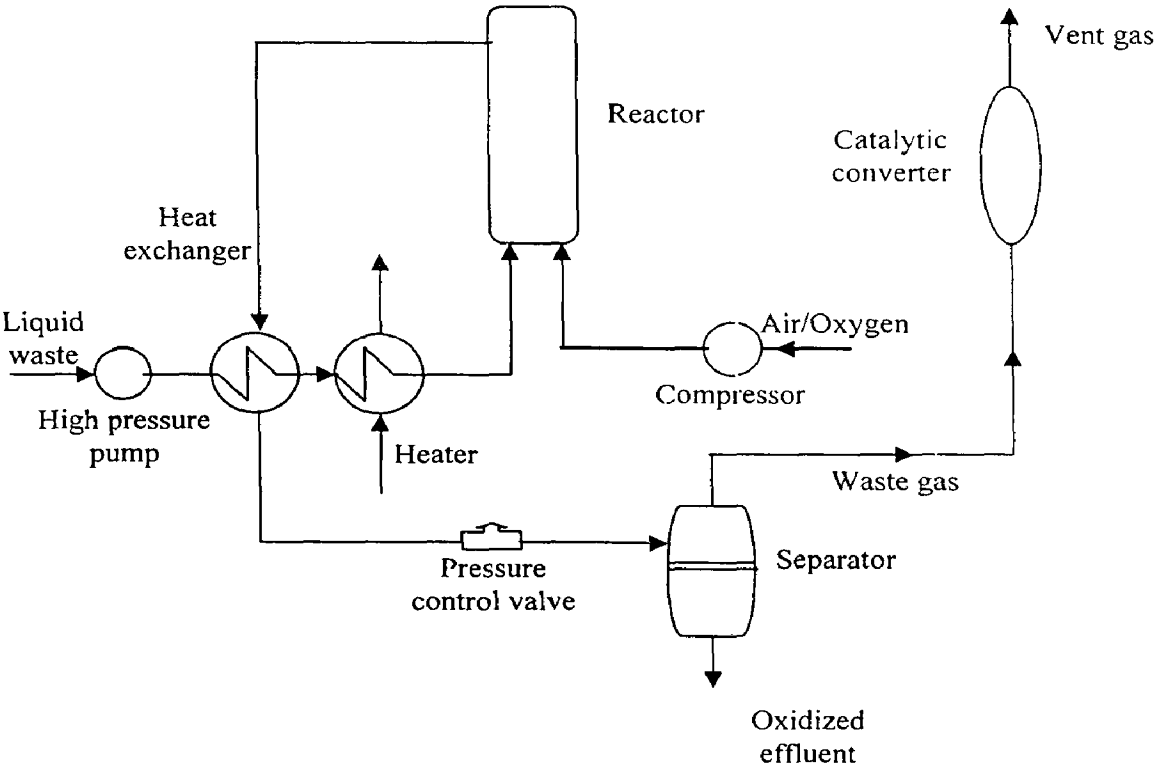


Fig. 2 Flow diagram of CWAO Process

The challenging operating conditions of wet air oxidation provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Thus, several types of heterogeneous catalysts were studied in the last decades, mostly based on supported or unsupported base metal oxides. This research paved the way for the development of several commercial catalytic WAO systems which achieve faster destruction rates at much lower temperatures and pressures.

1.4 CATALYSTS

The key issue in the effective catalytic oxidation of organics in waste waters is, however, finding a suitable catalyst. The conditions under which small amounts of organics dissolved in a large amount of water are oxidized force a severe demand on the physical and chemical properties of a catalyst. Hot acidic aqueous solutions can promote the solubility of some metal oxides in their higher oxidation states and consequently, deactivate an otherwise favorable catalyst. Some of the earliest studies employed the metals Pt, Pd, and Rh as catalysts for converting organic pollutants dissolved in waste water. (A. Rieche et al. (1959) [04]) showed that powdered coal and some types of ash were catalysts for the air-oxidation of phenol in waste water.

Intensified research activities in the seventies directed to the oxidation of organic pollutants dissolved in water have brought new and promising catalytic systems. Thus, A.Sadana et al. (1974) [05, 06] found that alumina supported copper oxide as an efficient catalyst for oxidation of aqueous phenol solutions in the temperature range of 96-246°C. Neither A.Sadana et al. (1974) [06] nor Goto et al. (1974) [22], which used the same catalyst and model pollutant to study the performance of a laboratory rotating basket reactor, have mentioned leaching of copper from the catalyst.

A.I. Njiribeako et al. (1978) [01, 02] found that copper in the form of cupric ions contributed about 20% to the total rate as a homogeneous catalyst when copper was supported by 33-alumina, while this figure increased up to 40% when alumina was replaced by silica.

Box et al. (1974) [17] designed an oxidation catalyst consisting of copper, manganese, and lanthanum oxide on a zinc aluminate spinel. Its catalytic activity was demonstrated in oxidation of acetic acid solutions (Levec J. et al. (1976) [33]) with no signs of early deactivation. The activity was found to be about one order of magnitude higher when compared with the iron oxide catalyst Smith J.M. et al. (1976) [69].

Sadana et al. (1974) [06] also showed that unsupported cupric oxide was not effective for oxidation of aqueous phenol solutions while copper and manganese oxides supported on alumina were active.

Smith J.M. et al. (1976) [69] found both palladium (0.1%) on 33-alumina and CuO.ZnO catalysts inactive for oxidation of acetic acid solutions. In contrary, CuO. ZnO was found quite active for oxidation of formic acid solutions [22].

Dissolved organics in waste waters were oxidized at 80 to 112°C and 14 to 61 bar by Chowdhury et al. (1975) [12] using various metals, metallic oxides, and salts: among solid catalysts platinum oxide gave best results. The Japanese patent (Takahashi S. et al. (1974) [64]) lists MnO_2 as an active catalyst for oxidation of organic pollutants in waste water at 60°C. Also, mixtures of oxides of Cu, Co, Ni and Fe, and Pt, Pd, Rh, Ru and Ir are reported S. lmamura, (1982)[65] as effective catalysts at 100°C for waste water purification, presumably by oxidation. At higher temperatures, copper oxide in combination with two of the following oxides CoO, Fe_20_3, CeO_2, SnO_2, NiO and ZnO are suggested S. lmamura, (1982)[65]. In the eighties a Imamura et al. (1982, 86, 88) [65-67] effectively employed different catalytic systems (Ru/Ce, Mn/Ce and Co/Bi) for oxidation of organics frequently found in waste waters.

Ito M.M. et al. (1989) [57] oxidized aqueous solutions of oxygen- and nitro-containing organic compounds by means of cobalt oxide. Recently, a catalyst capable of promoting oxidation of organics in aqueous solution below 150°C has been reported J. Levec, (1993) [34]. The catalyst consisting of CuO, ZnO and $A1_20_3$ promotes oxidation of phenol, chlorophenol, nitrophenol, butyl alcohol, methyl vinyl ketone at 130°C and oxygen partial pressure of 3 bar (J. Levec.(1990) [36]).

The oxides of copper, zinc and cobalt supported by aluminate cement also exhibited high activity in oxidation of phenol aqueous solutions A. Pintar, et al.(1992) [03]. When catalytic oxidation undergoes a free radical mechanism, there is no evidence in the literature that pretreatment of the catalyst is necessary. Sadana et al. (1974) [06] did note that the activity increased from the first to the second run but remained constant thereafter. In contrary, pretreatment was necessary in order to gain constant activity when the catalyst behavior followed an oxidation-reduction sequence J. Levec, et al. (1976) [33]. Smith J.M. et al. (1976) [69]. Goto, et al. (1974) [22].

1.4.1 Heterogeneous Catalytic Wet Oxidation Processes

In Japan, two CWO technologies have been developed in the late 80's by Nippon Shokubai [58] (NS-LC process) and Osaka Gas. Both processes rely on heterogeneous catalysts based on precious metals deposited on titania or titania-zirconia carriers. Compared to standard WO, these processes are able to oxidize two refractory compounds, namely acetic acid and ammonia, thus allowing direct discharge of treated water or reuse as industrial water.

The NS-LC [58] process involves a Pt-Pd/TiO_2- ZrO_2 honeycomb catalyst. Two-phase flow in vertical monoliths gives in a broad range of G-L velocities a very beneficial flow pattern, the slug flow (segmented gas-liquid flow). Since each liquid plug is sandwiched between two gas plugs, a recirculation pattern is developed within each liquid plug, which improves mass transfer significantly and prevents solids deposition. In addition, a thin liquid film is formed between the gas and the channel wall which allows high as a function of temperature in the LOPROX [48] WO process. Transfer rates while keeping the catalyst continuously wetted. Typical operating conditions of the NS-LC [58] process are temperature 220°C, pressure 4 MPa. In these conditions the oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches or exceeds 99%. In the absence of catalyst the removal efficiencies would be limited to 5-50% T. Ishii, (1991) [70].

The Osaka Gas CWO process is based on a mixture of precious and base metals on titania or titania-zirconia carriers (honeycomb or spheres). It has been demonstrated to work on several industrial and urban wastes:

1. A coal gasifier effluent in a pilot plant at British Gas's London Research Station [08]
2. Waste water from coke ovens [49].
3. Concentrated cyanide waste water of the Tuff-tilde process (a soft nitriding process for steel) [78].
4. Sewage sludge and residential wastes [49].

Treatment of waste water from coke ovens in a test plant built in 1979 with several reactors (0.30 m inner diameter, 6.50 m height, total capacity 6 m^3/ day). Highly concentrated COD and ammonia are decomposed to a level of 10 mg/l or less after 24 min contact time. Phenol and cyanide, the major pollutants present together with ammonia, are decomposed to levels below the detection limit. Furthermore, here is no detectable emission of NOx or SOx (M. Fukatawa (1993) [49]). Without catalyst, there is no removal of ammonia and the COD decomposition rate is very low. With a two to six fold increase of contact time, a residual COD value of ca. 1000 mg/l is left in the effluent (acetic acid).

1.4.2 Homogeneous Catalytic Wet Oxidation Processes

An alternative to insoluble precious metals catalysts is the use of homogeneous transition metal catalysts, which need however to be separated and recycled to the reactor or discarded. Several processes based on different variations of this concept have been developed in the last decade.

1.5 CATALYTIC WET AIR OXIDATION OF NITROGEN COMPOUNDS

During the treatment of nitrogenous pollutants, mineral forms of nitrogen (N-NH_3, N-NO_2, N-NO_3) are usually produced. Very similar conclusions have been deduced from the treatment of nitrobenzene, aniline or acrylonitrile using ferrous salts and hydrogen peroxide as an oxidation promoter (Chakchouk, 1993) [10]. In this case, a total mineralisation of organic nitrogen into N-NH_3 occurs. However, in some cases, the removal of organic intermediate species or even the initial pollutant is not total. Azobenzene and 4-4-dimethylazobenzene (Laha et al. 1990) [43] are the main oxidation products of aniline and p-toluidine with manganese dioxide: it is a partial oxidation. The wet oxidation decomposition of nitrophenol has been studied at 150°C and 200°C in a stirred autoclave. Nitrophenol was decomposed to give lower-molecular-weight compounds including formic and acetic acids (Kunishige et al., 1992 [40]). In the presence of a Pt catayst supported on TiO_2, the removal of total organic carbon (TOC) was 70%, whereas 0% is observed without the catalyst. Hao et al. (1994) [28] have treated 'red water', i.e. waste from the trinitrotoluene chemical industry. They pointed out the production of N-NH_3 and molecular nitrogen N_2 during catalytic wet air oxidation. In a similar way, Inoue et al. (1986) [32] have reported the efficiency of cobalt oxide as a catalyst during oxidation of ammonia. Organic compounds like urea, aniline and ethanolamine can be treated, and the NH_3 initially produced is oxidised to molecular nitrogen within a few hours in a batch reactor. According to Takahashi et al. (1987) [72], precious metals (Pd, Pt, Ru, Rh, etc.) deposited on ceramic are effective wet air oxidation catalysts. Again, the NH_3 initially produced is completely oxidised to molecular nitrogen. Imamura et al. (1982) [30] have tested ammonia oxidation with Co/Bi composite oxide (molar ratio: 5/1). The catalyst sharply increases the rate of ammonia transformation, probably to molecular nitrogen N_2. In the same way, these authors (Imamura et al., 1986) [31] have pointed out the very high activity of Mn/Ce composite oxide in ammonia elimination and oxidation to molecular nitrogen as shown in eq.1.10

$$2NH_3 + 3/20_2 \longrightarrow 3H_20 + N_2\,(I) \quad \ldots\ldots\ldots\ldots\ldots (1.10)$$

Recent catalytic studies using Wet Air Oxidation (WAO) of various Nitrogen and Oxygen containing organic compounds show ammonia and acetic acid to be the most difficult to oxidize. The most active solid catalysts are transition metal oxides (Mn/Ce, Cu/Zn, Co/Bi oxide systems) and supported noble metals (Pt, Ru). At present activity of the most widely used catalysts allows one to convert organic compounds to neutral gases at 533 K and PO_2 = 2 MPa in 1 h. Nevertheless, catalysts, designed for commercial application, possess at least two disadvantages. First, they show relatively low activity. Second, they are not stable enough. However, new materials and procedures used to prepare catalysts open new ways of catalyst improvement.

The CWAO process is capable of converting all organic contaminants ultimately to carbon dioxide and water, and can also remove oxidizable inorganic components such as cyanides and ammonia. The process uses air as the oxidant, which is mixed with the effluent and passed over a catalyst at elevated temperatures and pressures. If complete COD removal is not required, the air rate, temperature and pressure can be reduced, therefore reducing the operating cost.

CWAO is particularly cost-effective for effluents that are highly concentrated (chemical oxygen demands of 10,000 to over 100,000 mg/l) or which contain components that are not readily biodegradable or are toxic to biological treatment systems. CWAO process plants also offer the advantage that they can be highly automated for unattended operation, have relatively small plant footprints, and are able to deal with variable effluent flow rates and compositions.

The process is not cost-effective compared with other advanced processes such as biological processes for lightly contaminated effluents (COD less than about 5,000 mg/l).

Table 1.3. Typical results for conventional wet air oxidation, temperature = 200°C; catalyst: H_2O_2/Fe^{2+}; pH = 3.0; time = 60 min; Chakchouk (1993)[10]

	Concentration (g/liter)	**Organic compound removal (%)**	**N-NH3 /N-Org (%)**	**Organic carbon removal (%)**
Aniline	1	100	103	89
Nitrobenzene	1.35	99	>90	81
Pyridine	2	61	60	16
Acrylonitrile	2	50	52	- -

1.6 OBJECTIVE OF THE THESIS

This thesis describes the study undertaken on the application of some cheaper and easily available catalysts such as Copper, Cobalt and their combination supported activated carbon for catalytic wet air oxidation of nitrogen containing organic wastes in water. The emphasis is on the evaluation of activity and stability of these catalysts for use in liquid phase oxidation of nitrogen containing organic (oxygenates) compounds. It is also envisaged to enhance and consolidate research and strengthen institutional capability in catalytic oxidation of wastewater in India. Based on the reviewed literature, following objectives have been formulated:

i. To analyse the optimum conditions of reaction such as pH, catalyst concentration required.

ii. To develop efficient and cheaper treatment techniques for the removal of nitrogen containing organic compounds using non-noble metal based compounds.

CHAPTER II

LITERATURE REVIEW

2.0 INTRODUCTION

In this chapter we will discuss briefly different literatures available on various aspects of wet air oxidation of various compounds. Also the citation available on use of various catalysts for wet air oxidation process of waste water treatment, effect of various parameters on removal of nitrogen compounds form waste water and different types of reactors being used for wet air oxidation process of different compounds have been included.

Effect of temperature on removal/conversion efficiency and the selectivity has been studied by various researchers. These papers have been reviewed and a brief description of their work has been presented in this chapter. Some literature is also available on the study of the effect of various waste constituents. Comparative study of the catalyst activity by using various wastes has been done by some research workers. It has also been included in the chapter.

2.1 WET AIR OXIDATION PROCESS

Catalytic wet oxidation is a reaction involving an organic compound in water and oxygen over a catalyst. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Heterogeneous systems have the advantages over homogenous systems because the catalysts can be separated much more easily after the process. Although many studies have shown that metal oxide catalysts of transitional metals like Zn, Cu, Mn etc., are very effective for the removal of organic wastes, the use of noble metal catalysts for liquid phase oxidation is preferred since no leaching or dissolution of the active metal occurs even in hot and acidic conditions (Gallezot, 1996 [60]; Luck, 1999) [20].

Among the noble metal catalysts reported for liquid phase oxidation, platinum-supported catalysts seem to be promising. Platinum catalysts are well-known to be effective during aqueous phase oxidation of alcohols (Besson and Gallezot, 1999 [39]; and ammonia. However, there is still meagre information on the application of platinum catalysts for CWO of organic pollutants. Furthermore, in wet oxidation, the deactivation of platinum catalysts in liquid phase oxidation is not clearly addressed.

2.2 LITERATURE OVERVIEW

The literature available on wet air oxidation has been presented in this section.

Levec J. et al. (1995) [45] studied the catalytic liquid-phase oxidation of aqueous solutions of organics as a potential, advanced waste water treatment technology. Catalysts are briefly reviewed first, followed by mechanistic speculations and kinetics that have been proposed for liquid-phase oxidation of some model pollutants. Subsequently, oxidation reactors and potential process schemes are discussed.

Luck F. (1996) [20] studied wet air oxidation and presented a review of wet oxidation as a thermal aqueous phase process in which organic and inorganic substances in aqueous solutions or suspensions are oxidized by oxygen or air at elevated temperatures and pressures. Various catalysts have studied to reduce the severity of the reaction conditions. The main features of five commercially practised catalytic wet oxidation (CWO) processes for treating industrial waste waters have been analyzed and presented, along with highlights on several ongoing developments of new CWO technologies.

Deiber G. et al. (1997) [23] have shown studies that the aqueous wastes containing organic pollutants can be efficiently treated by wet air oxidation (WAO), i.e. oxidation by molecular oxygen in the liquid phase, under high temperature (200-325°C) and pressure (up to 150bar). However, organic nitrogen can be relatively resistant to oxidation and can be harmful to the environment. In the course of treatment, organic nitrogen (N-Org) is converted into ammonia (NHs), while organic carbon (C-Org) is converted mainly into carbon dioxide ($C0_2$). This can be done without catalysts. In the presence of Mn/Ce composite oxides, it is possible to transform ammonia into molecular nitrogen at a temperature close to 260°C. The direct conversion of organic nitrogen into molecular nitrogen also can be achieved using the same catalyst. This paper discusses the results obtained during the treatment of nitrogenous compounds like aniline, nitrophenol, alanine and ammonia. Laboratory investigations were conducted in a stirred batch reactor with Mn/Ce composite oxides as catalysts. Very limited amounts of nitrites and nitrates were observed with amines, but more significant quantities were found with nitro-compounds. The kinetics of oxidation of ammonia, organic compounds, and more particularly aniline, were investigated. The treatment of a real waste (process wastewater) was also investigated. The dependence of the transformation rate on various parameters (amount of catalyst, temperature, etc.) was established. The rates of oxidation are described by first-order kinetic laws with respect to the various nitrogen species (aniline, NH_3). Several parallel pathways are considered for the transformation of organic nitrogen, amongst which is an interaction with the catalyst surface.

Nikolay M. et al. (1998) [59] prepared several solid catalysts (Co3O4/g-Al2O3, Fe2O3/g-Al2O3, Mn2O3/g-Al2O3, Pt/g-Al2O3, Ru/CeO2, Ru/C) to remove N-containing organic contaminants while processing toxic and hazardous industrial waste waters using wet oxidation by air (WAO). The autoclave tests of catalysts were done to reveal the main advantages of catalysts in water presence at high pressures and temperatures. Catalyst activity was determined with regard to oxygen interaction with model mixtures (water organic contaminant: acetonitrile, carbamide, dimethyl formamide, or multicomponent mixture of aliphatic alcohols). Activity tests were done in a static reactor under ideal mixing regime. Reagents and products were monitored using gas chromatograph Cvet-560, Millichrom-1 HPLC, and routine chemical analysis. Optimum process conditions for the best catalyst (Ru/graphite-like carbon) are as follows: partial oxygen pressure 1.0 MPa, temperature = 473-513 K. At 0.5-5.0 MPa total pressure and 433-523 K temperature catalysts show high water-resistance and high activity level (residual content of toxic compounds is less than 1%, and no NOx and NH_3 are detected).

Gang L. et al. (1999) [42] showed that no metal oxide particles form on alumina at copper loadings below 10% (by weight). At higher loadings a CuO phase was detected. The fact that the performance of 10 wt% Cu/Al_2O_3 was better than that of 15 wt% (Cu–

Al- 15) supports the conclusion that a $CuAl_2O_4$ like surface phase is more active than a CuO phase in the ammonia oxidation reaction. NH_3 TPD profiles on Cu–Al-10 indicate that both surface oxygen and lattice oxygen can react with NH_3 to produce N_2. However, surface oxygen is much more active than lattice oxygen at low temperature. NH_3 TPD on CuY catalysts shows three types of active centers. Two of these are active at low temperature (below 200 °C) and one is active at a higher temperature (above 300 °C). The existence of low temperature active centers indicates that ammonia oxidation at low temperature on copper catalysts is possible. According to the UV spectra, the [Cu–O–Cu]2C-like species or small copper oxygen aggregates are responsible to the low temperature active centers. However, the amount of low temperature active centers or the concentration of [Cu–O–Cu]2C species is small prior to NaOH treatment. The NaOH treatment of CuY increases the amount of low temperature active centers. The above results apparently indicate that the environment or the type of active copper species is very important for low temperature ammonia oxidation and is strongly related with different supports and preparation methods.

Barbier J. et al. (2002) [37] in this paper the Oxidation of aniline and ammonia were carried out on mono- and bimetallic noble metal catalysts (Pt, Ru, Pd, etc.) prepared by impregnation and supported on cerium oxides. In liquid phase, at high temperature (150–250 ˚C) and high pressure of oxygen (20 bar), a Ru/CeO_2 catalyst is able to achieve the elimination of refractory nitrogenous organic products like aniline. The greatest interest of CWAO compared to the classical biological one, is that the selectivity towards molecular nitrogen is much higher (>90%). Indeed, in this process, ammonium ions give essentially N_2, via hydroxylamine and below 200 ˚C. At higher temperatures the rate of conversion is extremely high but nitrite and nitrate ions appear in the effluent. On a $RuPd/CeO_2$ catalyst, the optimal temperature for ammonia conversion is then 200 ˚C. In these conditions, the N_2 selectivity is up to 90%.

Masende, Zacharia P.G. (2003) [51] have studied the catalytic performance of graphite supported platinum (5-wt %) catalyst in liquid phase oxidation using a continuous stirred tank (CSTR) slurry reactor in order to determine the proper operation window. The study was carried out in a temperature range of 120 to 180°C and in a total pressure range of 1.5 to 2.0 MPa. Other operational variables employed were oxygen partial pressure (0.01-0.8 MPa), initial phenol feed concentration (0.005-0.07M), and catalyst concentration from 1 to 10 kgcat.mL. It was found that the extent of oxygen coverage on the platinum surface determines the reaction pathway and selectivity to CO_2 and H_2O. Complete oxidation of phenol to CO_2 and H_2O could be achieved at 150°C when the reaction proceeds within the range of weight specific oxygen loads of 0.15 to 0.35 mol.s-1.kgPt-1 and at stoichiometric oxygen excess in the range of 0 to 80%. The activity of the platinum catalyst remained high when the residual partial pressure of oxygen in the reactor was kept below 150 kPa. Higher residual oxygen partial pressure resulted into deactivation of the platinum catalyst (over-oxidation), which was temporary and could be reversed at reducing conditions. The formation of p-benzoquinone, followed by the formation of polymeric products was also favoured at higher oxygen load, which resulted into permanent deactivation of the platinum catalyst (poisoning). While the platinum surface was vulnerable to poisoning by carbonaceous compounds when insufficient oxygen was used, a fully reduced platinum surface favoured the formation of acetic and succinic acids which are difficult to oxidize. Higher temperatures can enhance the activity of the platinum catalyst, while at lower temperatures catalyst deactivation occurs with increased formation of polymeric products and lower selectivity to CO_2 and H_2O. In order to maintain the catalyst within the proper operation window, a CSTR is the preferred reactor.

Wu Q. et al. (2003) [62] studied the kinetics study of phenol oxidation by catalytic wet air oxidation (CWAO) using aqueous copper nitrate as homogeneous catalyst and based on the free radical mechanism a kinetics model is established where the electron transfer from copper to phenol is assumed to initiate the formation of free radicals. According to this model, the reaction orders are found to be approximately 1.0, 0.5 and 0.5 with respect to phenol, oxygen and copper concentrations, respectively. In order to verify the proposed kinetics, a series of CWAO experimental tests were done at various temperatures (313–333 K), oxygen partial pressures (0.6 – 1:9 MPa), and copper concentrations (0 –13 mg l –1). The experimental data were found to agree well with the model.

Zacharia P.G. (2003) [79] studied the catalytic wet oxidation of phenol in a slurry phase CSTR using platinum on graphite support as a catalyst. The investigation was carried out in the temperature range of 120-180°C and at total pressure of 1.8 MPa, while the phenol feed concentration was varied between 5 and 70 mol/m3 and oxygen partial pressures between 0.01 and 0.8 MPa. It was found that both the oxygen load and the stoichiometric oxygen excess determine the extent of oxygen coverage on the platinum surface, which influences the reaction pathways and selectivity to CO_2 and H_2O. A fully oxidized platinum surface resulted into catalyst deactivation which favoured of various polymeric products. Whereas free platinum surface was vulnerable to poisoning by carbonaceous compounds, a fully reduced platinum surface favoured the formation of acetic and succinic acids which are difficult to oxidize. A reaction scheme for platinum catalysed phenol oxidation in liquid phase have been proposed.

Wijdan Aljailawi (2003) [76] studied the performance of packed-bed reactor in eliminating phenol via a catalytic wet oxidation process (CWO) over Al- Fe pillared clay was investigated. Both catalytic and non-catalytic reactions were conducted under relatively mild condition .The effects of temperature, pressure, gas flow rate, liquid flow rate, and operation mode (down flow, up flow) were thoroughly explored. The catalyst deactivation was examined by monitoring two phenomena: leaching of catalyst's active sites into the liquid phase, and formation of solid organic polymers on the catalyst's surface. FAZA has shown great stability even after three weeks of experimental runs, and high conversion yields of phenol were obtained. Optimization of CWO process in packed bed reactors has been a focal point of many researchers for decades. In general, this operation can be optimized by improving reactor design, locating the optimal operating conditions, and utilizing stable catalysts. Therefore, there is a constant search for catalysts that could offer qualities such as: high selectivity to desired end products, low deactivation rate, high stability at optimal operating conditions.

Oliviero L. et al. (2003) [41] reviewed the literature dealing with the catalytic wet air Oxidation (CWAO) of various nitrogenous compounds, mainly produced in chemical and pharmaceutical industries. Many studies dealing with oxidation of aniline are often chosen as a model molecule of pollutant of dye industries. First, the results obtained with CWAO were compared with those obtained with other oxidation processes. Particular attention is paid to the selectivity towards organic by-products (specially, azo, nitroso and nitro compounds, phenolic compounds and carboxylic acids) as well as towards several inorganic forms of nitrogen (NH_4+, N_2, NO_2-, NO_3-). In a second part, the review focuses on the mechanism of chemical reactions that can explain the formation of the observed products. Usually, similar catalysts can be used for CWAO of oxygen-containing (phenol, carboxylic acids) and nitrogen-containing organic compounds. Ammonia is one of the most refractory by-product formed during catalytic WAO of the nitrogen-containing organic pollutants and is itself a pollutant. For this reason, recent reports about its oxidation by the CWAO process are finally reviewed. Very high selectivities to dinitrogen can be obtained on certain noble metal catalysts. As a rule, catalysts active and selective for ammonia oxidation are different (nature of active phase, support, etc.) from the solids proven to be the best catalysts for CWAO of organic compounds. Multifunctional catalysts are, thus, required for the treatment of nitrogenous organic compounds.

Masende (2004) [52] studied the catalytic activity of platinum catalysts such as Pt/graphite, Pt/TiO_2, Pt/Al_2O_3, and Pt/active carbon 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. The catalytic activity of platinum catalysts is significantly influenced by the surface coverage of oxygen on the platinum surface. Deactivation due to over-oxidation is gradual for Pt/graphite with a metal dispersion of 5.3% as compared to Pt/TiO_2, Pt/Al_2O_3 and Pt/AC, which have metal dispersions of

15.3%, 19.5% and 19.0%, respectively. 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.

Masende, Zacharia P.G. (2004) [53] has studied the paper deals with the catalytic performance of graphite supported platinum (5-wt%) catalyst in liquid phase phenol oxidation in a continuous stirred tank (CSTR) slurry reactor. The study was carried out for a temperature range of 120 to 180 °C and for a total pressure of 1.5 to 2.0 MPa. Other operational variables employed were oxygen partial pressure (0.01 - Pa), initial phenol feed concentration (5-70 mol/m^3) and catalyst amount (0.2 – 12.0 g of Pt/graphite). The selectivity and activity of the platinum catalyst depend strongly on the transfer rate of oxygen to the catalyst. Carbon dioxide and water are the only products when the reaction proceeds at oxygen gas-liquid mass transfer limitation conditions. In surplus of oxygen, the side products p-benzoquinone, maleic acid, and low molecular weight carboxylic acid were detected. A model was developed that predicts the performance of phenol oxidation in a CSTR.

Table 2.1 Listing of studies on catalytic wet oxidation of aqueous phenol.

S.No.	Catalyst	Reactor Type	Temp ($^{\circ}$C)	Press. (atm)	C_0 (g/L)	Conversion (%)	Reaction time(min)	Reference
1	Ru/CeO_2	S	200	10	2.0	94.8	60	Imamura et al., 1985
2	$Pt/\gamma-Al_2O_3$	S	200	10	1.0	58	175	Higashi et al., 1991
3	Cr_2O_3	F	390	241	0.5			Ding et al., 1995
4	V_2O_5	F	390	241	0.5			Ding et al., 1995
5	MnO_2 (TGS-3)	S	50-60	1	.5-2.0	90	30	Jie er al., 1991
7	$CuO/\gamma-Al_2O_3$	TB	120-160	6.0-12.0	5.0	80	30	Fortuny et al., 1995
8	V_2O_5/Al_2O_3	F	390-410	241	.23-8.4		8	Ding et al., 1995
9	MnO_2/CeO_2	F	220	10	2.0	92.7	20	Imamura et al., 1988
10	CuO-ZnO/	FB	380-390	230	5.0	0.25		Krajnc and Levec, 1994
11	CuO-ZnO-CoO	TB	50-210	3-8.0	0.1-0.5	100	1	Pintar and Levec, 1994
12	CuO-CoO-TiO_2	S	14-200	0.8-1.8	4-5.5	85	30	Kochetkova et al., 1992b
13	Pt/Al_2O_3	S	130-175	2.0-25	.13-10	100		Larachi,Hamoudi et al., 1998
14	MnO_2/CeO_2	S	80-130	.13-10	100			Larachi,Hamoudi et al., 1998
15	Pt/TiO_2	B & TB	15-205	35-47	.2-1.2	60	400	Clayton et al., 2002
16	Al-Fe pillared clay	B	< 70	1	5.4E-06	100	130	Papayannakos et al., 2000
17	CuO-ZnO-Al_2O_3	S	105-132	5.6				Pintar and Levec, 1992
18	Active Carbon with Ni,V,Fe	TB	120-160	20-50	0.005	100	5500	Tukac and Hanika, 1997
19	Ru/TiO_2	TB	150-200	50	5	90	1800	Bessonet al., 1999
20	Cu-203T	BSTR	127-180	3.2-16	4-1150			Santos et al., 2001

Boutarbouch M.N.D. et al. (2004) [50] investigated the conversion of N_2O in the presence of NO and CO over steam-activated FeZSM-5 in the temperature range of 473–873 K. Individually, both CO and NO have a positive effect on the N_2O conversion, leading to a lower operation temperature with respect to direct N_2O decomposition. At low partial pressures, the catalytic effect of NO as O_2 desorption-accelerator is more effective than the reducing effect of CO. At high partial pressures, the N_2O removal is faster with CO than with NO at low temperature. Small amounts of NO in the feed are sufficient to severely inhibit the reduction of N_2O with CO, approaching the activity of the binary N_2O + NO system. The CO conversion is more negatively affected by NO than the N_2O conversion, decreasing progressively with an increased partial NO pressure. The catalyst showed a very low activity in the reduction of NO with CO, evidencing the inability of steam-activated FeZSM-5 to dissociate the NO molecule. The N_2O conversion is decreased in the presence of small NO amounts, but no longer inhibited at higher partial NO pressures. The dual role of NO, acting as a promotor in N_2O decomposition and as an inhibitor in N_2O reduction with CO, can be explained attending to the iron species involved in the various reactions. A recent in situ spectroscopic study [J. Catal. 223 (2004) 13] has demonstrated that both isolated iron ions and oligonuclear iron clusters in FeZSM-5 participate in the reaction of N_2O + CO. The present results suggest that NO selectively inhibits the reduction of N_2O of isolated iron sites by strong NO adsorption, particularly in the low-temperature range, blocking CO and N_2O activation. As a consequence the reaction mechanism shifts to that of NO-assisted N_2O decomposition, mainly involving oligo nuclear iron species.

Gianguido R. et al. (2004) [24] studied the interaction of NO, ammonia (NH_3), hydrazine (N_2H_4) and hydroxylamine (NH_2OH) on Fe_2O_3/Al_2O_3 model catalyst. The data support the idea that hydrazine can be intermediate in the oxidation of ammonia to nitrogen, while hydroxylamine-type species, can be intermediate in the oxidation of ammonia to NO. On the contrary to those observed over Fe_2O_3/TiO_2 previously studied, hydroxylamine-type species are formed at relatively low temperature, indicating that Fe_2O_3/Al_2O_3 is less selective in SCR reaction with ammonia.

2.3 MOTIVATION FOR THE PRESENT STUDY

In this study, we establish that *"Catalytic Wet Air Oxidation is one of the few processes that do not turn pollution from one form to another, but actually eliminate it"*. And in today's world the greatest challenge for mankind is to deal with the various form of pollution present in our day to day life. Water is one of the basic need for sustaining on this planet as mentioned in chapter I the fresh water sources in the world are only 3% of the total water present on our planet and out of this 03% only 21 % of the water is available for human need, so it is the need of present time to treat our waste water streams so that the water available can be used to its optimum.

Nitrogen is one of the pollutants found in waste water in many forms and to treat nitrogen containing waste water wet air oxidation is the most suitable technique. Again catalytic WAO is one of the most feasible and new technique in finding a new approach for removal of nitrogen from wastewater. The treatment will deal with the use of economic and stable catalyst for effective oxidation at comparable conditions.

2.4 CONCLUDING REMARKS

In this chapter literature available on wet air oxidation of various organic wastes, effects of various operating parameters on wet air oxidation, effect catalysts and different reactors used for the effluent treatment plant have been reviewed. This forms the basis for our study of removal of nitrogen containing organic compounds (pyridine) from waste water.

CHAPTER III

EXPERIMENTAL SETUP AND PROCEDURE

CHAPTER III

EXPERIMENTAL SETUP AND PROCEDURE

3.0 INTRODUCTION

The model reactions were chosen based on the characteristics of common or typical industrial wastewater generating toxic wastes. The model reactions were pyridine oxidation. The compound represent typical nitrogen based organic pollutant present in the aqueous environment, and offer a range of composition, physical and chemical properties, susceptibilities to oxidation and potential for deactivation of catalysts. The catalytic wet air oxidation of model compound (pyridine) was studied in a batch reactor (see fig 3.1). The analysis of liquid samples was performed by means of UV-Visible Spectrophotometer.

Copper catalysts were used in the present studies, namely: $CuSO_4$, and Cu (5 wt%)/Co (5 wt%)/ C, were used in this study. The activity of the catalyst and the optimum reaction conditions were analysed.

3.1 ANALYSIS OF LIQUID SAMPLES

In each experiment, the progress of the reaction and the catalytic activity were monitored by the measurement of the reactor effluent composition as a function of time. At appropriate intervals or at the end of experiment the composition of the outlet liquid samples was determined by an UV Visible Spectrophotometer. First of all the absorbance of the sample was scanned on the spectrophotometer. The scan peak value of the wavelength is 256 nm for the pure and diluted pyridine samples. After scanning the wavelength peak for pyridine the calibration curve was obtained by analyzing different know concentrations of pyridine sample and a calibration curve was drawn to determine the concentration of unknown samples.

3.2 CATALYST PREPARATION

The two catalysts $CuSO_4$ (copper sulphate) and Cu-Co/C (copper 5% wt – cobalt 5% wt. supported on carbon) were used in the experiments. The laboratory grade copper sulphate is used directly in the reaction while the other catalyst Cu-Co/C was prepared in the laboratory the procedure of catalyst preparation is discussed below.

3.2.1 Preparation of Cu-Co/C catalyst

Nitrate salt of copper and cobalt were weighed as 1 gm each and mixed with 8 gm of activated carbon in cleanly rinsed beaker, the mixture was transferred to a clean beaker and diluted with distilled water, and the pH of the mixture was maintained at 7.5. The beaker was then kept for stirring for 30 minutes then the mixture was allowed to precipitate in the beaker. The precipitate was separated and washed 3 – 4 times with water. The catalyst was dried overnight at 110 °C in an oven. Calcination in a silica crucible was then done from 200 °C to 600 °C for 6 hours. Stepwise calcinations was started from 200 °C with 50 °C temperature in constant steps of 30 minutes upto 600 °C. After reaching 600 °C the catalyst was kept for 2 hours at this temperature. Stepwise calcinations helped in getting a uniform structure of the catalyst.

3.3 EXPERIMENTAL SETUP DESCRIPTION

The experiments were conducted in a bath reactor in the temperature range of 120 to 180°C and at total pressure 09 bars. Other experimental and reactor operating conditions were as listed in Table 3.1.

Table 3.1 Standard reactor operating conditions

	Standard	Range
Temperature, °C	150	150 - 160
Total pressure, bar	09	09
Initial pyridine concentration, mg/lit	10	10
Volume of liquid in the reactor, ml	250	250
Mass of $CuSO_4$ in the reactor, gm/Lit		2-5
pH	7.8	4.0

The reactor along with all its accessories is shown in the fig. 3.1 a schematic presentation of the high-pressure batch reactor is shown below. The reactor is a 500 ml volume stainless steel (S.S. 316) single cut section the heating element covered with asbestos rope is wrapped around and on which magnesia paste is placed to avoid heat loss and direct contact with the heating element. The reactor is sealed with a Teflon and heating pressure gasket and bolted it can withstand a pressure of about 10-15 bars without noticeable leakage. The reactor has with one inlet for oxygen, one outlet for product along with a temperature indicator cum controller thermocouple, digital pressure indicator and a magnetic stirrer. The reactor set-up is schematically presented in Fig. 3.1. During reaction the reactor was kept at constant temperature within ± 3 °C. The liquid outlet of the reactor contains a S.S. needle valve which is connected to a condenser. The liquid samples taken out through the condenser were analysed by an UV spectrophotometer for residual pyridine concentration in the product.

The oxygen is fed by connecting an oxygen cylinder to the oxygen inlet as shown in the figure. The feed is fed from the sample inlet bolt and then the thermocouple connected with the PID indicator cum controller is attached to the reactor. The supply to the reactor is provided through an AC Variac which supplies constant current to the heating element around the reactor. The reactor is placed on a magnetic stirrer with heating plate to avoid loss of heat through the bottom of the reactor.

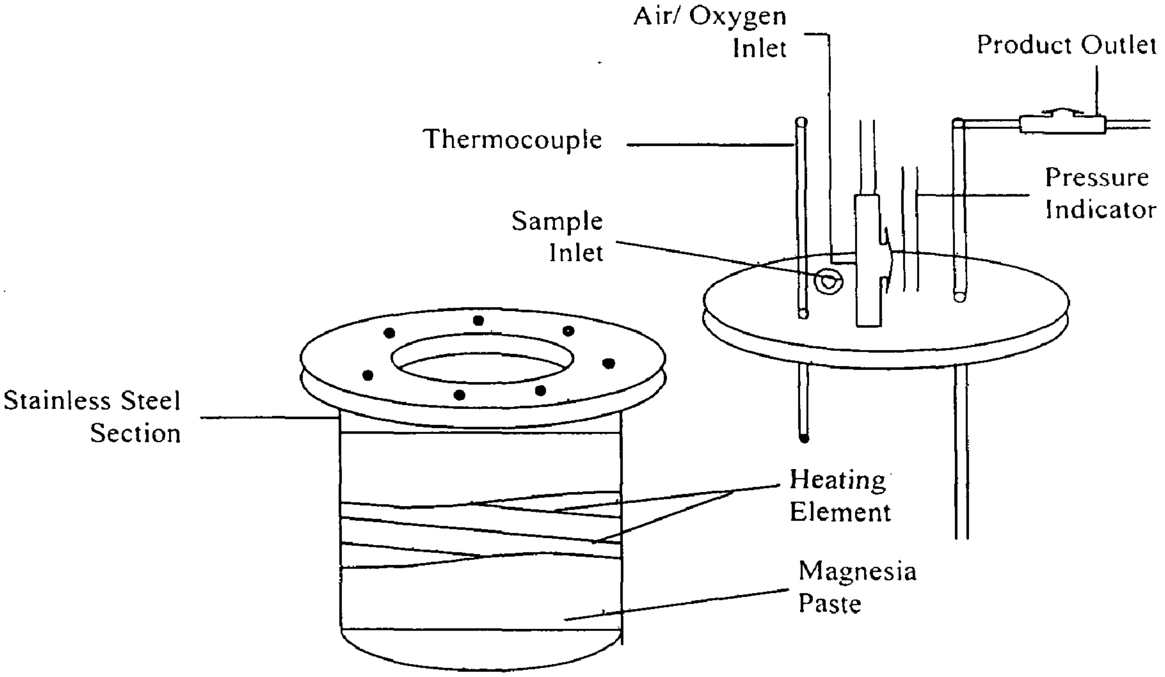


Fig 3.1 Layout of Reactor Specifications

3.4 REACTOR START-UP PROCEDURE

The reactor start up procedure was tested with two different ways as described below:

In the first procedure (Pyr-O_2-Sim), i.e. simultaneous feed of pyridine and oxygen were made in the reactor before starting the heating. 250 ml of pyridine sample conc. 10 mg/l and given mass of dry catalyst was introduced into the reactor. After closing the reactor, oxygen was introduced into the reactor at a fixed pressure and the mixture was stirred to keep the catalyst in suspension. After the oxygen is fed at the desired pressure in the reactor, heating of the reactor was started. When the reaction temperature and pressure were attained. The reaction was monitored by digital temperature indicator cum controller and digital pressure indicator for final temperature and pressure respectively.

In the second start-up procedure (Pyr-First), the catalyst along with 250 ml of pyridine sample (conc. = 10 mg/l) was introduced into the reactor. Then after closing the reactor heating was started. After the desired reactor temperature was attained the pressure of the reactor was increased to 9 bar by introducing oxygen from an external oxygen cylinder connected to oxygen inlet. The reactor was then run for the complete reaction time.

In our experimental procedure we used the second method of reactor start up for conducting the experiments, as in the first case the pressure can not be controlled by feeding the oxygen at the startup of reaction.

CHAPTER IV

RESULTS AND DISCUSSION

4.0 CALIBRATION CURVE

The experiments were performed as described in Chapter III. The pyridine concentration in a sample were obtained from the calibration curve plotted as pyridine concentration of a known sample as a function of absorbance at 256 nm..

The calibration curve for the determination of pyridine sample concentration obtained by means of UV-Visible Spectrophotometer is shown in fig. 4.1 and the equation of the curve and the R^2 value of the curve is also given in equation 4.1 and 4.2 The equation obtained from the graph is:

$y = 90.311x - 348.68$ .... (4.1)

$R^2 = 0.988$ .... (4.2)

where,

y = pyridine concentration, mg/l

x = absorbance at 256 nm wavelength

4.1 SAMPLE REACTOR CONDITIONS WITHOUT CATALYST

Initially the reactor was run without catalyst, and pyridine sample concentration 10 mg/l, pH – 4, temperature 150 °C, total pressure of 9 bar and reaction time of 1 hour. No significant results were observed and only a very little conversion had taken place with 4.2 % removal of pyridine. The reaction conditions are shown in table 4.1 (a) % (b).

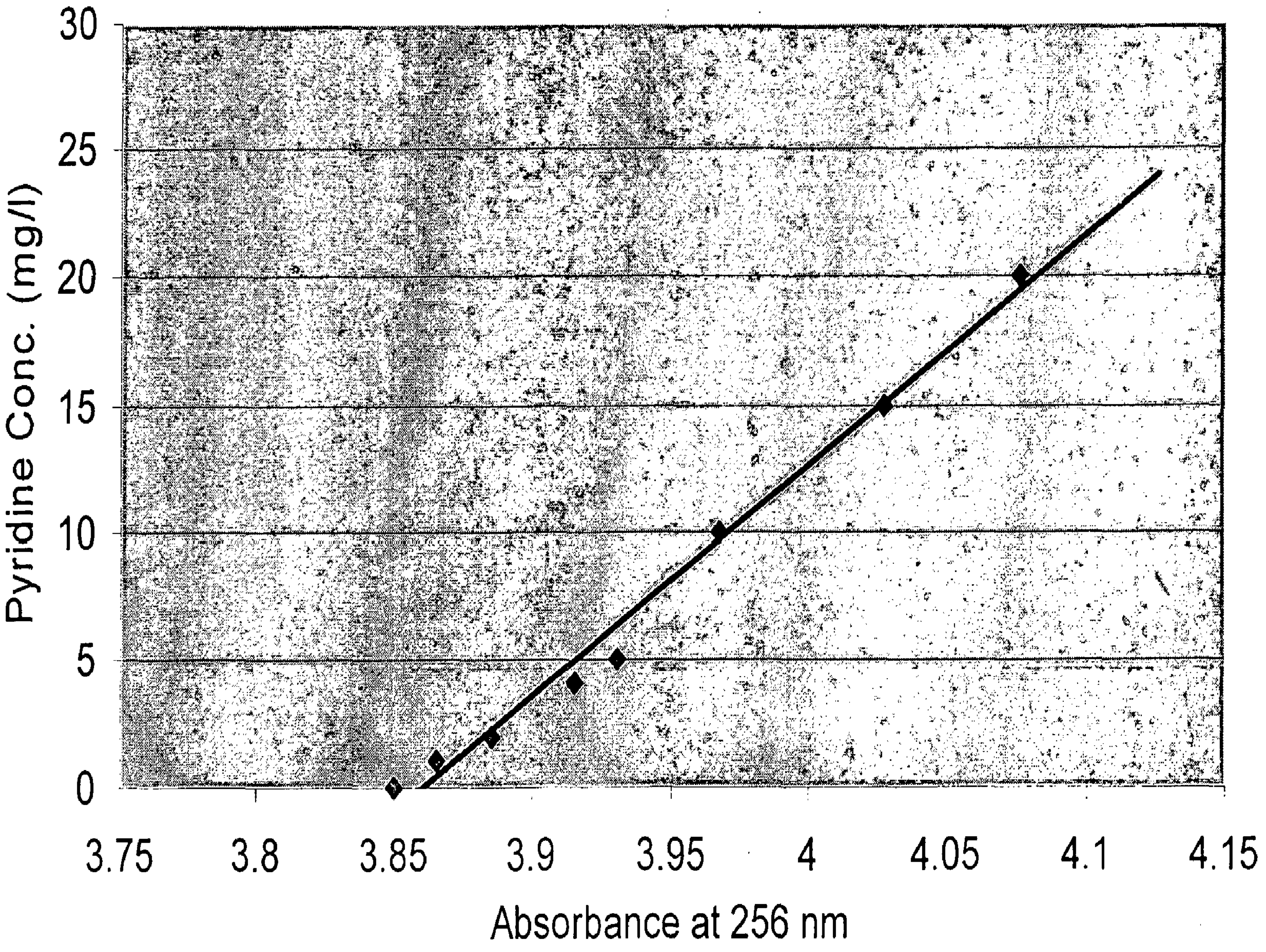


Fig. 4.1 Calibration curve for pyridine conc. v/s absorbance

4.2 EFFECT OF pH ON % REMOVAL OF PYRIDINE

(a) Using $CuSO_4$ Catalyst (Homogenous)

Experiments were carried out with synthetic samples containing pyridine concentration of 10 mg/l. $CuSO_4$ was used as the catalyst with a concentration of 2 mg/l. The temperature of the reaction and the total pressure of the reaction was 150 °C and 9 bar respectively. The reaction was carried out for 1.5 hours; the data is presented in table 4.2. It is observed that when the pH was varied from 2 to 10 pH 4 gave the maximum removal of 56 %. Below pH 4 and above pH 4 the % removal declined. The reaction conditions are shown in table 4.2

Similar results at 160 °C are presented in fig. 4.3 the results indicate clearly an initial pH of the sample to be 4 as optimum value. The reaction conditions are shown in table 4.3

(b) Using Cu-Co/C Catalyst (Heterogeneous)

Similar reaction conditions are used here, where same as in section (a). The results are presented in fig 4.4. It is observed that the heterogeneous catalyst Cu-Co on Carbon also have optimum reactivity when the initial pH of the pyridine sample was 4. The reaction conditions are shown in table 4.4

The data at 160 °C using Cu-Co/C catalyst are presented in fig 4.12 with similar observation – pH 4 as optimum value. The reaction conditions are shown in table 4.5

It may be noted that in all the above cases just described the % removal of pyridine at 160 °C is higher then that obtained at 150 °C. In case of Cu SO_4 catalyst the % removal increased from 56% at 150 °C to 64.3 at 160 °C and with Cu-Co/C catalyst the % removal of pyridine was enhanced from 53.4 % at 150 °C to 57.4 % at 160 °C.

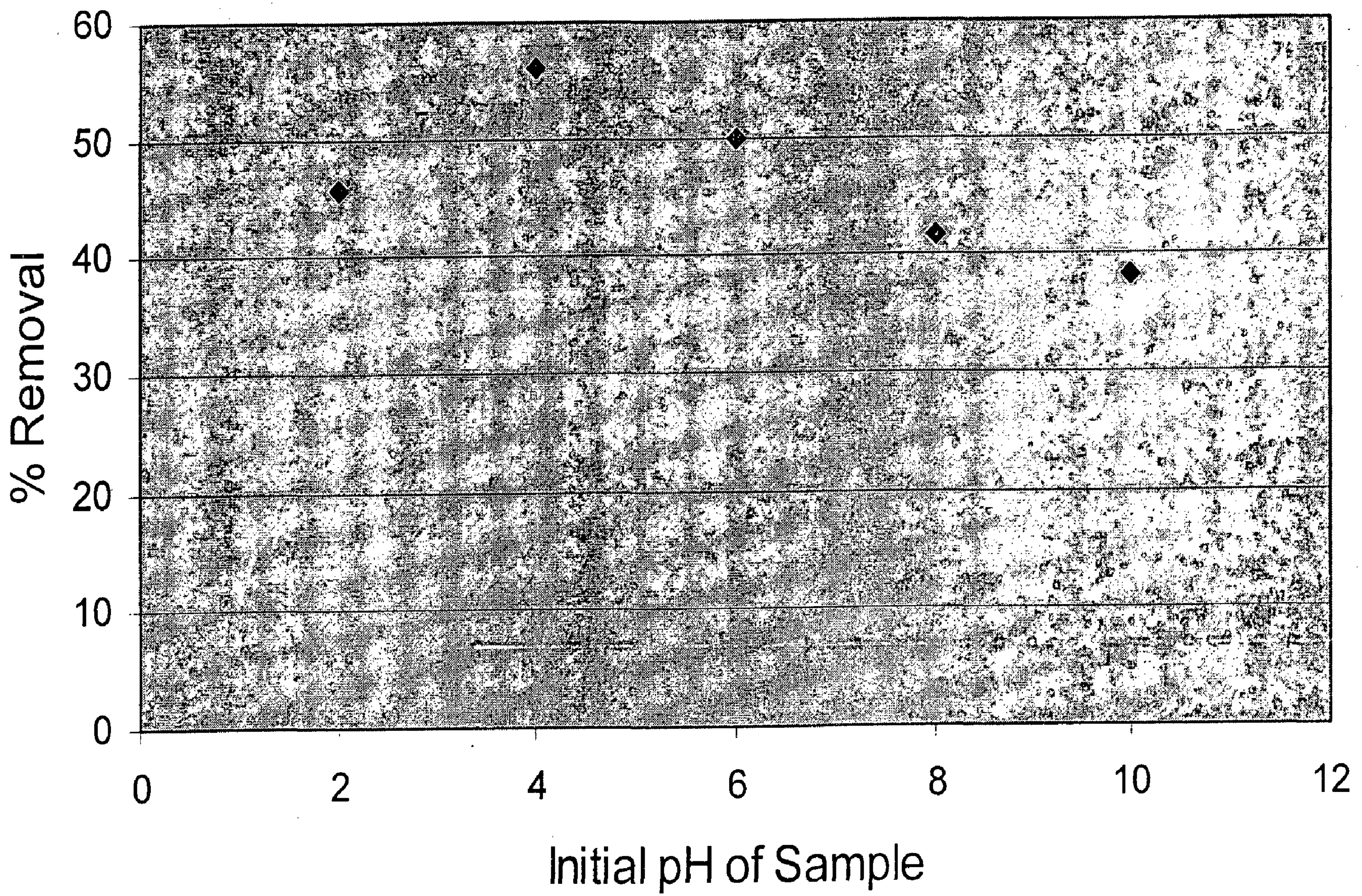


Fig. 4.2 Effect of pH on % removal of pyridine using $CuSO_4$
T =150 °C, P_T = 9 bar, C_o = 10 mg/l

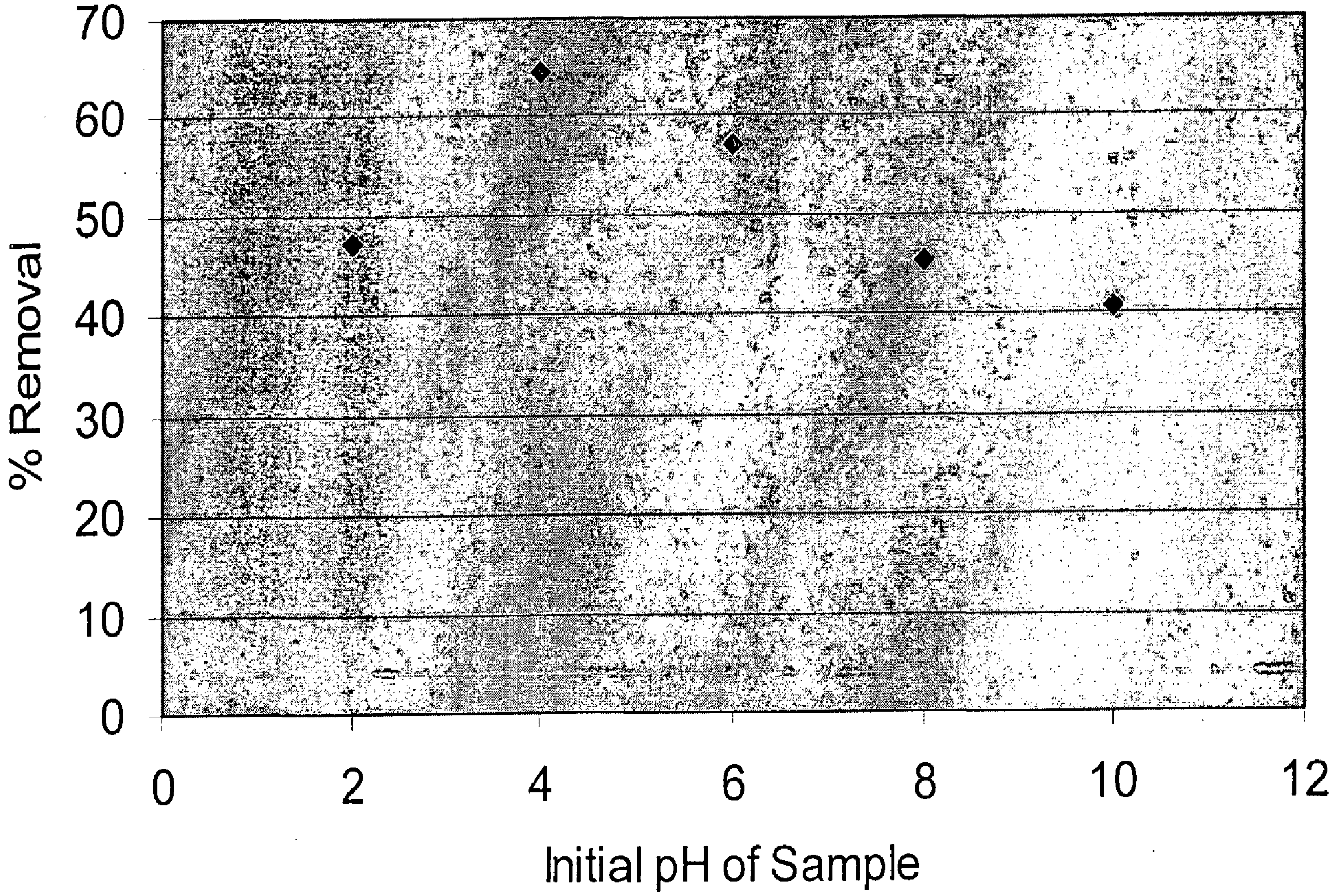


Fig. 4.3 Effect of pH on % removal of pyridine using $CuSO_4$
T =160 °C, P_T = 9 bar, C_o = 10 mg/l

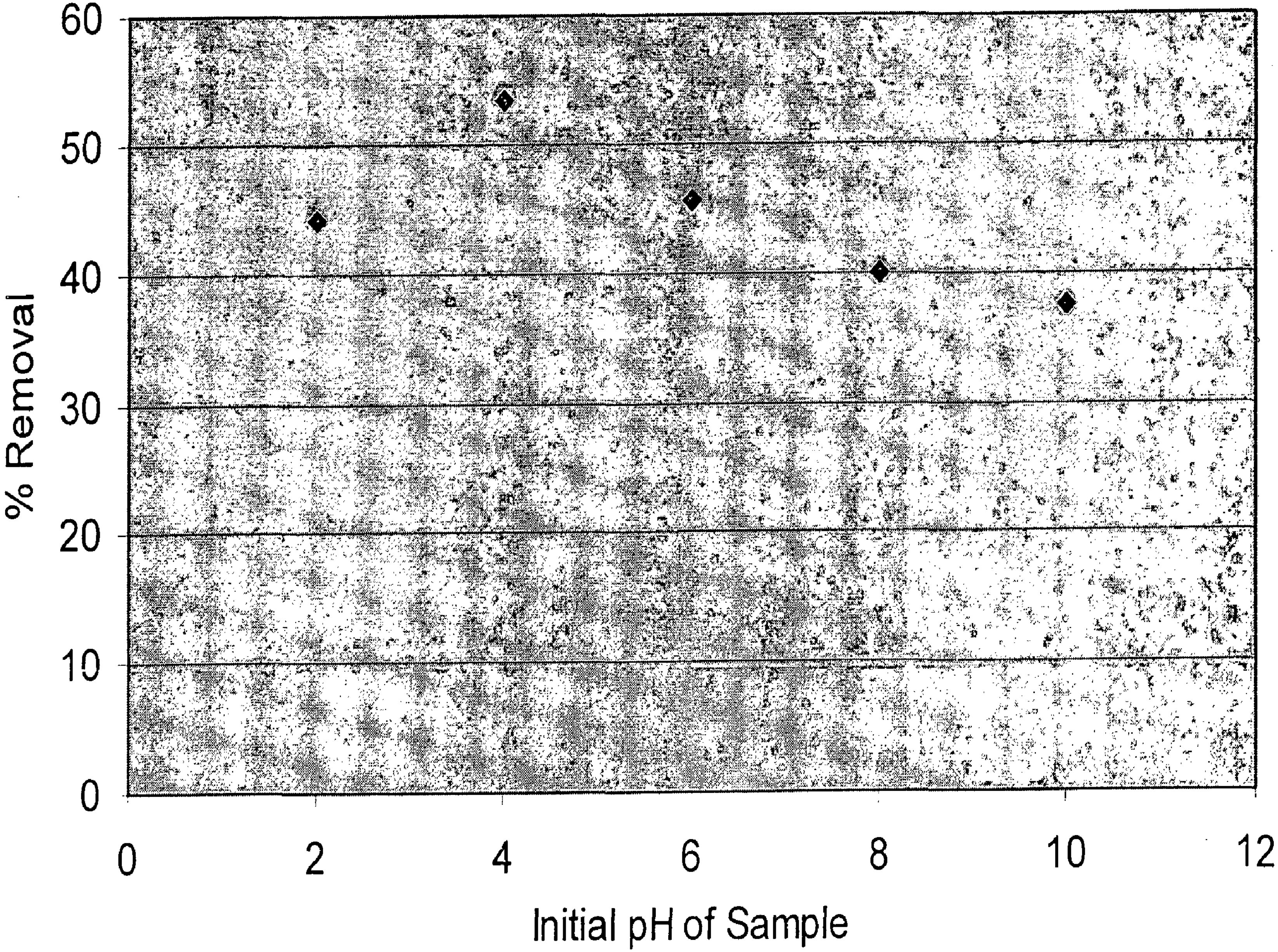


Fig. 4.4 Effect of pH on % removal of pyridine using Cu-Co/C
T =150 °C, P_T = 9 bar, C_o = 10 mg/l

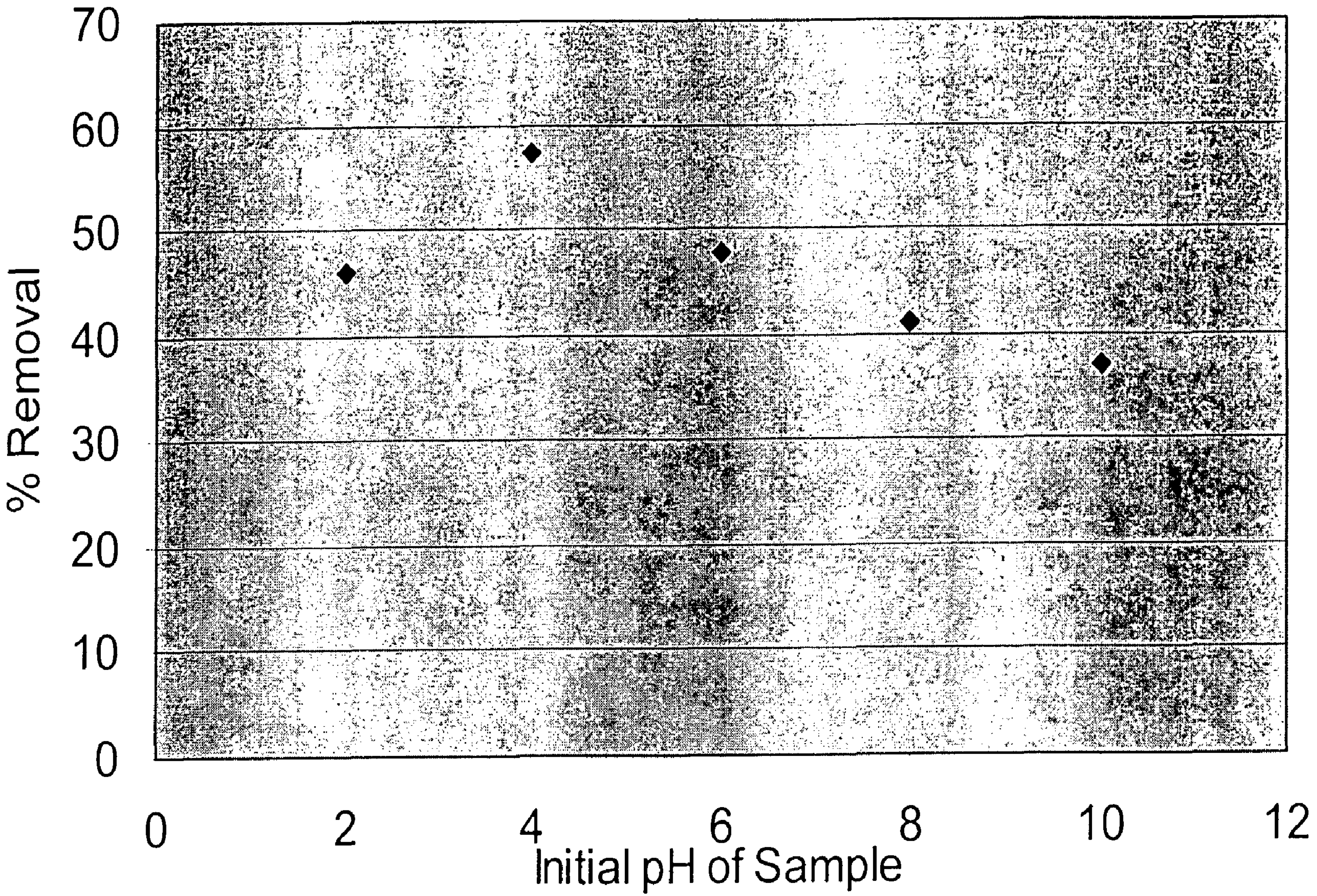


Fig. 4.5 Effect of pH on % removal of pyridine using Cu-Co/C
T =160 °C, P_T = 9 bar, C_o = 10 mg/l

4.3 EFFECT OF CATALYST CONCENTRATION ON % PYRIDINE REMOVAL

(a) Using $CuSO_4$ catalyst (Homogenous)

The experiments were performed using catalyst $CuSO_4$ with 2 mg/l concentration, the catalyst concentration was varied from 2 to 5 mg/l. The results are presented in fig 4.6. The initial sample concentration was 10 mg/l having pH maintained at its optimum value 4. The temperature was maintained at 160 ^{0}C and the total pressure 9 bar, the reaction time was 1.5 hours. The reaction conditions are shown in table 4.6.

It was observed that with increase in catalyst concentration from 2 mg/l onwards the % pyridine removal increases rapidly upto concentration 4 mg/l and thereafter the increase is not appreciable. We therefore conclude that the catalyst concentration of 5 mg/l is an optimum value of catalyst concentration.

(b) Using Cu-Co/C catalyst (Heterogeneous)

The reaction conditions using Cu-Co/C catalyst were exactly same as described in section 4.3 (a). The results are presented in fig. 4.7. The % removal of pyridine increases rapidly with increase in catalyst concentration from 2 mg/l onwards. It is observed that the rate of increase of % removal is rather slower after 4 mg/l concentration. However no optimum value was observed with in the range of studies conducted. The reaction conditions are shown in table 4.7.

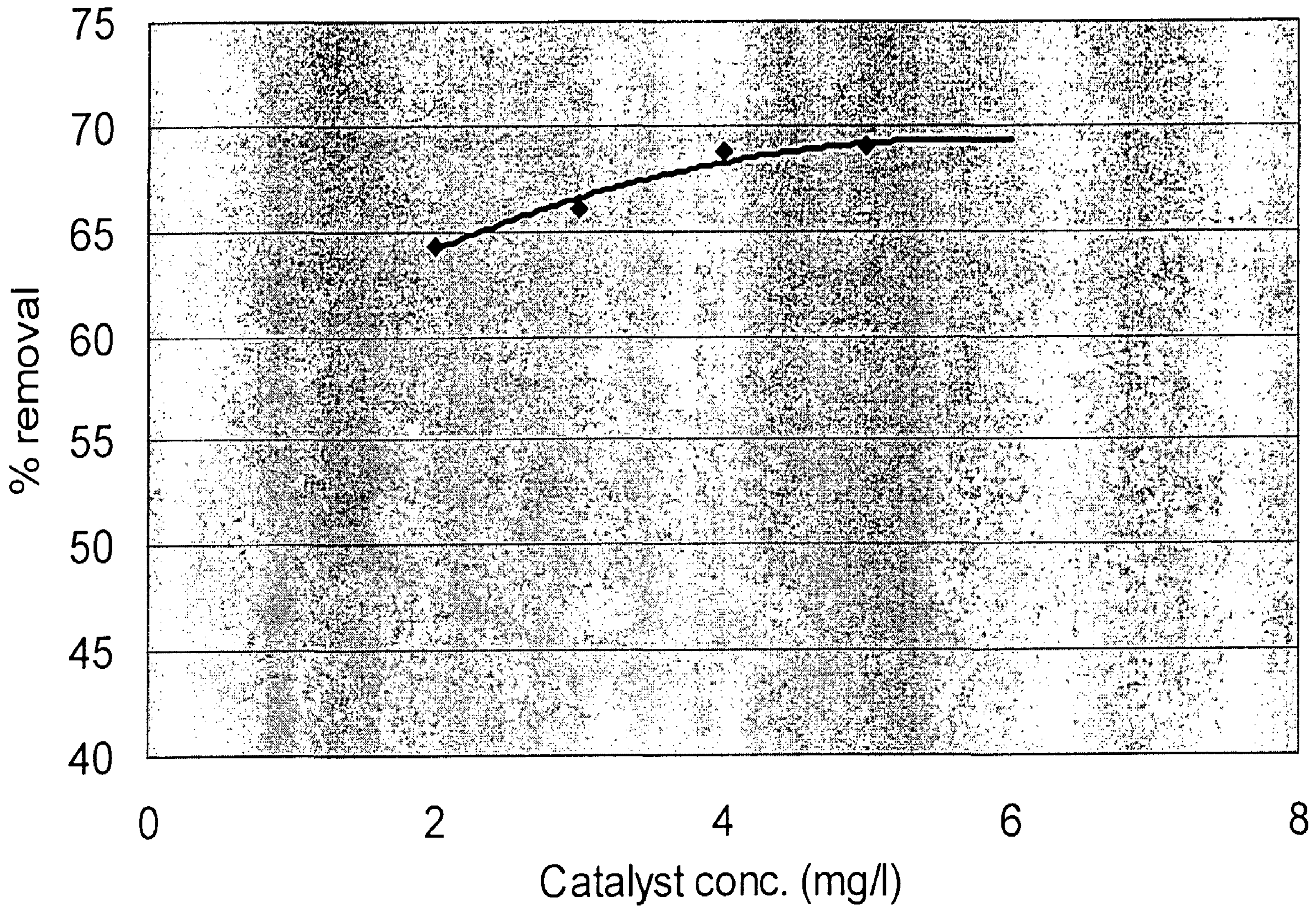


Fig. 4.6 Effect of catalyst conc. on % removal of pyridine using $CuSO_4$
$T = 160\ ^{o}C$, $P_T = 9$ bar. $C_o = 10$ mg/l, t = 1.5 hr, pH = 4

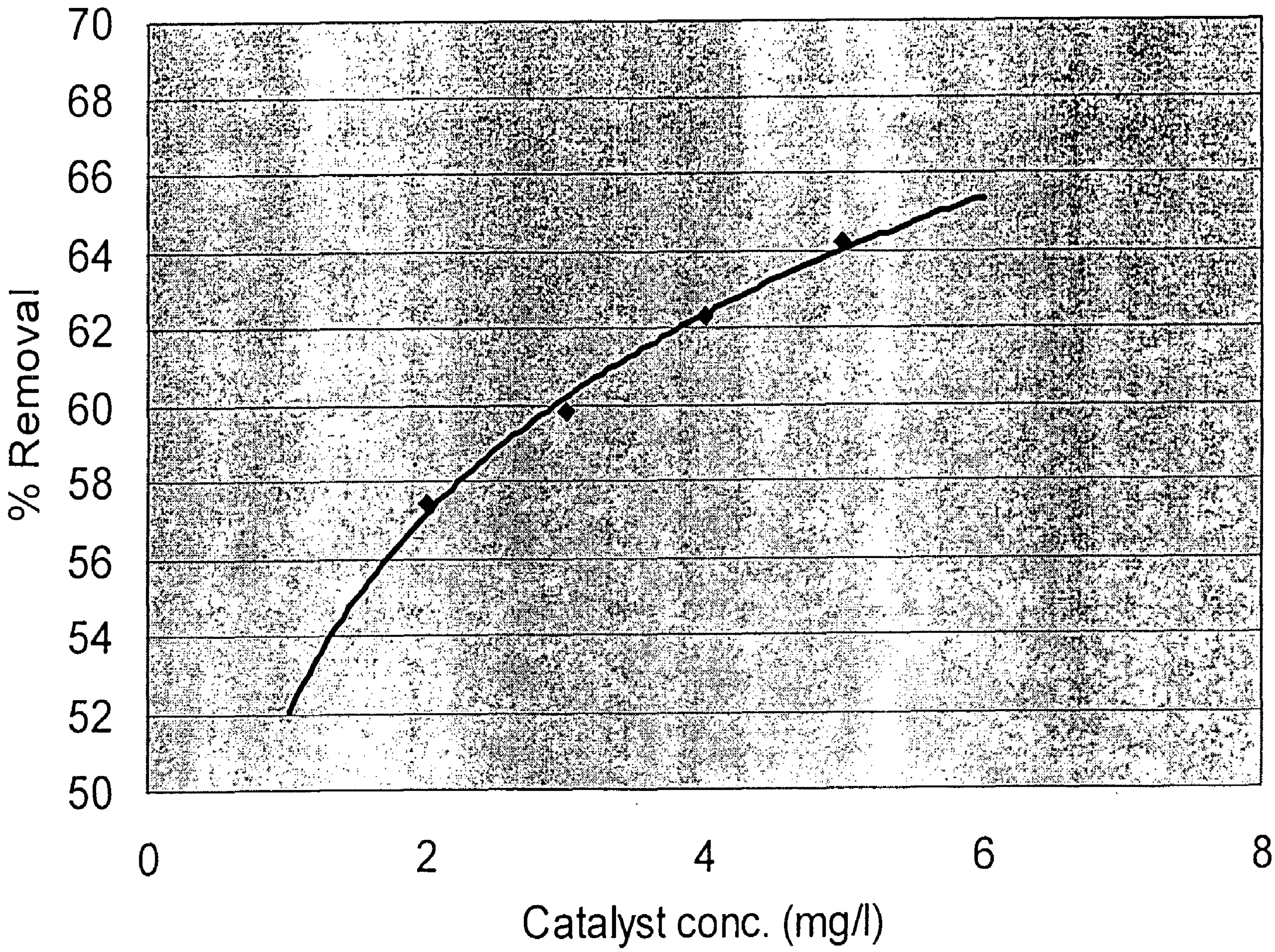


Fig. 4.7 Effect of catalyst conc. on % removal of pyridine using Cu-Co/C
T =160 °C. P_T = 9 bar, C_o = 10 mg/l, t = 1.5 hr, pH = 4

4.4 COMPARATIVE ACTIVITY OF DIFFERENT CATALYSTS FOR % REMOVAL OF PYRIDINE

Fig. 4.8 presents % removal of pyridine at different concentrations of catalyst $CuSO_4$ and Cu-Co/C. The % removal in each case is increased with increase in catalyst concentration, initially faster followed by a slower rate with $CuSO_4$ having a higher % removal in comparison to Cu-Co/C catalyst at 5 mg/l catalyst concentration. The % removal at 160 °C, 9 bar total pressure were 69 % approx and 64.2 % respectively after 1.5 hrs reaction time.

Fig. 4.9 presents % pyridine removal after 1 hour as a function of time for various catalysts. Fig. 4.9 presents % removal of pyridine as a function of reaction time using catalyst $CuSO_4$ and Cu-Co/C at the reaction conditions; $T = 160\ ^{o}C$, $P_T = 9$ bar, catalyst concentration = 5 mg/l.It is observed that the % removal of pyridine increases with time, with $CuSO_4$ having higher conversion in comparison to Cu-Co/C at 2 hour of reaction time the % removal using $CuSO_4$ and Cu-Co/C catalyst were 75.1 % and 71.8 % respectively as shown in fig. 4.10. The reaction conditions are shown in table 4.8 and 4.9 respectively.

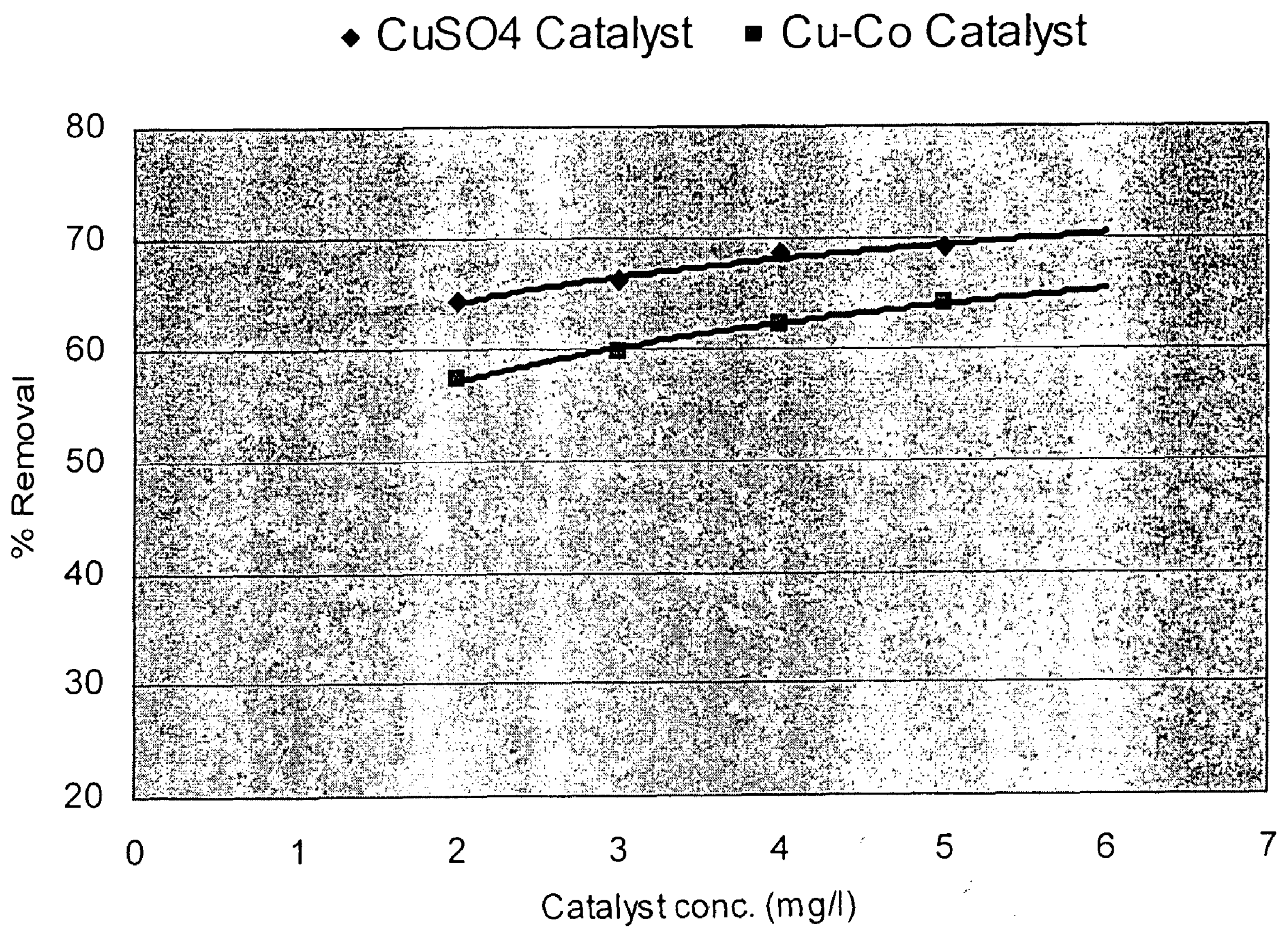


Fig. 4.8 % removal of pyridine at different conc. of different catalysts
T =160 °C, P_T = 9 bar, C_o = 10 mg/l, t = 1.5 hr, pH = 4

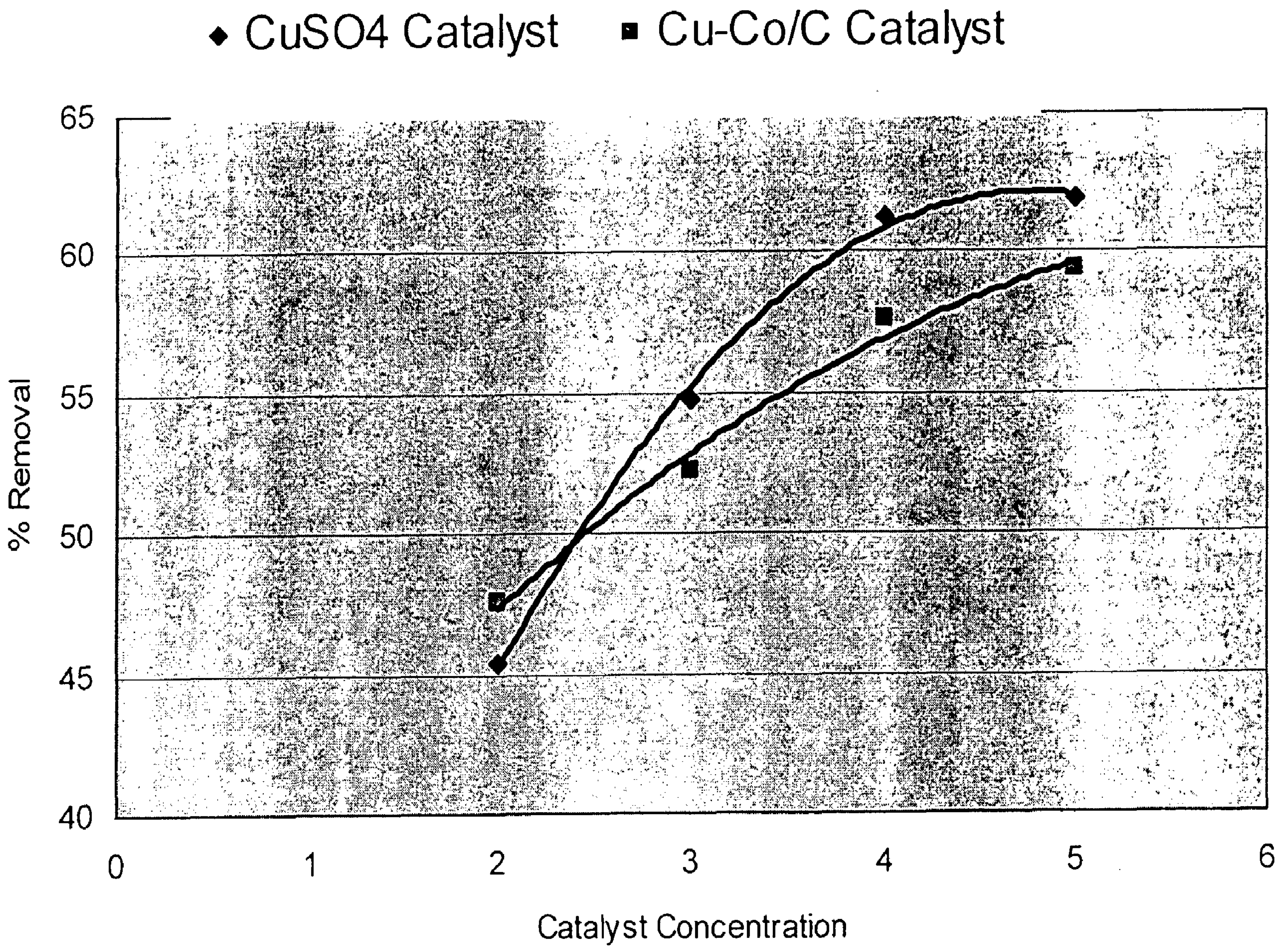


Fig. 4.9 Effect of catalyst conc. of different catalyst on % removal of pyridine
T =160 °C, P_T = 9 bar, C_0 = 10 mg/l, t = 1 hr, pH = 4

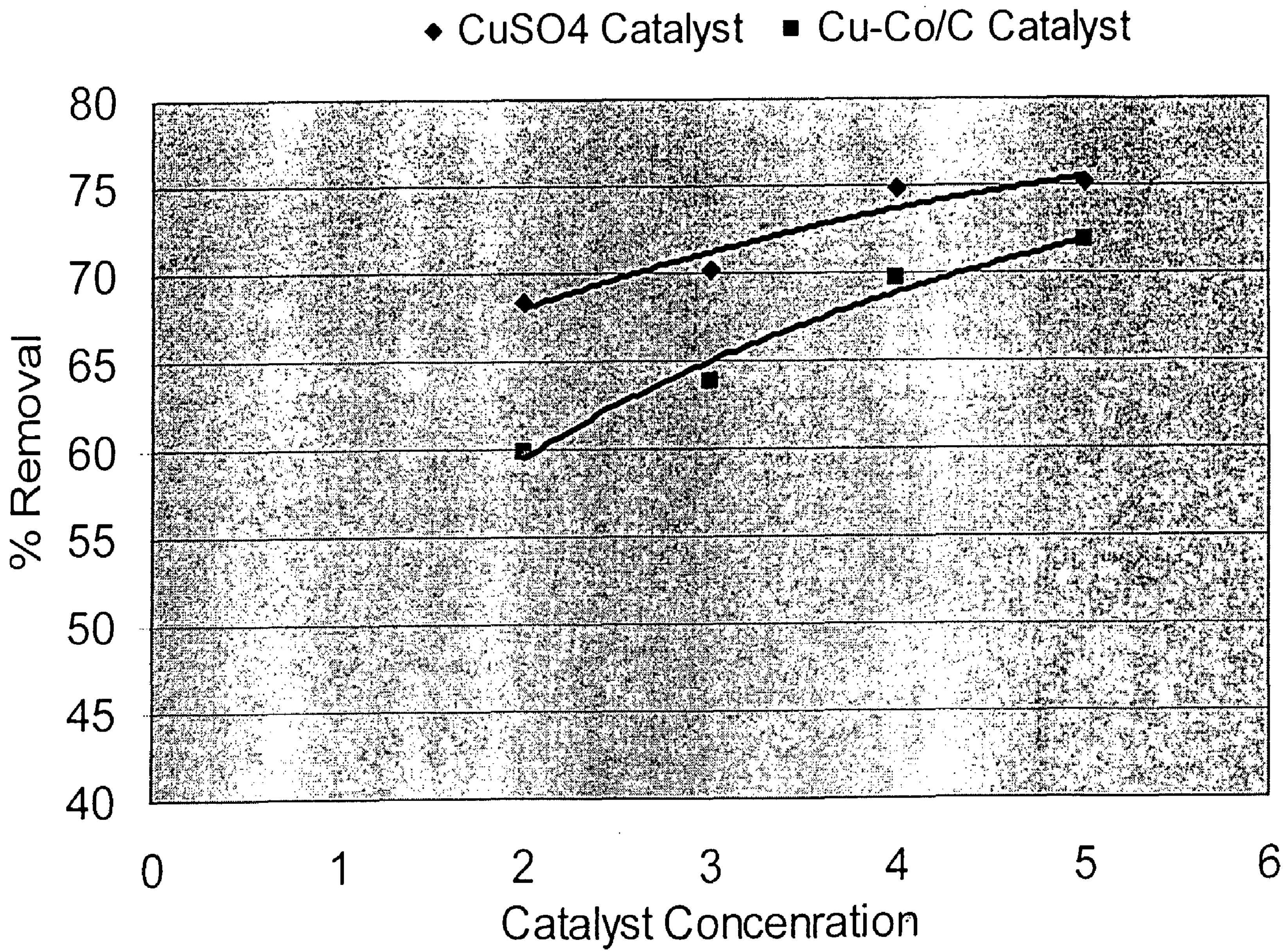


Fig. 4.10 Effect of catalyst conc. of different catalyst on % removal of pyridine
T =160 °C, P_T = 9 bar, C_o = 10 mg/l, t = 2 hr, pH = 4

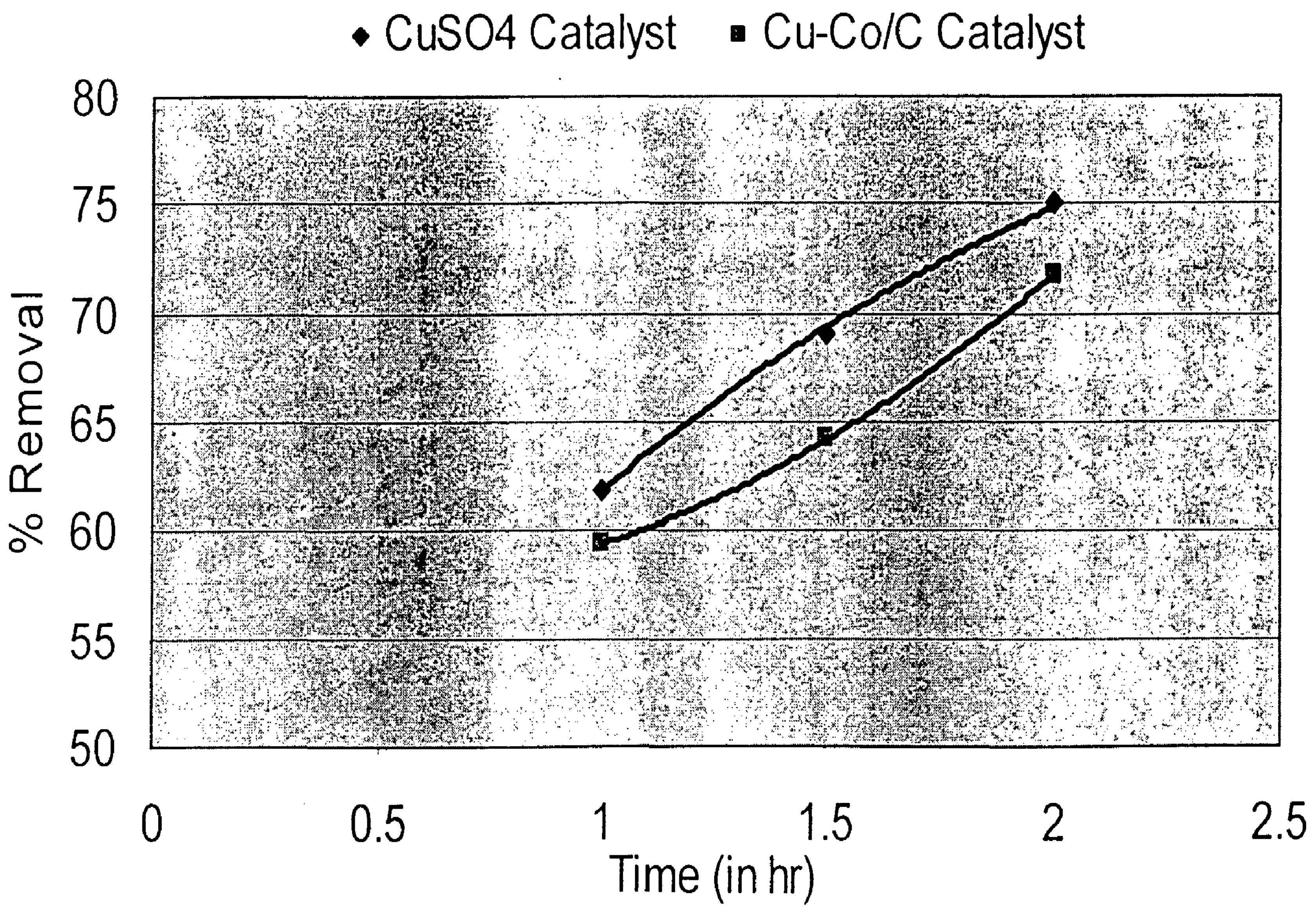


Fig 4.11 % removal of time as a function of reaction time using catalyst $CuSO_4$ and Cu-Co/C

T =160 °C, $\dot{P}_T$ = 9 bar. C_0 = 10 mg/l. t = 2 hr, pH = 4 Catalyst Conc. = 5 mg/l

4.5 KINETIC PARAMETER STUDIES

The rate constant for pyridine removal was assumed to be the function of the concentration of the substrate as well as the oxygen partial pressure. Since in all the runs the partial pressure of the oxygen is kept constant, the rate constant of the reaction would invariably be a function of substrate concentration. Levee et al. (2000) proposed Ist order kinetics with respect to total organic carbon removal of butyric acid. The global equation rate was also mentioned in eqn (1.9). In most cases, a first-order reaction with respect to the organic substrate was observed (Lixiong et al., 1991).

We also consider the rate to follow a first order kinetics and try to show through the experimental data for its applicability.

For a first order reaction we may write,

$$-r_A = -\frac{dC_A}{dt} = kC_A \qquad \text{..........(4.3)}$$

where,

C_A = concentration of substrate (pyridine)

For the concentration of substrate we can write

$C_A = C_{AO}(1 - X_A)$

$$-C_A \frac{d(1-X_A)}{dt} = k\,C_{AO}(1-X_A)$$

or, $$-k\,dt = -\frac{1}{(1-X_A)}\,d\,X_A$$

$$k\,t = -\ln(1-X_A) \qquad \text{.............(4.4)}$$

For determining rate constant of the reaction of a Ist order equation a plot between $-\ln(1-X_A)$ Vs reaction time in hours is plotted. Rate constant for each catalyst was found at temperatures of 160 °C of operation. The catalysts were $CuSO_4$ and Cu-Co/C and the concentration was varied from 2mg/l to 5 mg/l. The partial pressure of the air in all the cases is supposed to be constant and the reactor pressure was also kept constant between 9 bars. The pH value has already been optimized at 4.

Figure 4.12 represent a plot of $-\ln(1-X_A)$ Vs reaction time in hours. From this plot its is observed that the value of the rate constant with respect to pyridine removal using

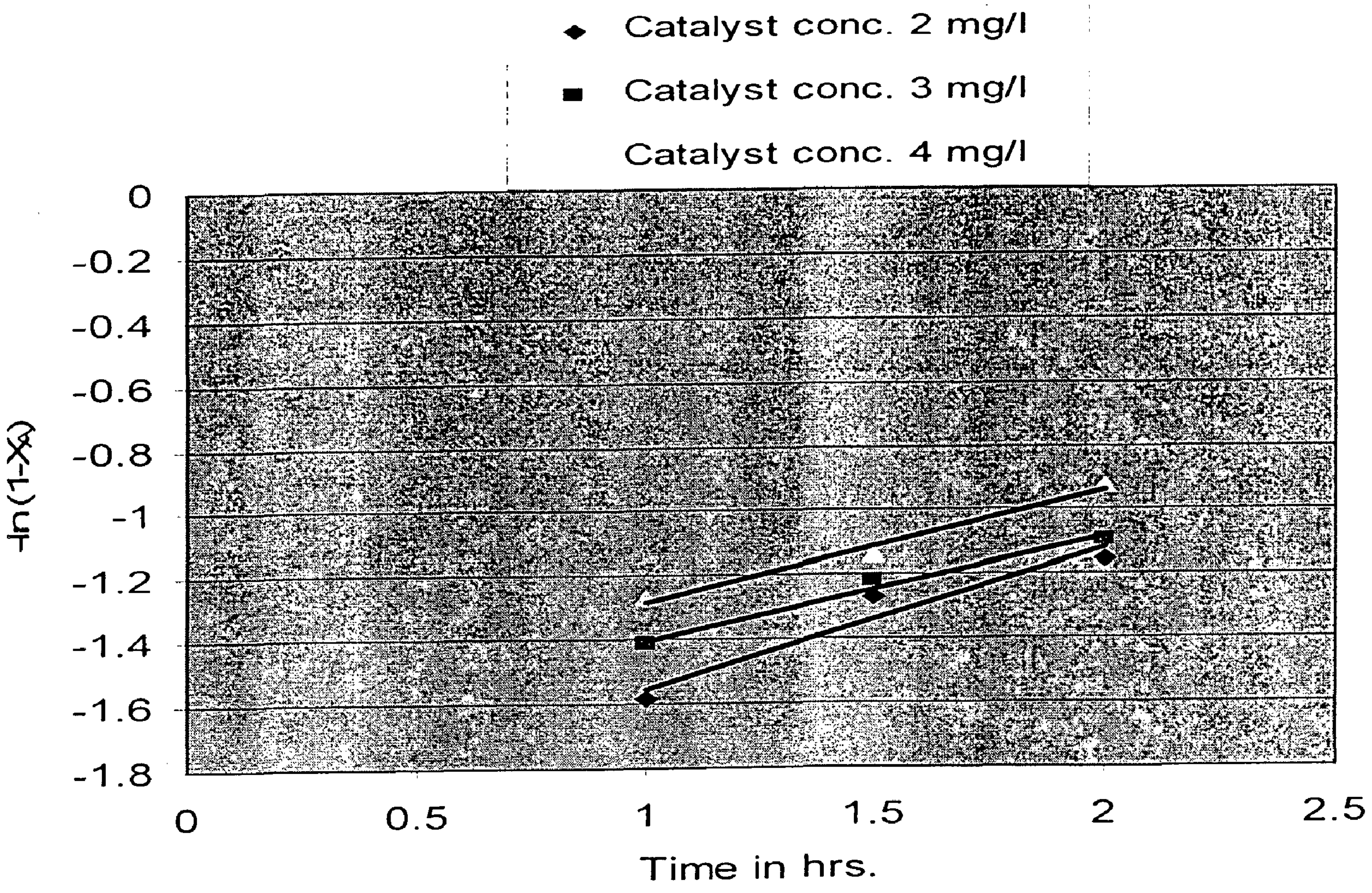


Fig 4.12 Kinetic plot of - ln(1-X_A) v/s reaction time for $CuSO_4$ catalyst

T =160 °C, P_T = 9 bar, C_o = 10 mg/l, t = 2 hr, pH = 4

$CuSO_4$ fits a straight line thus showing the validity of first order rate expression. The values of rate constant using $CuSO_4$ at two different temperatures 150 °C and 160 °C were tabulated in table 4.10.

$y = 0.436x - 1.9907$ .... (4.5)

$R^2 = 0.9381$ .... (4.6)

$y = 0.32x - 1.7237$ .... (4.7)

$R^2 = 0.9852$ .... (4.8)

$y = 0.348x - 1.6343$ .... (4.9)

$R^2 = 0.98$ .... (4.10)

Equations (4.5) and (4.6), gives the relation between $-\ln(1-X_A)$ Vs reaction time (in hours) for $CuSO_4$ catalyst concentration of 4 mg/l. The equation and the R^2 value of the relation indicate that the data fits almost a straight line, showing the validity of the first order expression.

Similarly equations (4.7) and (4.8) as well as (4.9) and (4.10) shows the validity of the first order rate expression for catalyst concentration of 3 mg/l and 2 mg/l respectively.

The values of rate constant for different catalyst concentrations of $CuSO_4$ are shown in table 4.10.

Table 4.10 Rate constant for different concentrations of $CuSO_4$

Time in hrs	**Catalyst Conc. 2mg/l**	**Rate Constant hr^{-1}**	**Catalyst Conc. 3mg/l**	**Rate Constant hr^{-1}**	**Catalyst Conc. 4mg/l**	**Rate Constant hr^{-1}**
1.0	-1.587	-1.58719	-1.415	-1.41585	-1.272	-1.27257
1.5	-1.272	-0.84838	-1.221	-0.81389	-1.141	-0.76069
2.0	-1.151	-0.57529	-1.095	-0.54764	-0.924	-0.46213

Figure 4.13 represent a plot of $-\ln(1-X_A)$ Vs reaction time in hours. From this plot its is observed that the value of the rate constant with respect to pyridine removal using Cu-Co/C fits a straight line thus showing the validity of first order rate expression. The values of rate constant using Cu-Co/C at two different temperatures 150 °C and 160 °C were tabulated in table 4.11.

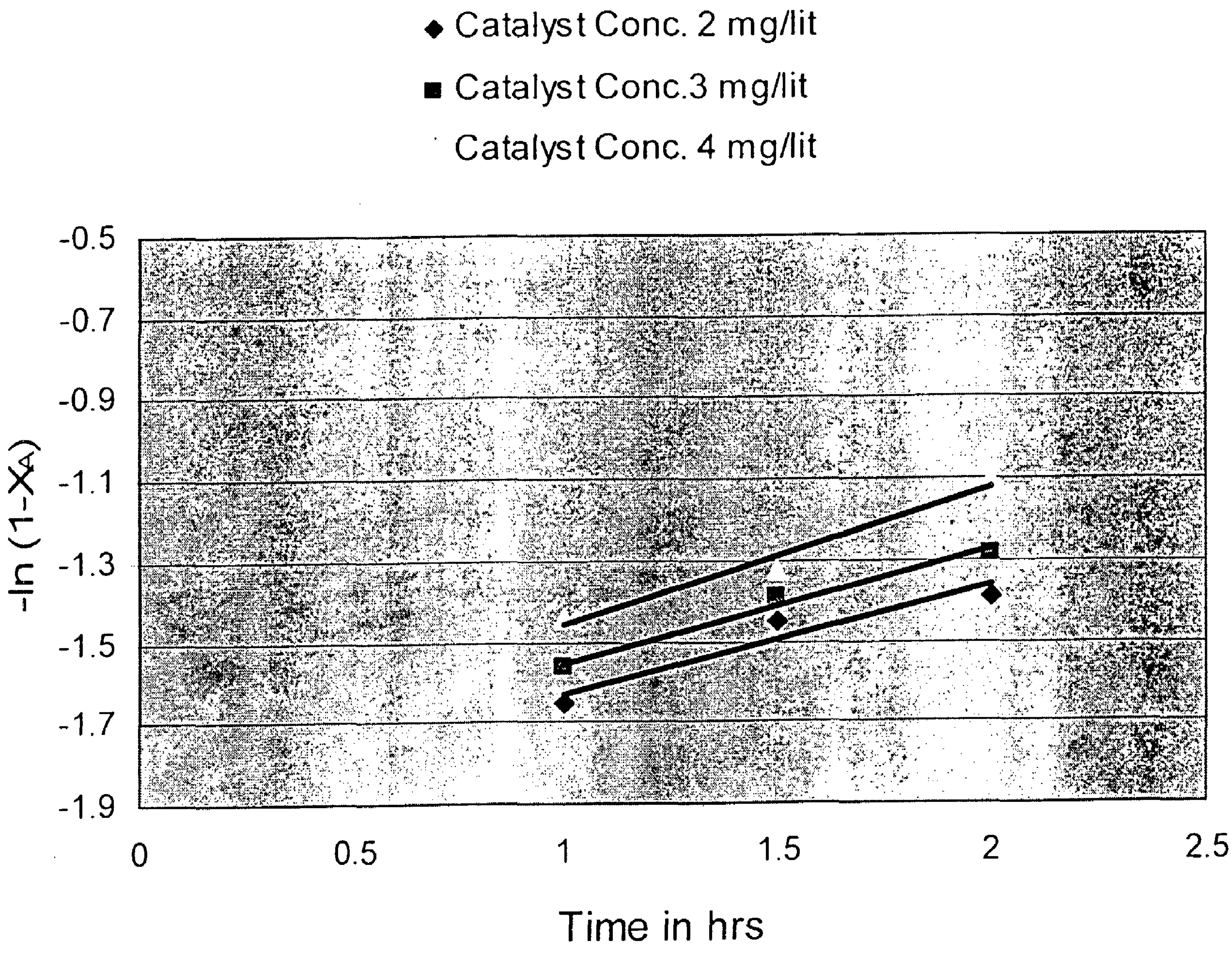


Fig 4.13 Kinetic plot of - $\ln(1-X_A)$ v/s reaction time for Cu-Co/C catalyst

$T = 160\ ^{o}C$, $P_T = 9$ bar, $C_o = 10$ mg/l, t = 2 hr, pH = 4

$y = 0.267x - 1.8985$ .... (4.11)

$R^2 = 0.9082$ .... (4.12)

$y = 0.278x - 1.8307$ .... (4.13)

$R^2 = 0.9804$ .... (4.14)

$y = 0.336x - 1.797$ .... (4.15)

$R^2 = 0.9702$ .... (4.16)

Equations (4.11) and (4.12), gives the relation between $-\ln(1-X_A)$ Vs reaction time (in hours) for Cu-Co/C catalyst concentration of 4 mg/l The equation and the R^2 value of the relation indicate that the data fits almost a straight line, showing the validity of the first order expression.

Similarly equations (4.13) and (4.14) as well as (4.15) and (4.16) shows the validity of the first order rate expression for catalyst concentration of 3 mg/l and 2 mg/l respectively. The values of rate constant for different applied catalyst concentrations of Cu-Co are shown in table 4.11.

Table 4.11 Rate constant for different concentrations of Cu-Co/C

Time in Hours	Catalyst Conc. 2mg/l	Rate Constant hr^{-1}	Catalyst Conc. 3mg/l	Rate Constant hr^{-1}	Catalyst Conc. 4mg/l	Rate Constant hr^{-1}
1.0	-1.656	-1.65632	-1.564	-1.56444	-1.444	-1.44456
1.5	-1.449	-0.96618	-1.391	-0.92752	-1.327	-0.88472
2.0	-1.389	-0.6944	-1.286	-0.64324	-1.108	-0.55428

CHAPTER V

CONCLUSIONS

CONCLUSIONS

Based on the experimental results the following conclusions may be drawn:

(a) The homogenous catalyst $CuSO_4$ and the heterogeneous catalyst Cu-Co/C have optimum activity at the initial pH of pyridine solution as 4.

(b) The catalyst concentration of 5 mg/l was found to be nearly optimum as the increase in the % removal of pyridine was very little when the catalyst concentration was increased beyond 5 mg/l.

(c) The experiment conducted at reaction temperature 150 °C and 160 °C showed that the % removal was higher at 160 °C. Using $CuSO_4$ catalyst the % removal increased from 56 % at 150 °C to 64.3 % at 160 °C at optimum pH – 4.

(d) The % pyridine removal was observed to increase as the reaction time was increased from 1 to 2 hours for both the catalysts $CuSO_4$ and Cu-Co/C/. After 2 hours of reaction time the % conversion with $CuSO_4$ was 75.1 % in comparison to 71.8 % with Cu-Co/C.

CHAPTER VI

RECOMMENDATIONS

RECOMMENDATIONS

Based on the experimental work conducted the following recommendation may be made for future work:

(a) Experiments should be conducted at even higher pressure and temperature to minimize the reaction time.

(b) The catalyst based in geolites, modified geolites and perovskite type oxides may also be studied for the removal of nitrogen containing organic compounds from the waste water.

(c) In order to correlate the activity pattern with the type of catalyst, the catalyst must be characterized by BET surface area pore size, pore volume, SEM and TGA/DTA.

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APPENDIX

APPENDIX

4.1 SAMPLE REACTOR CONDITIONS WITHOUT CATALYST

4.1.1 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10 mg/l
Catalyst	---------
Catalyst concentration	---------
pH	7.8
Temperature	150 °C
Pressure	09 bar
Reaction Time	1.0 hour

4.1.2 After reaction conditions:

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.967	
Final concentration of sample* (mg/l)	9.58	04.2

* calculated from calibration curve

4.2 EFFECT OF INITIAL pH ON PYRIDINE REMOVAL USING $CuSO_4$ CATALYST

4.2.1 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10mg/l.
Catalyst	$CuSO_4$
Catalyst concentration	02 mg/l
Reaction Time	1.5 hour
Temperature	150 °C
Pressure	09 bar

4.2.2 After reaction conditions (initial pH = 10)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9293	
Final concentration of sample* (mg/l)	6.18	38.2

4.2.3 After reaction conditions (initial pH = 08)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9254	
Final concentration of sample* (mg/l)	5.83	41.7

4.2.4 After reaction conditions (initial pH = 06)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9165	
Final concentration of sample* (mg/l)	5.02	49.8

4.2.5 After reaction conditions (initial pH = 04)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9096	
Final concentration of sample* (mg/l)	4.4	56.0

4.2.6 After reaction conditions (initial pH = 02)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9211	
Final concentration of sample* (mg/l)	5.44	45.6

4.3 EFFECT OF INITIAL pH ON PYRIDINE REMOVAL USING $CuSO_4$ CATALYST

4.3.1 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10mg/l
Catalyst	$CuSO_4$
Catalyst concentration	02 mg/l
Reaction Time	1.5 hour
Temperature	160 °C
Pressure	09 bar

4.3.2 After reaction conditions (initial pH = 10)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9265	
Final concentration of sample* (mg/l)	5.93	40.7

4.3.3 After reaction conditions (initial pH = 08)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9216	
Final concentration of sample* (mg/l)	5.48	45.2

4.3.4 After reaction conditions (initial pH = 06)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9149	
Final concentration of sample* (mg/l)	4.88	51.2

4.3.5 After reaction conditions (initial pH = 04)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9004	
Final concentration of sample* (mg/l)	3.57	64.3

4.3.6 After reaction conditions (initial pH = 02)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9193	
Final concentration of sample* (mg/l)	5.28	47.2

4.4 EFFECT OF INITIAL pH ON PYRIDINE REMOVAL USING Cu-Co/C CATALYST

4.4.1 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10mg/l
Catalyst	Cu-Co/C
Catalyst concentration	02 mg/l
Reaction Time	1.5 hour
Temperature	150 °C
Pressure	09 bar

4.4.2 After reaction conditions (initial pH = 10)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9302	
Final concentration of sample* (mg/l)	6.26	37.4

4.4.3 After reaction conditions (initial pH = 08)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9273	
Final concentration of sample* (mg/l)	6.00	40.0

4.4.4 After reaction conditions (initial pH = 06)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9211	
Final concentration of sample* (mg/l)	5.44	45.6

4.4.5 After reaction conditions (initial pH = 04)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9125	
Final concentration of sample* (mg/l)	4.66	53.4

4.4.6 After reaction conditions (initial pH = 02)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9227	
Final concentration of sample* (mg/l)	5.58	44.2

4.5 EFFECT OF INITIAL pH ON PYRIDINE REMOVAL USING Cu-Co/C CATALYST

4.5.1 Before reaction conditions:

Parameters	**Values**
Initial Sample Concentration	10mg/l
Catalyst	Cu-Co/C
Catalyst concentration	02 mg/l
Reaction Time	1.5 hour
Temperature	160 °C
Pressure	09 bar

4.5.2 After reaction conditions (initial pH = 10)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9306	
Final concentration of sample* (mg/l)	6.3	37.0

4.5.3 After reaction conditions (initial pH = 08)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9260	
Final concentration of sample* (mg/l)	5.88	41.2

4.5.4 After reaction conditions (initial pH = 06)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9189	
Final concentration of sample* (mg/l)	5.24	47.6

4.5.5 After reaction conditions (initial pH = 04)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9080	
Final concentration of sample* (mg/l)	4.26	57.4

4.5.6 After reaction conditions (initial pH = 02)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9208	
Final concentration of sample* (mg/l)	5.41	45.9

4.6 % REMOVAL OF PYRIDINE USING CATALYST AT DIFFERENT CONCENTRATION ($CuSO_4$)

4.6.1 Before reaction conditions:

Parameters	**Values**
Initial Sample Concentration	10mg/l
Catalyst	$CuSO_4$
pH	04
Reaction Time	1.5 hour
Temperature	160 °C
Pressure	09 bar

4.6.2 After reaction conditions (Catalyst Conc. = 03 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8984	
Final concentration of sample* (mg/l)	3.39	66.1

4.6.3 After reaction conditions (Catalyst Conc. = 04 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8955	
Final concentration of sample* (mg/l)	3.13	68.7

4.6.4 After reaction conditions (Catalyst Conc. = 05 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8956	
Final concentration of sample* (mg/l)	3.1	69.0

4.7 % REMOVAL OF PYRIDINE USING CATALYSTS AT DIFFERENT CONCENTRATIONS (Cu-Co/C)

4.7.1 Before reaction conditions:

Parameters	**Values**
Initial Sample Concentration	10mg/l
Catalyst	Cu-Co/C
pH	04
Reaction Time	1.5 hour
Temperature	160 °C
Pressure	09 bar

4.7.2 After reaction conditions (Catalyst Concentration = 03 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9054	
Final concentration of sample* (mg/l)	4.02	59.8

4.7.3 After reaction conditions (Catalyst Concentration = 04 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9026	
Final concentration of sample* (mg/l)	3.77	62.3

4.7.4 After reaction conditions (Catalyst Concentration = 05 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9005	
Final concentration of sample* (mg/l)	3.58	64.2

4.8 % REMOVAL OF PYRIDINE USING DIFFERENT CATALYSTS AT DIFFERENT CONCENTRATIONS ($CuSO_4$)

4.8.1 Before reaction conditions:

Parameters	**Values**
Initial Sample Concentration	10mg/l
Catalyst	$CuSO_4$
pH	04
Reaction Time	1.0 hour
Temperature	160 °C
Pressure	08-10 bar

4.8.2 After reaction conditions (Catalyst Concentration = 02 mg/l)

:Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9213	
Final concentration of sample* (mg/l)	5.46	45.4

4.8.3 After reaction conditions (Catalyst Concentration = 03 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9109	
Final concentration of sample* (mg/l)	4.52	54.8

4.8.4 After reaction conditions (Catalyst Concentration = 04 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9037	
Final concentration of sample* (mg/l)	3.87	61.3

4.8.5 After reaction conditions (Catalyst Concentration = 05 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9031	
Final concentration of sample* (mg/l)	3.81	61.9

4.8.6 Before reaction conditions:

Parameters	**Values**
Initial Sample Concentration	10mg/l
Catalyst	$CuSO_4$
pH	04
Reaction Time	2.0 hour
Temperature	160 °C
Pressure	08-10 bar

4.8.7 After reaction conditions (Catalyst Concentration = 02 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8959	
Final concentration of sample* (mg/l)	3.16	68.4

4.8.8 After reaction conditions (Catalyst Concentration = 03 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.8940	
Final concentration of sample* (mg/l	2.99	70.1

4.8.9 After reaction conditions (Catalyst Concentration = 04 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.8888	
Final concentration of sample* (mg/l)	2.52	74.8

4.8.10 After reaction conditions (Catalyst Concentration = 05 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.8884	
Final concentration of sample* (mg/l)	2.49	75.1

4.9 % REMOVAL OF PYRIDINE USING DIFFERENT CATALYSTS AT DIFFERENT CONCENTRATIONS (Cu-Co/C)

4.9.1 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10mg/l
Catalyst	Cu-Co/C
pH	04
Reaction Time	1 hour
Temperature	160 °C
Pressure	08-10 bar

4.9.2 After reaction conditions (Catalyst Concentration = 02 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9189	
Final concentration of sample* (mg/l)	5.24	47.6

4.9.3 After reaction conditions (Catalyst Concentration = 03 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9138	
Final concentration of sample* (mg/l)	4.78	52.2

4.9.4 After reaction conditions (Catalyst Concentration = 04 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9078	
Final concentration of sample* (mg/l)	4.24	57.6

4.9.5 After reaction conditions (Catalyst Concentration = 05 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9058	
Final concentration of sample* (mg/l)	4.06	59.4

4.9.6 Before reaction conditions:

Parameters	Values
Initial Sample Concentration	10mg/l
Catalyst	Cu-Co/C
pH	04
Reaction Time	2.0 hour
Temperature	160 °C
Pressure	08-10 bar

4.9.7 After reaction conditions (Catalyst Concentration = 02 mg/l)

Parameters	Values	% removal
Absorbance on Spectrophotometer	3.9053	
Final concentration of sample* (mg/l)	4.01	59.9

4.9.8 After reaction conditions (Catalyst Concentration = 03 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.9010	
Final concentration of sample* (mg/l)	3.62	63.8

4.9.9 After reaction conditions (Catalyst Concentration = 04 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8944	
Final concentration of sample* (mg/l)	3.03	69.7

4.9.10 After reaction conditions (Catalyst Concentration = 05 mg/l)

Parameters	**Values**	**% removal**
Absorbance on Spectrophotometer	3.8921	
Final concentration of sample* (mg/l)	2.82	71.8

CHAPTER IV

RESULTS AND DISCUSSION