Nanocatalyst in Remediating Environmental Pollutants

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ABSTRACT

Remediation of pollutants is a concerning topic for current environmental scenario. remediation is a control against pollutants to prevent the damage of the environment using nano-catalyst. alumina supported titanium catalysts (0.5 wt.%,1 wt.%,1.5 wt.%, 2 wt.%) were prepared by excess solution impregnation on alumina oxide support and used for catalytic wet air oxidation (CWAO) of oxalic acid. the oxidation of oxalic acid was performed in a three-neck round bottom glass reactor with a capacity of 1 L. The reactions were conducted by Ti/γ-Al_2O_3 catalysts under different process conditions, such as temperature from 60^0c to 90^0c and pressure from 1 bar to 15 bar, flow-rate is 1 L/min and Ti loading from 0.5 to 2.5 wt.%. the oxalic acid conversion (88.29%) was achieved using the Ti/γ-Al_2O_3 catalyst at 90^0C and 1.0 wt.% Ti metal loading. The influence of the titanium sintering (reducing treatment) was studied to modify the oxygen transfer from the gas phase onto the metallic active site of the catalyst and also to determine the effect of this treatment on the catalytic activity and stability. The activation energy for oxalic acid conversion was found to be 73.01 kJ mol^{-1} at the temperature range 60-90^0C. The support and catalysts were characterized by using different techniques such as BET, TGA. Here the alumina supported catalyst are used because it increased the catalyst activity and selectivity. (Ti/γ-Al_2O_3) catalyst are used for the remediation of environmental pollutants because of its low cost and easy availability to the market, high surface area, high pore diameter, high melting point and thermal stability.

LIST OF ABBREVIATIONS

AC : Activated Carbon

AOP : Advanced Oxidation Process

ARP : Advanced Reduction Process

ACC : Automobile Catalytic converter

BP-ANN : Backpropagation Artificial Neural Network

BET : Braunner-Emmett-Teller

BOD_5 : Biochemical Oxygen Demand

BPA : Bisphenol A

CNFs : Carbon Nanofibers

CNTs : Carbon Nanotubes

CWAO : Catalytic Wet Air Oxidation

CWPO : Catalytic Wet Peroxide Oxidation

COD : Chemical Oxygen Demand

CSD : Chemical Solution Deposition

CVD : Chemical Vapor Deposition

CFD : Computational Fluid Dynamics

CSTR : Continuous Stirred Tank Reactor

DFT : Density Functional Theory

EC : Electrocoagulation

EMSI : Electron Metal Support Interactions

EDCs : Endocrine Disrupting Chemicals

EDX : Energy Dispersive X-ray

FBR : Fluidized Bed Reactors

FTIR : Fourier Transform Infrared Spectroscopy

HWB : Hancili Region Bentonite Rock

HEO : High Entropy Oxide

HISWW : High Ionic Strength Wastewater

HTC : Hydrothermal Carbonization

HTL : Hydrothermal Liquefaction

ICP-AES : Inductively Coupled Plasma Atomic Emission Spectrometers

MCM-41 : Mobil Composition of Matter No. 41

MONPs : Metal Oxide Nanoparticles

MWCNTs : Multi Walled Carbon Nanotubes

DMF : N,N-Dimethylformamide

DATB : Novel Decamethonium Bromide

TBBS : N-Terl-Butyl-2-Benzothiazoles-Ulfenamide

p-HBA : p- Hydroxy Benzoic Acid

PPE : Phenethyl Phenyl Ether

ROC : Removal of Catalyst

RTD : Residence Time Distribution

RSM : Response Surface Methodology

SEM : Scanning Electronics Microscopy

FeSAC : Sewage Sludge Derived Activated Carbon

SPC : Silica Pillared Clay

SBRs : Still Batch Reactors

sCOD : Soluble Chemical Oxygen Demand

SAF : Sustainable Aviation Fuels

$LaCoO_3$: Synthesized Lanthanum Cobalt Oxide

TPD-MS : Temperature -Programmed Desorption Mass Spectrometry

TPR : Temperature Programmed Reduction

TGA : Thermogravimetric Analysis

tCOD : Total Chemical Oxygen Demand

TOC : Total Organic Carbon

TEM : Transmission Electron Microscopy

TBRs : Trickle Bed Reactors

TOF : Turnover Frequency

UV : Ultra Violet

WT : Wastewater Treatment

WWTPs : Wastewater Treatment Plants

WAO : Wet Air Oxidation

XRD : X-Ray Diffraction

XPS : X-Ray Photoelectron Spectroscopy

DEDICATED

TO

MY PARENTS & SIBLINGS

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Water, the lifeblood of our world, sustains all living organisms and ecosystems. After industrial pollution, there has been an increase in the number of industries and so has increased the number of pollutants which adversely affect the environment. These pollutants affect the quality of air as well as water. Water contamination ranks among the most urgent issues of our day, right up there with air pollution. Many factors contribute to water pollution, each of which introduces harmful pollutants that upset the brittle equilibrium of aquatic ecosystems. The effects are extensive and far-reaching, nevertheless of the source-industrial discharge of heavy metals and chemicals, agricultural runoff including pesticides and fertilizers, or the constant inflow of plastic waste matter into our waterways. As pollutants infiltrate rivers, lakes, and oceans, they not only disrupt fragile ecosystems but also pose grave risks to aquatic health as well as human health and well-being. Industrial effluent was generate waste water and these industrial waste water when discharged without proper treatment causes damage to the environment as well as human health. Some wastewater has higher concentration of certain chemicals while some are more dilute. Oxalic acid is present in dilute form in industrial waste water and is mainly used in different industries like that petrochemical, textile or pharmaceutical processes [Roy et al, 2014]. Although traditional methods such as distillation, adsorption and extraction are effective, they are not preferred because of their high separation cost under dilute feed conditions as well as transfer of pollutants from one medium to another [Balcı et al, 2023]. According to the wastewater with poor biodegradability, advanced oxidation technologies such as Fenton reaction, photo catalytic oxidation, electrochemical oxidation, catalytic wet air oxidation (CWAO). Among them, CWAO is one of the most promising water treatment methods, through wet oxidation process to degrade high-concentration, toxic and harmful pollutants. CWAO has the

advantages of mild reaction conditions, high treatment efficiency, fast reaction rate, small equipment, recyclable resources and low secondary pollution [Chai et al, 2023]. Traditional wastewater treatment techniques include physicochemical, thermal and biological treatment methods which are widely applied for the removal of pollutants. Incineration is appropriate for effluents with chemical oxygen demand (COD) over 150 mg L^{-1} but it is extremely energy consuming and generates further problems due to the hazardous emissions of dioxin and furan [Debellefontaine et al. 1996]. For wastewaters with higher amounts of COD (5-150 g L^{-1}) hot oxidation techniques i.e. wet air oxidation, wet peroxide oxidation and supercritical wet air oxidation are more convenient. In recent years, catalytic wet air oxidation (CWAO) and catalytic wet peroxide oxidation (CWPO) have received a lot of 16 attention in the research field of wastewater treatment [Perathoner & Centi 2005, Kim & Ihm 2011]. Both homogeneous and heterogeneous catalysts have been studied in CWPO and particularly in CWAO. Therefore, various materials such as metal oxides, carbon materials and noble metals have been widely studied in the abatement of organic pollutants from wastewater streams [Bhargava et al. 2006, Cybulski 2007]. The catalytic wet air oxidation (CWAO) is one of the most interesting techniques for achieving a meaningful extent of organic pollutant mineralization at moderate temperatures, moderate pressures and at a relatively short time in the presence of a highly active catalyst [Bensouilah et al, 2020]. In many industries was produced wastewaters which containing highly concentrated bio-toxic and recalcitrant organic pollutants. Their direct discharge into aquatic environment can result in a serve impact on both environmental and human health. Physical and biological treatments, traditional treatment technologies which was incapable to organic pollutants removing because of their toxicity and refractory nature. One of the most efficient and economically viable technology was catalytic wet air oxidation used to remove effluents, especially for effluents with high organic loads, where other chemical treatments was not possible or not as

efficient [Saidulu et al, 2021]. The increasing population and expansion of chemical industries lead to the generation of hazardous organic compounds, posing significant environmental threats. Various wastewater treatment methods have been developed, including bio-treatment, physical separation, and chemical oxidation techniques like wet oxidation, wet peroxide oxidation, and supercritical wet oxidation. However, these methods often face challenges such as high operating costs or low efficiency, making them unsuitable for growing industrial demands. Consequently, there is a need for superior technologies to address these challenges. Catalytic wet air oxidation (CWAO) has emerged as a promising solution, leveraging well-designed catalysts to efficiently convert toxic pollutants into harmless products like CO_2, N_2, and H_2O, offering an effective approach for industrial wastewater treatment [Ali et al, 2021]. Acetic, oxalic, propionic, and butyric acids serve as effective model systems because they are commonly formed during the oxidation of various complex organic compounds. Additionally, they are resistant to chemical oxidation, making them ideal for studying oxidation processes [Gomes et al, 2005]. The catalytic wet air oxidation of oxalic acid was observed using alumina supported Pt catalyst. Oxalic acid was very refractory to oxidation with low molecular weight organic substance, serves as a valuable model system due to its presence in the degradation pathways of many complex organic compounds. The conditions employed in this process are conducive to various catalyst deactivation phenomena, including poisoning, sintering, metal leaching, and coke formation [Roy and Saroha, 2014].

1.1. Source of waste water

Industry is believed to be the main source of organic pollutants in wastewater that ultimately reach aquatic eco-systems. Research shows that these environments contain trace

concentrations of a variety of pollutants, such as industrial compounds, personal care products, and endocrine disrupting chemicals (EDCs), typically micrograms per litre (μg/L) or measured in nanograms per liter (mg/L) [Bensouilah et al, 2020]. In many industries wastewater was produced highly concentrated bio-toxic and organic pollutants. These pollutants directly discharged into the aquatic environment, these are affected both environment and human health. Physical and biological wastewater treatment technologies are the conventional wastewater treatment technologies which are unable organic pollutants

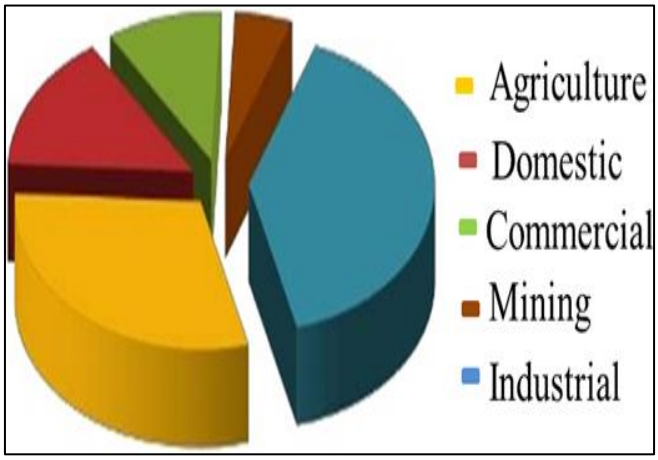


Fig.1. Sources of wastewater (Lakshmi Machineni, 2020)

removing due to their toxicity and refractory [F.M. Santos et al, 2021]. For drinking water, surface water is the source, for agricultural activities source is irrigation water and for industrial activities source is process water. As day to day progress, settlement of human and development had concentrated water resources. As such oceans, lakes and rivers were located in the densely populated and commercially developed areas [Roy et al, 2010].

1.2. Different pollutants names and their uses from wastewaters

1.2.1. Organic material

Carbon, hydrogen, nitrogen, oxygen and other elements and could either be carbohydrate, protein or fat which was contained in organic wastes. The source of organic materials of wastewater was plants, animals or source of synthetic. This all pollutants go in wastewater by the human wastes, paper products, detergents, cosmetics, foods and from agricultural, commercial, and industrial sources. The existence of organic matter in water increases the request for oxygen by organisms involved in decomposition, minimizing the amount of dissolved oxygen available to other living things in the water. When dissolved oxygen drops below a particular level, it impacts the health and metabolism of aquatic organisms, resulting in their fatalities. [Akpor et al, 2014].

1.2.2. Heavy metals

It was most man made pollutants, showed in wastewater like industrial, petroleum contamination and sewage disposal [Santos et al, 2005]. Zinc, copper and iron are the example of some heavy metals which stated to be necessary in aquatic environment due to their nature various biochemical processes, it was detrimental when high concentration present [Samir and Ibrahim, 2008]. Considered poisonous and carcinogenic, the majority of heavy metals represent major risks to human health as well as the environment and wildlife in receiving waterways. Even at very high concentrations, a number of heavy metals, including arsenic, copper, zinc, and nickel, have been shown to be hazardous. [Akpor et al, 2014]

1.2.3. Microbes

It was the majority source of microorganisms waterborne that cause human disease, it comes from wastes fecal which emission by animals or humans [Kris, 2007]. Pollutants was eliminated from from hyper-thermal, acidic, hyper-saline, or basic industrial waste by using microbes [Bala et al, 2022]. Most ordinary microbial pollutants in wastewater was bacteria, it cause a broad range of infections like as skin and tissue infections, diarrhea, dysentery etc. Giardia and Cryptosporidium was the major pathogenic protozoans which associated with wastewater. Those protozoans present more dominant in wastewater than any other environmental source [Akpor and Muchie, 2011]. Rotavirus, Astrovirus, Adenovirus, Norwalk virus, Picobirna virus, and Enterovirus was noticeable enteric viruses related to diarrhea [Some et al, 2021]. Microbial contaminants can also enter the body in other ways, such as during surgical procedures at a hospital or dentist.

1.2.4. Acetic acid

In many other compounds acetic acid is one of the simplest carboxylic acids. Acetic acid (systematically named ethanoic acid) was an organic compound with the chemical formula CH_3CO_2H (also written as CH_3COOH). It has a colourless liquid when it undiluted formed also called glacial acetic acid. Irritation to the nose, throat, and lungs due to inhalation of acetic acid. This substance was corrosive and concentrated vapor of inhalation can cause serious damage to the lining of these organs and later cause breathing difficulties. Repeated exposure may cause sensitization if swallowed, this material can cause severe burns to the oral cavity and gastrointestinal tract, which can lead to vomiting, diarrhea, circulatory failure, kidney failure and death. Sensititation of skin was the uncommon result of exposure.

According to industries report acetic acid discharge paper manufacture and paper products, meat and meat products, textile products and chemicals [J Kulkarni et al, 2013].

1.2.5. Phenol

Phenol, present in wastewater was dangerous if discharge untreated. It create serious risks to living organisms. Phenol was exsist in effluent that contain chemical and pharmaceutical industries like as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. This is a highly corrosive and neurotoxic substance [Naguib et al, 2020]. Phenols cause harmful side effects such as a sour taste in the mouth, diarrhea, vision problems, and the dark urine excretion. It is also toxic to fish. Toxicity levels typically range between levels of 10 to 24 mg/l for humans and 9 to 25 mg/l of toxicity levels for fish. The lethal concentration of phenol in the blood is approximately 150 mg/100 ml. Hot gas or steam stripping, adsorption, ion exchange solvent extraction, oxidation, phase transfer catalysis, and biological treatment processes was used for removal and/or phenol recovery. Phenol wastewater is treated with activated carbon in fixed bed/moving bed/fluidized bed. When inhaled, it is quickly absorbed through the skin and lungs. When an appropriate amount of phenol is ingested, it is detoxified by binding with sulfuric acid or glucuronic acid and excreted in the urine [Gad et al, 2008].

1.2.6. Oxalic Acid

Oxalic acid is mainly occurs in many plants and vegetables and also produced molds of metabolism. It is extensively used in chemical industry which more toxicity features. Oxalic acid is corrosive to the eyes and skin and is classified in the acute eye and skin irritation

toxicity category [Hasan et al, 2023]. It is also very irritating when inhaled and damages the respiratory tract. Acute exposure also causes stomach inflammation, decreased calcium levels, nervous system effects, and kidney damage in humans. The production of oxalate, dextrin, tartar, celluloid, tartaric acid, purified methyl alcohol, glycerin and stable hydrogen cyanide was used by oxalic acid. Oxalic acid had also been used in medicine of veterinary, as a hemostatic [Martínez-Huitle et al, 2008].

1.3. Different treatment technologies for effluent treatment

1.3.1. Wet air oxidation (WAO)

For treatment of effluent WAO is the most important and useful method. For the incineration process organic pollutants concentration of CWAO is very low which was expensively not efficient the result would be given marginal saving and toxic effluents because of additional cost of fuel or heat recovery. Total organic carbon such as insoluble polymers, waste water and organic compounds was removed to applied WAO process. At the condition of very high temperature and pressure are necessary to remove efficient pollutants by using WAO method [Lee et al, 2000]. Wet air oxidation (WAO) is a important technology which consists of mineralizing organic carbon through oxidation to CO_2, holds great promise for industrial wastewater treatment and recycling if investment and operating costs are significantly reduced. This can be achieved through the use of catalysts that accelerate the rate of oxidation to CO_2, improve overall carbon reduction, and allow operation under milder temperature and pressure conditions than would be required without a catalyst [Beziat et al, 1999]. WAO is the liquid-phase oxidation of organic or oxidizable inorganic components using oxygen (usually air) 2 at high temperatures (125-320°C) and pressures (0.5-20 MPa). Molecular oxygen and matter both was improved with contact that was to be oxidized. At high

temperatures, organic materials are converted to carbon dioxide and water. The concentration of dissolved oxygen and the oxidation rate was increased by the maintained of high pressure in the liquid phase [Kumar et al, 2006]. Dissolved oxidation pollutants or suspended in water

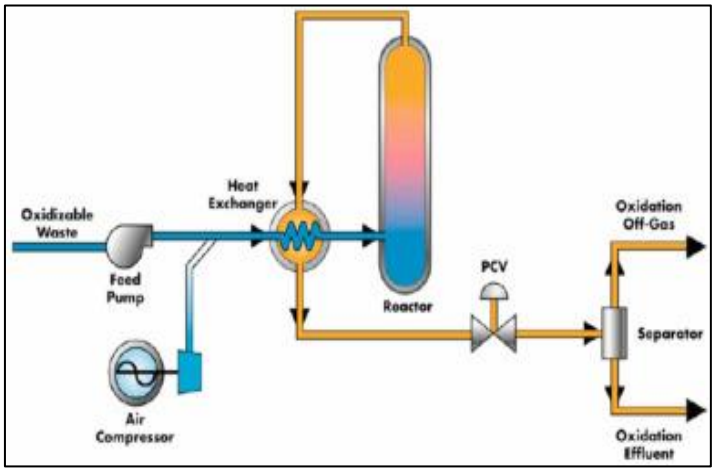


Fig.2. Wet air oxidation process (Gerd Brunner, 2014)

using pure oxygen or air that present in the wet air oxidation process. This occurs under highly intense pressure and temperature conditions. Wet Air Oxidation (WAO) is frequently employed for treating wastewater with organic compounds like phenolic derivatives. It's used when concentrations are too high for biological treatment yet too dilute for incineration with energy recovery [Bouabdellah et al, 2021].

1.3.2. Catalytic wet air oxidation (CWAO)

The advanced catalytic wet air oxidation process is used with various catalysts that had been pretend to reduce order of oxidation strength conditions. The CWAO process is to be most attractive method to used catalysts and achieved high conversion at the condition of lower temperature and pressure [Lee et al, 2000]. Catalytic WAO can be performed using a catalyst dissolved in the reaction medium. From the treated water through additional separation process soluble catalysts such as transition metal cations (essentially copper) had to be

recovered. The liquid phase is easily separated using either batch or continuous processes of heterogeneous catalyst, but must be stable for long periods in acidic, oxidizing, and often chelating reaction medium [Beziat et al, 1999]. Wet air catalytic oxidation (CWAO) is widely used to speed up the reaction rates and reduce the severity of conditions. Several homogeneous and heterogeneous catalysts were used. It is important to use a catalyst system that is stable and does not wash out in solution due to reaction with acid [Kumar et al, 2006]. For industrial wastewater treatment one promising method was used that is catalytic wet air oxidation method. It efficiently reduces chemical oxygen-demanding substances using an oxidizing agent under moderate conditions (125-220°C, 5-50 bar pressure) with the assistance of a suitable catalyst [Gomes et al, 2005].

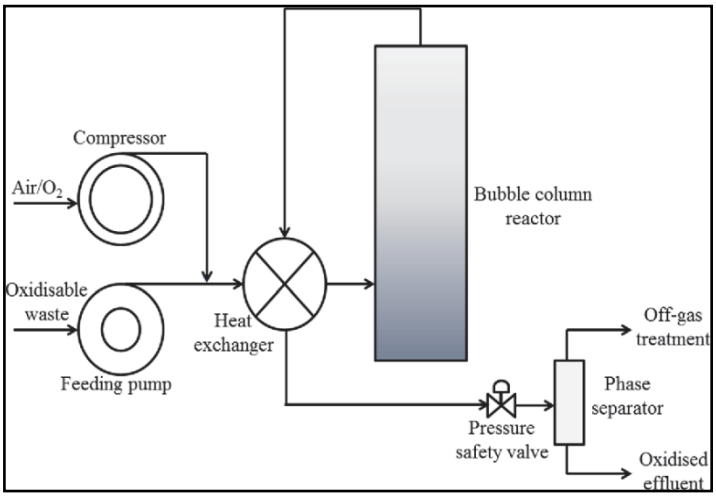


Fig.3. Catalytic wet air oxidation process **(**A Heponiemi, 2015)

Table 1: Process data of CWAO using different metals and support [Roy et al, 2010].

Metal	**Support**	**Substrate**	**T (^{0}C)**	**P (MPa)**
Pt	γ-Al_2O_3	Acetic acid	> 200	2
Ru, Ir, Pd, Ag, base metals	CeO_2, TiO_2, ZrO_2	Acetic acid	200	2
Pt	γ-Al_2O_3	Maleic acid	>120	>0.4
Ru	CeO_2	Maleic acid	>160	2
Pt	C	Carboxylic acids	>20	>0.1
Pt	C	Carboxylic acids	200	0.69
Pt	γ-Al_2O_3, resin	Carboxylic acids	80	0.1
Ir	C	Butiric acid	200	0.69
Pt, Ru, Rh	TiO_2, CeO_2, C	Phenol/acrylic acid	170	0.2
Pt	γ-Al_2O_3	Phenol	>155	2
Pt, Ag	MnO_2/CeO_2	Phenol	>80	0.5
Ru	C, CeO_2/C	Phenol	160	2
Pt	C	P-chlorophenol	170	2.6
Pt, Ru, Pd, Ir	CeO_2	Ammonia	>150	2
Pd	C	Ammonia	280	2
Pt	SDB resin	Ammonia	>110	<0.28
Pt, Ru, Pd, Ir	TiO_2, CeO_2, C	Ammonia	>150	1.5
Ru	TiO_2, ZrO_2	Kraft effluent	190	5.5
Pd-Pt-Ce	γ-Al_2O_3	Kraft effluent	>130	>1.5

1.3.3. Incineration Process

Incineration is the most important and largely implemented of the sludge thermo-chemical treatment processes. The feed organics eliminated by using incineration process which is more effective, little odour produced and generates a stable solid ash product and substantially reusable. Incineration stands out as the most efficient treatment method due to its high reduction capacity, remarkable reduction capabilities, complete treatment of waste, and minimal pollution. Additionally, it offers the benefit of electricity generation. This makes it the primary waste treatment method in China currently and is expected to remain so in the future [Miao et al, 2021]. Incineration reactors are mainly structured as fluidized beds. Fluidized beds is working at 800-900°C temperature and under atmospheric pressure. It is flammable in the presence of air. Incineration of wastewater solids takes place in two steps. The first is drying the solids, so that their temperature is increased to the required point where water evaporates in the solids. The second step is the real combustion of the solids of volatile fraction. Combustion can only occur after enough water is removed [Sakai et al, 2000]. Recent advancements grow in the incineration process that involve hot gas, like air, in a rotary kiln to decompose explosive waste. This technology consistently maintained and monitored huge quantities of waste materials. Incineration facilities can be reduced by more than 100 times by decreasing the need for storage space. Furthermore, NOx emissions can be reduced substantially, from 285 to 25 grams of NO_2 equivalent per kilogram of energy material. [Cho et al, 2020]. The method is hygienic, effectively destroying all vectors and pathogens. It reduces waste volume, making disposal easier. It doesn't produce any odor and the resulting residue is degradable. The process has high plant cost, can cause secondary pollution, and produces toxic intermediates.

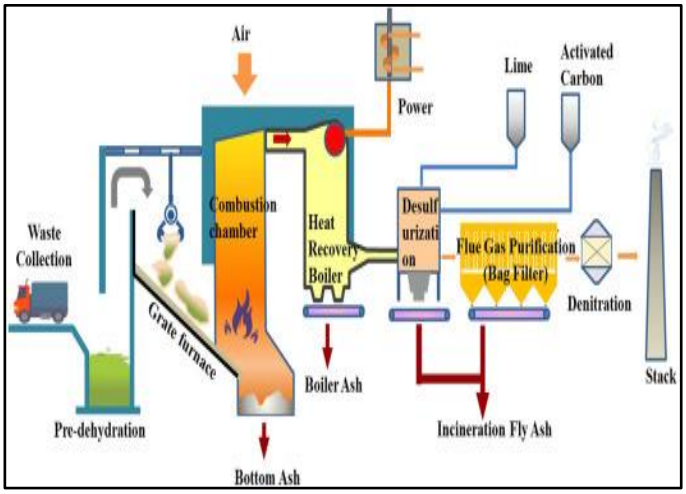


Fig.4. Incineration process of wastewater (V Funari, Elsevier-2022)

1.3.4. Adsorption Process

Adsorption occurs when molecules or ions in the bulk phase of a gas or liquid accumulate on a solid surface. The substance utilized for adsorption is known as the adsorbent, and the molecules or ions are the adsorbates. It is not uncommon for liquid to be used as an adsorbent. Adsorption is a surface phenomenon that affects only the surface of the adsorbent, without the adsorbate penetrating inside the structure of the adsorbent. The opposite mechanism, the desorption of molecules from the adsorbent surface, is called desorption [Rathi et al, 2021]. The process has low operational cost, relatively high efficiency, design simplicity, is non-toxic, and is regenerative. It has low selectivity of the adsorbent, disposal problems, and is non-destructive. It requires high investment and the adsorbent rapidly saturates.

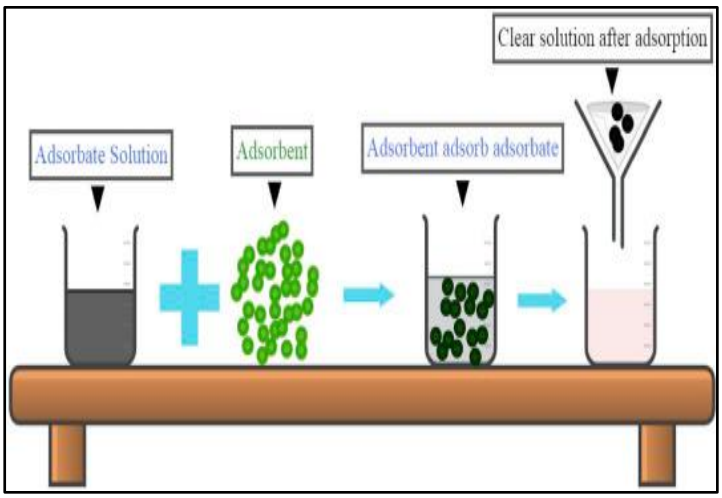


Fig.5. Adsorption process (Rathi et al, 2021)

1.3.5. Electrolysis Process

Electrolysis is a technology that applies electricity to wastewater. The electric current destabilizes the dissolved colloidal particles and changes the charge of the suspended particles, allowing for water purification. Compared to conventional treatment, wastewater can be treated more efficiently. It is effective to remove non-biological and even toxic components from waste streams. The system is small, modular, and portable, and it runs softly. The electrolysis process is shown as either batch or continuous operation. It is a complicated process that involves a variety of chemical and physical phenomena and uses disposable electrodes to introduce ions into wastewater. During this process, coagulants are created in situ by electrolytic oxidation of iron (Fe) and aluminum (Al) electrodes that serve as anodes, releasing ions continually into the system. These ions help neutralize particle charges, initiating coagulation. They can then remove unwanted contaminants like metal

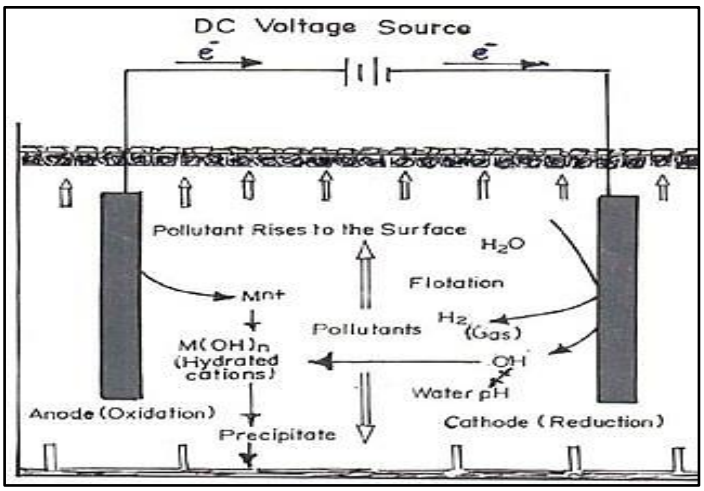


Fig.6. Electrolysis Process (Waterman Engineers hazardous waste, Chopra et al, 2011)

hydroxide and metal phosphate flocs either through chemical reactions and precipitation or by causing colloidal materials to merge, facilitating their removal via Electrocoagulation (EC) [Chopra et al, 2011). The technique has extremely low carbon emissions and produces no greenhouse gasses. Because of the higher quality of treatment, it increases water conservation. It is not necessary to maintain temperature, pH, or biomass at particular values. It runs silently and doesn't use any oxygen from the atmosphere. Because there are few moving components, maintenance and operation are much easier. Although representing a discontinuous process with potential electrode inhibition, the performance to cost ratio is high.

1.3.6. Electrocoagulation Process

Electrocoagulation is a process of water purification that used to remove contaminants in aqueous environment by micro-electric current. It is an alternative to chemical coagulation (CC), in which a metallic coagulant is released into the water by electrolytic dissolution of electrodes. EC structure of an electrolytic cell with two electrodes (anode and cathode) that is

immersed in the conductive solution to be treated and connected to an external power source. Electrocoagulation (EC) offers a merging of coagulation, flotation, and electrooxidation in one method that likely serving as an alternative to chemical coagulation. This occurs when the anode energizes the water, causing it to be converted into hydroxyl (OH^-) and hydrogen (H_2) by electrolysis at the cathode, resulting in the formation of coagulants in the solution [An et al, 2023]. The goal of electrocoagulation is to establish a voltage gap between

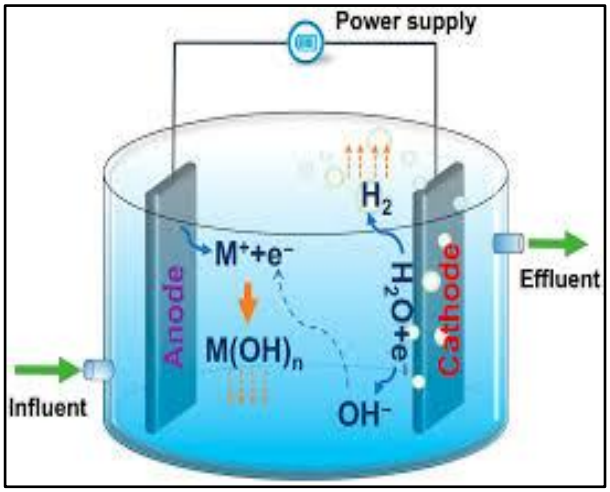


Fig.7. Schematic diagram of electrocoagulation process (Mao et al, 2023)

electrodes within a colloidal dispersion, causing colloidal migration to the electrodes. Electrocoagulation produces positively charged ions from the electrodes when an electric current is applied, allowing heavy metals to be neutralized [Carvajal-Flórez et al,2019]. The process is used for fine particle removal and effectively removes metals, color, and turbidity. It involves multiple steps, is toxic if improperly used, produces high sludge, and has high operational costs.

1.3.7. Evaporation Process

For choosing an alternative process, evaporation is being considered which as increasing number of effluent treatment applications. Effective in concentrating or removing salts, heavy metals, and various harmful substances from solutions. It can also be used to recover useful by-products from solutions or to concentrate liquid waste before further processing or final disposal. This process is applied to produce high quality and reusable distillates [Gupta et al, 2012]. At the time of evaporation, as some of the solvent (usually water) evaporates, the solution is concentrated, leaving behind a brine solution containing substantially all of the dissolved solids or solutes from the original feedstock. It can be performed in solar evaporation ponds or using commercially available evaporation equipment. The evaporation process is conducted through a metal heat transfer surface and heat is transferred condensing vapor to the cold solution. The solvent (usually water) is to evaporate, increasing the concentration of the solute due to absorbed heat. The generated steam can either be released into the atmosphere or condensed and reused [Mariah et al, 2006]. Evaporation has been studied for lignocellulosic ethanol production, but has not been extensively used due to its high energy requirements and a paucity of boilers capable of burning high ash content materials. The wastewater evaporation system's process flow diagram is illustrated in the above figure. The system primarily removes suspended solids (such as insoluble lignin) from the wastewater stream, resulting in a residual thin stillage containing about 8.5% dissolved solids. Approximately 70% of these dissolved solids are organic, while the remaining 30% are inorganic [Tobin et al, 2020). The process is expensive, non-destructive, and has high energy consumption.

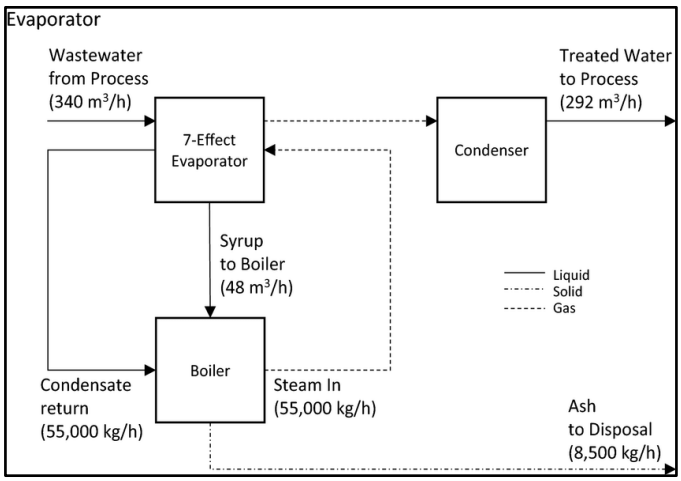


Fig.8. Evaporation Process (Tobin et al, 2020)

1.3.8. Biological Treatment

One of the most environmentally friendly and cost-effective methods for removing pollutants from wastewater is biological treatment. Biological treatment in wastewater treatment plants (WWTPs) is divided into two lines: wastewater treatment (WT), which aims to remove organic carbon and nutrients from wastewater, and sludge treatment, which focuses on the disposal of waste activated sludge. This method is preferred over chemical treatment because it requires less chemical and energy while removing pollutants effectively, making it the most cost-effective and ecologically friendly choice for municipal wastewater treatment. Biological processes use a variety of microorganisms, including naturally occurring, commercial, specialized group, and acclimatized sewage sludge. These microbes oxidize organic materials, converting it into less complex compounds like methane (CH_4), carbon dioxide (CO_2), and water (H_2O). Depending on the process, this oxidation takes place under anaerobic, semi-aerobic, or aerobic circumstances. In wastewater treatment facilities, activated sludge serves as an inoculum and is essential to the biological process of starting microbial reactions. To remove different types of contaminants from wastewater, different biological treatment processes are used, such as membrane bioreactors, trickling filters, and

the traditional activated sludge process. Still, biological wastewater treatment has high capital and operating costs because it usually takes a long time and requires a large amount of space for water treatment and storage.

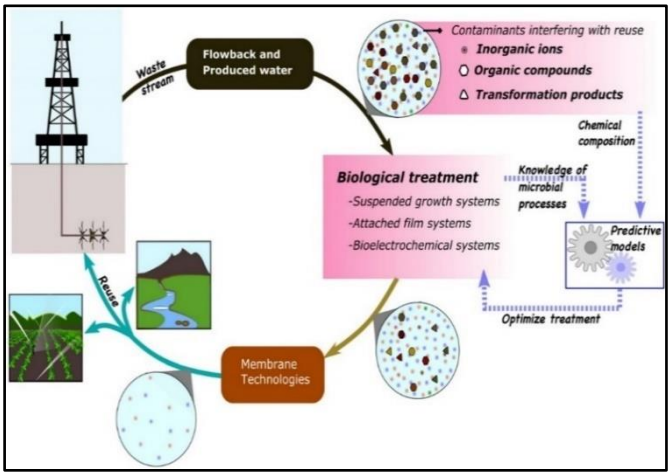


Fig.9. Biological treatment process (M. Acharya et al, 2020)

1.4. Choice of metals for catalyst synthesis

1.4.1. Single metal

Single metal catalysts consist of one type of metal, which present in forms like nanoparticles, thin films, or supported materials, with surface atoms directly interacting with reactants to enhance the catalytic activity. These are-

1.4.1.1. Iron (III) nitrate nonahydrate salt

Iron (III) nitrate nonahydrate, chemical formula as $Fe(NO_3)_3 \cdot 9H_2O$, is a hydrated version of iron(III) nitrate, comprising iron, nitrogen, oxygen, and water molecules. The chemical formula $Fe(NO_3)_3$ represents iron(III) nitrate, where iron has a +3 oxidation state and is bonded to three nitrate ions (NO_3^-), each with a -1 charge. The term "nonahydrate" signifies that the compound contains nine water molecules (H_2O) per formula unit, forming weak hydrogen bonds with the iron (III) nitrate ions [Material science manufacturer, American

elements]. Molecular weight of this metal is 404 g/mol. Iron nitrate nonahydrate is valuable for catalyst synthesis because of its iron content. Iron-based catalysts are extensively employed in diverse chemical reactions such as oxidation, reduction, and hydrogenation processes.



Fig.10. Iron metal salt (Sigma-Aldrich website)

Iron-based catalysts often exhibit good stability under reaction conditions, contributing to their utility in industrial processes. Iron-based catalysts often exhibit good stability under reaction conditions, contributing to their utility in industrial processes. Iron, being abundant and cost-effective compared to other transition metals used in catalyst synthesis, is economically advantageous. Iron nitrate nonahydrate can act as a precursor for producing iron oxide or iron-containing nanoparticles, which possess catalytic activity across various chemical reactions. Additionally, iron-based catalysts generally demonstrate robust stability under reaction conditions, enhancing their suitability for industrial processes.

1.4.1.2. Cobalt nitrate salt

Cobalt nitrate, with the formula $Co(NO_3)_2$, comprises cobalt ions (Co^{2+}) and nitrate ions (NO_3^-), where cobalt exhibits a +2 oxidation state. Typically appearing as a reddish-brown

crystalline solid, it dissolves in water to yield a pink solution. Cobalt nitrate is soluble in water and may absorb moisture from the air due to its slight deliquescence. However, it is toxic if ingested or inhaled, necessitating caution and appropriate safety measures during handling to avoid adverse health effects from prolonged exposure. Cobalt nitrate is utilized in catalyst synthesis by impregnating it



Fig.11. Cobalt nitrate salt (Fairsky Industrial co. limited)

onto diverse carrier materials like alumina, silica, or zeolites. The interaction between cobalt ions and these supports impacts the catalyst's activity, selectivity, and stability. Moreover, cobalt is less expensive compared to other transition metals makes cobalt nitrate an economically feasible choice for large-scale catalyst production [Chemistry formula article].

1.4.1.3. Manganese dioxide powder

Manganese dioxide powder is a fine, granular compound with a dark brown to black colour and a metallic luster. It comprises manganese ions (Mn^{4+}) and oxide ions (O^{2-}) with the chemical formula MnO_2. Stable under normal conditions, it decomposes at high temperatures, releasing oxygen. Used widely as a catalyst in chemical processes like sulfuric acid production, it also aids in oxidation reactions and water treatment, removing iron and

manganese ions. While generally safe when handled correctly, prolonged exposure to manganese dust or fumes can lead to respiratory and neurological health risks. Manganese dioxide powder's high surface



Fig.12. Manganese dioxide powder form

area, stemming from its fine, granular structure, offers numerous active sites for catalytic reactions, thereby boosting catalyst efficiency. Its capability to undergo redox reactions allows it to seamlessly switch between oxidation states, providing it versatile in facilitating both oxidation and reduction reactions. Particularly valuable is its proficiency in transferring oxygen atoms during catalysis, crucial for oxidation reactions. Additionally, its cost-effectiveness compared to other catalysts gives it an attractive choice for extensive industrial applications.

1.4.4. Platinum salt

Platinum metal salts, notably platinum (II) chloride ($PtCl_2$), are widely utilized as catalyst precursors, especially in the creation of platinum-based catalysts. Various synthesis including impregnation, precipitation, sol-gel, and deposition-precipitation methods to prepare catalysts by platinum salt.



Fig.13. Platinum metal salt

1.4.2. Bi-metal

By combining two distinct metals, bi-metal catalysts can improve catalytic qualities such as activity, selectivity, and stability. This is because the metals work in concert to produce better results than single-metal catalysts. Bi-metal catalyst can be used in hydrogenation, oxidation, hydrogenation, polymerization and hydrocracking process. Some examples of bi-metal catalysts are Co-Fe, Ti-Mn, Pt-Ru, Pd-Cu, Ni-La, Au-Pt etc. Catalysts that are bimetallic can enhance selectivity for desired reactions and reduce activation energy. Longer catalyst lifetimes can result from the mixture of metals since it can increase resistance to sintering and poisoning.

1.5. Selection of support for catalyst synthesis

1.5.1. TiO_2 support

Titanium dioxide (TiO_2) is widely utilized as a catalyst support due to its unique properties and versatility. It offers high surface area, chemical stability, photocatalytic activity, biocompatibility, and support for metal nanoparticles, making it suitable for a broad range of catalytic applications across various industries.



Fig.14.TiO_2 supported metal

1.5.2. Ceria (CeO_2) support

Cerium dioxide (CeO_2), or ceria, is widely employed in catalyst synthesis due to its versatility and unique properties. As a support material, ceria provides numerous advantages, including high surface area, oxygen storage capacity, thermal stability, promotion of metal dispersion, resistance to poisoning, and environmental friendliness. Ceria acts as a promoter for dispersing metal particles evenly on it surface. When utilized as a support material for metal catalysts, ceria prevents aggregation of metal particles, thereby maximizing catalytic efficiency. Ceria-supported catalysts are versatile and applicable across various reactions like

oxidation, hydrogenation, dehydrogenation, and SCR of nitrogen oxides. The broad versatility of ceria as a support material enables its use in diverse catalytic processes.



Fig.15. CeO_2 supported salt

1.5.3. Zeolite Support

Zeolites, crystalline aluminosilicate minerals with a distinct structure and microporous nature, serve as common support materials in catalyst synthesis. Their unique properties make them invaluable for this purpose. It has a high surface area. This ample surface area facilitates numerous active sites for catalytic reactions to take place. Zeolite showed various properties like high thermal and chemical stability, that appropriate for harsh reaction conditions, such as high temperatures and corrosive surroundings.



Fig.16. Zeolite support

1.6. Choice of reaction

The selection of metals for catalyst synthesis is adjust to the particular reactions they are intended to catalyze. Various metals are utilized based on their suitability for different types of reactions. Here are some common metals employed for multiple catalytic processes:

Hydrogenation and Dehydrogenation Reactions

Platinum (Pt), Palladium (Pd), Nickel (Ni), Ruthenium (Ru), Rhodium (Rh)

Oxidation and Reduction Reactions

Platinum (Pt), Palladium (Pd), Gold (Au), Silver (Ag), Copper (Cu)

Hydrogenation of Unsaturated Compounds

Palladium (Pd), Platinum (Pt), Nickel (Ni), Ruthenium (Ru)

Dehydrogenation of Alcohols or Hydrocarbons

Copper (Cu), Chromium (Cr), Iron (Fe), Platinum (Pt)

Water-Gas Shift Reaction

Iron (Fe), Copper (Cu), Zinc (Zn), Nickel (Ni)

Fischer-Tropsch Synthesis (FTS)

Iron (Fe), Cobalt (Co), Ruthenium (Ru), Nickel (Ni)

Methanol Synthesis

Copper-Zinc Oxide (Cu-ZnO), Copper-Chromium Oxide (Cu-Cr_2O_3), Copper-Aluminum Oxide (Cu-Al_2O_3)

Selective Catalytic Reduction (SCR) of NOx

Vanadium (V), Titanium (Ti), Iron (Fe), Cobalt (Co)

Olefin Polymerization

Zirconium (Zr), Titanium (Ti), Chromium (Cr), Nickel (Ni)

Alkylation and Isomerization Reactions

Aluminum (Al), Platinum (Pt), Nickel (Ni), Palladium (Pd)

1.7. Methods for preparation of bulk catalyst and support

Different catalyst preparation methods provide control over key characteristics like particle size, surface area, morphology, and composition. Researchers can strategically choose methods to precisely adjust these properties, aiming to improve catalytic activity, selectivity, and stability. Achieving effective dispersion of active components on support materials is vital for optimizing catalyst performance. Various preparation techniques offer different levels of control over this dispersion, ensuring uniform distribution and accessibility of catalytic sites, thereby enhancing catalyst performance. Consideration of scalability is crucial in catalyst preparation for industrial applications. Certain methods are preferred due to their simplicity, reproducibility, and cost-effectiveness, making them more suitable for large-scale production. Certain catalyst preparation methods may utilize hazardous chemicals or energy-intensive processes. Researchers may choose environmentally friendly or safer methods that reduce the use of toxic reagents or energy consumption.

1.7.1. Co-precipitation method / Precipitation method

Precipitation process is one of the most willey employed catalyst preparation technique and may be used to prepared either by single component catalyst or supported catalyst (Al_2O_3 /TiO_2) or mixed catalyst. In co-precipitation, multiple metal salts dissolve in a solvent, to produce a homogeneous solution. A precipitating agent, like a base, is added under controlled conditions, leading to the formation of insoluble metal hydroxides or compounds. This results in the precipitation of the desired catalyst components. The precipitate is separated, washed, dried, and calcined to form the final catalyst material. Co-precipitation enables the synthesis of catalysts with uniform composition and intimate mixing of multiple active components.

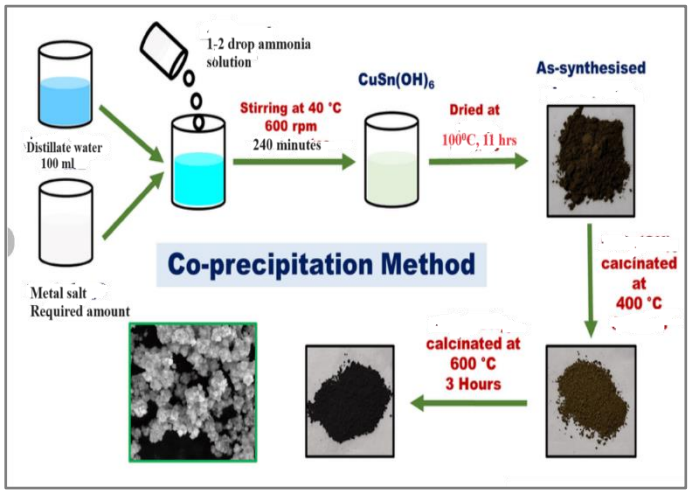


Fig.17. Co-precipitation method (Muni Babu et al, 2022)

1.7.2. Sol-gel Method

A material science solvents process is a method for producing solute materials from small molecules. The method is used for the fabrication of metal oxide especially oxide of silicon and titanium. Sol-gel catalysts have a high surface area, vital for boosting catalytic activity. This expanded surface area facilities greater exposure of active sites to reactants, improving their interaction and ultimately enhancing catalytic performance. The sol-gel method is a

cost-effective process permit precise control over chemical composition because of its low reaction temperature. It shows applications in ceramics production as a molding material and intermediate product for metal oxide thin films. Materials produced through this method which are utilized across various fields such as optics, electronics, energy, surface engineering, biosensors, pharmaceuticals, and separation technologies like chromatography. It is commonly used in industrial synthesis of nanoparticles with diverse compositions. The process involves creating a homogeneous sol from precursors, which is then converted into a gel. Subsequently, the solvent is removed from the gel, leaving behind a dried material [Bokov et al, 2021]. The sol-gel method is a proven technique for producing high-quality metal oxide nanoparticles (MONPs) and mixed oxide composites, offering precise control over material texture and surface properties. It typically involves five main steps: hydrolysis, polycondensation, aging, drying, and thermal decomposition. Sol-gel synthesis is a easy,



Fig.18. Sol gel method (Chkirida et al, 2019)

rapid, and cost-effective method with several advantages, including low processing temperatures, uniformity in material production, and the ability to form complex structures or composite materials. [Parashar et al, 2020]. The sol-gel method is highly regarded for

material fabrication due to its cost-effectiveness, stability, reproducibility, and affordability. It can be utilized to produce a wide range of materials, including ceramics, thin-film coatings, and nanoparticles, enabling a diverse array of applications [Shafiee et al, 2021].

1.7.3. Chemical Vapor Deposition (CVD) method

A chemical vapor deposition method is a most important process to cleave a carbon atom containing. Flowing through the catalyst nanoparticle to generate carbon atom. Chemical vapor deposition (CVD) is a traditional method employing gaseous carbon sources like hydrocarbons or CO over a metal catalyst to create diverse carbon materials such as carbon fibers and filaments. However, it was Endo and his research group who initially reported the use of CVD technique to produce multi-walled carbon nanotubes (MWCNTs) [Khan et al, 2016].

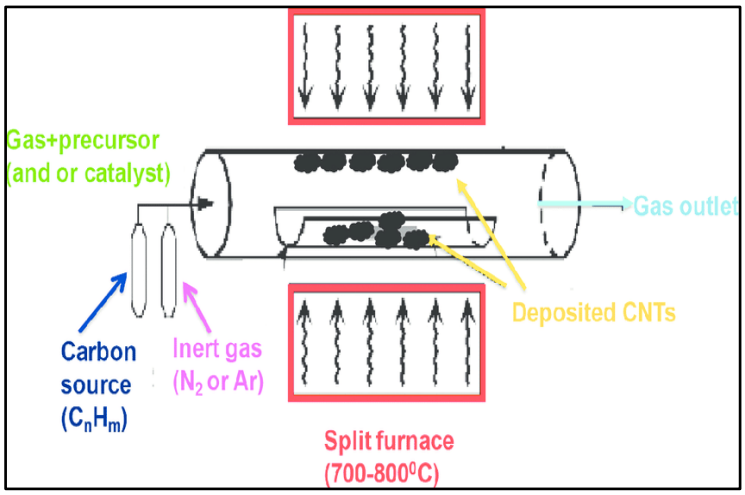


Fig.19. Schematic diagram of chemical vapor deposition setup (Khan et al, 2016)

Chemical vapor deposition (CVD) processes offer high deposition rates and can operate at low temperatures. They provide upper-level control over morphology, crystal structure, and orientations compared to chemical solution deposition (CSD), making them ideal for

deposition of thin film preparation. CVD is widely used for achieving highly conformal coatings on 3-D substrates in various devices. However, it has drawbacks, including the potential release of toxic gases, substrate temperature effects causing phase changes or grain growth, dopant diffusion in microelectronic components, and the possibility of poor adhesive between the film and substrate, leading to film contamination [Zhang et al, 2016].

1.7.4. Hydrothermal Synthesis

Hydrothermal synthesis involves producing high-quality crystals in hot water under high pressure and above its boiling point. This method is popular due to its simplicity, allowing control by adjusting solvent, temperature, and pressure to influence ionic reaction equilibria. Since the mid-20th century, hydrothermal processing has rapidly evolved for fabricating micro or nanoscale materials. From the early 1990s, non-aqueous solvents have been introduced for various hydrothermal reactions, including "ammino-thermal," "glycol-thermal," and "alcohol-thermal" methods. Additionally, a new approach called "solvothermal" has emerged for synthesizing materials using non-aqueous solvents [Zhang et al, 2016]. This method is applied due to its low process temperature and ease of particle size control. It offers several merits, including the simple equipment use, catalyst-free growth, cost-effectiveness, homogeneous yields, eco-friendliness, and lower risk compared to alternative fabrication methods. Particularly fitting for plastic electronics and microelectronics due to its low reaction temperature, it allows for precise adjustment of particle size and morphology by tuning precursor concentration, reaction temperature, and time under hydrothermal conditions [Shafiee et al, 2021].

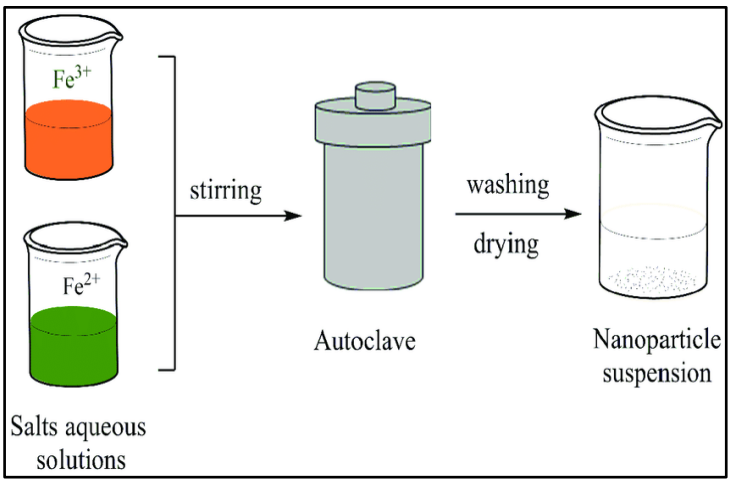


Fig.20. Hydrothermal synthesis of IONPs (Bustamante-Torres et al, 2022)

1.8. Choice of reactor for Catalytic Wet Air Oxidation (CWAO)

The selection of a reactor for catalytic wet air oxidation (CWAO) based on factors like feedstock characteristics, desired reaction conditions, catalyst attributes, and economic considerations. Common reactor types for CWAO encompass stirred tank, fixed-bed, fluidized bed, supercritical water, and packed bed reactors. Various feedstocks may demand specific reactor types to ensure ideal reaction conditions and catalyst performance. For instance, feedstocks with high viscosity or solid content may require reactors with efficient mixing capabilities, like stirred tank reactors. The properties of catalyst such as stability, activity and selectivity are influenced by reactor selection, ensuring optimal performance. Additionally the factors are impact the reactor selection like that capital and operating costs, as well as scalability. Ultimately, the choice of reactor is tailored to the specific requirements of the CWAO process, balancing performance and cost-effectiveness.

1.8.1. Continuous Stirred Tank Reactor (CSTR)

A continuous stirred tank reactor (CSTR) is a stirred tank that is continuously fed and discharged. They are used on a large scale. Based on decades of experience and behavioral knowledge, CSTR is well-characterized and readily available from 1 mL to over 10 m^3. They can handle solids and provide long residence times, but the resulting residence time distribution (RTD) is wide. Control of residence time can be improved by connecting multiple CSTRs in series for solids handling, ease of scale, and better mixing at the expense of mechanical complexity [Cherkasov et al, 2023].

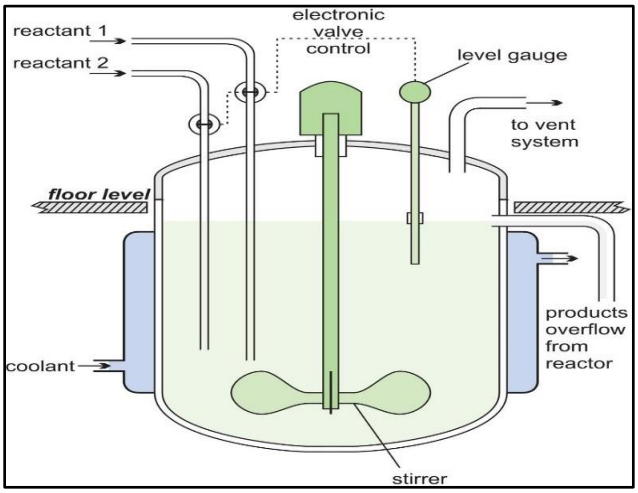


Fig.21. continuous stirred tank reactor

1.7.2. Batch Reactor

Still batch reactors (SBRs) were widely used all over the world in 1920s for treating municipal and industrial wastewater. They were successfully implemented in Europe, China, and the United States for this purpose. SBR technology offers several differences compared to conventional wastewater treatment methods. It provides flexibility in operation, allowing for changes in sequence phase and metabolic function. It was worked effectively at low

retention times and gives control over microbial populations. Additionally, SBRs can run in treatment of wastewater with various reactor configurations to enhancing their adaptability and efficiency [Suresh et al, 2011].

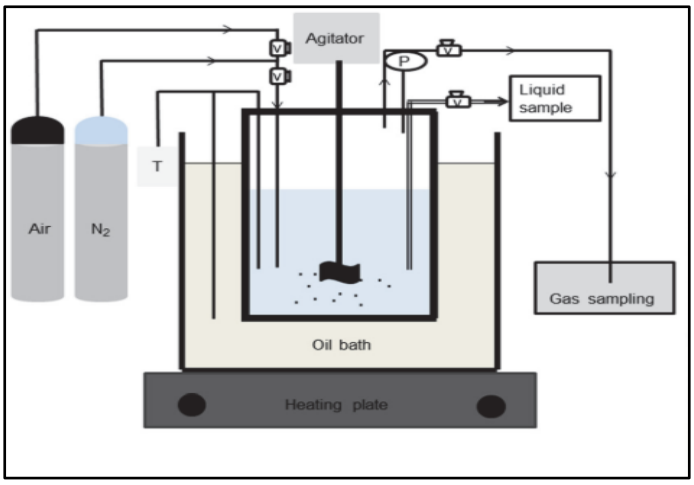


Fig.22. Still batch reactor (Heponiemi et al, 2015)

Still batch reactor was operated in batch mode to provide operational flexibility and improved process control. The SBR cycle conclude distinct treatment phases, including fill, react, settle, decant, and idle, each with a specific duration that can be adjusted based on the required treatment level [Singh et al, 2021].

1.7.4. Fluidized Bed Reactor

The fluidized bed method, also called the suspended carrier biofilm method, utilizes solid particle fluidization to maintain a fluidized system, enhancing interaction between solid particles and liquid for effective cleaning. Microorganism development in the fluidized bed reactor (FBR) is evaluated by assessing the number of living cells in the biofilms and the liquid phase surrounding the support medium [Chandran et al, 2023].

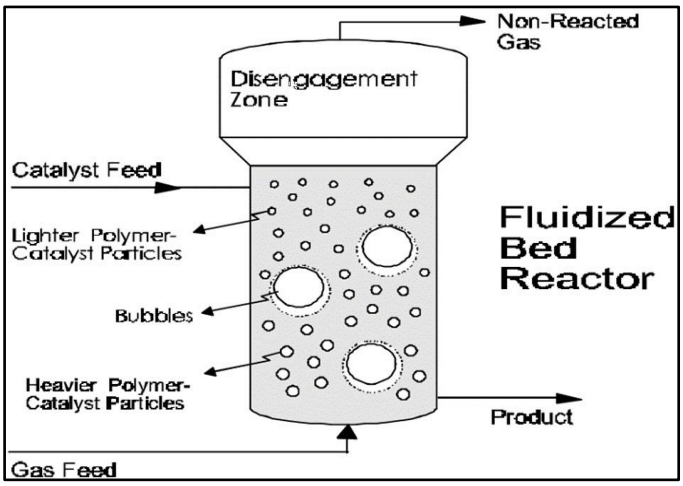


Fig.23. Schematic diagram of fluidized bed reactor (Fernandes et al, 2000)

1.7.5. Trickle bed reactor

catalytic liquid-phase oxidation of organics in wastewaters employing a trickle-bed reactor. Pre-filtered wastewater is pumped to operating pressure, and brought to the reactor operating temperature by a feed/effluent heat exchanger. A compressed air/oxygen stream at stoichiometric excess is fed contemporaneously to the top of the trickle bed reactor [Levec and Pintar, 2007]. The continuous oxidation experiments were conducted using a stainless steel reactor with a diameter of 1 cm and a length of 20 cm, filled with 7-7.5 g of carbon. The reactor was placed in an electric oven for heating and temperature regulation. Prior to operation, the reactor underwent a leak check at room temperature using air at pressures of 25 bar or 50 bar. If no leaks were detected, the operating pressure was adjusted using a pressure reducing valve, and the pollutant solution was supplied from a 5-liter feed tank to the reactor via a high-pressure pump. The liquid flow rate was measured using a liquid mass flow meter installed after the liquid dampers in the pump's exit line. The liquid and air streams were mixed downstream and preheated to the desired reaction temperature in a 1-meter-long coil

positioned inside the oven [Stüber et al, 2011]. various industries including petroleum, petrochemical, and chemical sectors, as well as in wastewater treatment, biochemical, and electrochemical processing were used Trickle-bed reactors (TBRs). In the petroleum industry, these reactors are working under adiabatic conditions, operating at high temperatures and pressures, often involving hydrogen and organic liquids. TBRs are particularly suited for performing intense exothermic reactions like the hydrogenation of unsaturated hydrocarbons [Ramírez-Castelán et al, 2017].

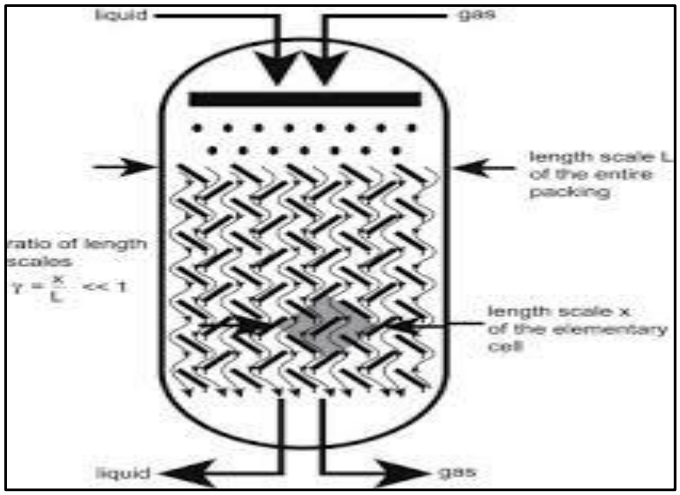


Fig.24. Trickle bed reactor (Ramírez-Castelán et al, 2017)

1.7.6. Packed Bed Reactor

A packed bed reactor is a tubular reactor used to cultivate biomass or microbial pellets, facilitating metabolic activities on their surfaces. It features a screen and metal support grid near the bottom to aid in supporting the microbial pellets [Chandran et al, 2023].

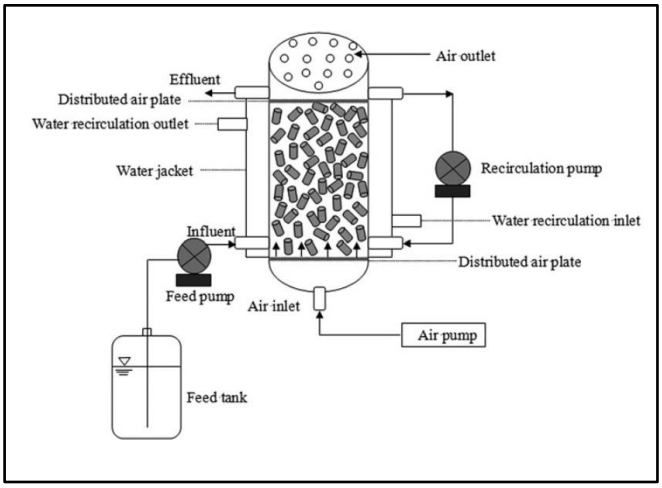


Fig.25. Schematic diagram of packed bed reactor (Lin et al, 2015)

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

Shan et al. (2023), focuses on provoking working catalysts for Catalytic Wet Air Oxidation (CWAO) of phenol in wastewater, the operation is working on active and stable performance at lower temperatures. Pt-M (M=Pb, Cu) alloy structures are constructed, with Pt mainly in the form of Pt^0 and M mainly as M^{2+}. The Pt-Pb/XC-72R catalyst shows high activity and stability in CWAO at 100°C, observing over 75% TOC degradation in five sequent cycles. Conversely, Pt-Pb/EC-300 destroy rapidly, with TOC degradation decay from 91.2% to 47.1% after five cycles. Substitute Pt-Pb using Pt-Cu nanoparticles serving high catalytic activity and stability, with raised Cu^{2+} concentration which is improve working on CWAO. Adjust the chemical state of the second metal in Pt-based bimetallic alloys show effective in developing catalysts for CWAO technology. Xiaoxia Ou et al. (2022), explores catalytic wet oxidation (CWAO) of phenol in high-ionic-strength wastewater (HISWW) using a Mn-Ce-Ox catalyst and discovered the effect of high NaCl concentrations. The mixture of Mn-Ce-Ox and NaCl increase phenol and total organic carbon (TOC) conversions, that is- 98% and 85% respectively, and it changes after 24 hours with 200 g L^{-1} NaCl and 1.0 g L^{-1} Mn-Ce-Ox. Under same conditions, conversions are decreased to about 41% for phenol and 27% for TOC when NaCl is not used. Lowering carbon deposition and encouraging catalyst reoxidation and surface oxidation lead to increased mineralization when NaCl is applied. Further evidence of the Mn-Ce-Ox catalyst's potential for useful HISWW treatment comes from the saltwater system's ability to regenerate it effectively. Balc1 et al (2023)., investigated the catalytic represented of Silica Pillared Clay (SPC) supports and synthesized silica amounts from SWy-2 clay mineral and Hançılı region bentonite rock (HWB). The consolidation of iron (Fe) and/or titanium (Ti) is used in various combinations enhanced catalytic performance in

Catalytic Wet Peroxide Oxidation (CWPO) of phenol. Fe-loaded SPCs displayed excellent performance compared to Ti-loaded ones. Phenol conversion raised with catalyst amount and temperature, and lower pH preferred catalyst effectiveness. Aromatic intermediates converted into carboxylic acids across time and conductive to relatively low total organic carbon (TOC) conversion. The highest catalytic activity was shows with high silica content Fe-SPCs synthesized from both host clays, gain complete conversion within 60 minutes under particular conditions. The SWy-2 based catalyst maintained its performance after three cycles. Peng et al. (2018), study investigates of Pt nanoparticles on Pt/CeO_2 catalysts' working in toluene oxidation. Size-adjustable Pt nanoparticles (1.3-2.5 nm) are successfully loaded using CeO_2 nanorod support. Pt particle size dominance the structure and chemical properties of Pt/CeO_2 catalysts, its affect the Pt dispersion, Pt-O Ce bonds, Ce^{3+}, and oxygen vacancies on ceria. Another investigations are the Pt/CeO_2-1.8 sample displayed the catalytic performance is very good due to a Pt dispersion and oxygen vacancy concentration on ceria promotor. TOF values depends on dispersion of Pt, oxygen vacancy concentration, and both properties expressed that the reaction rate is impacted by both exposed Pt atoms and oxygen vacancies. The Pt/CeO_2-1.8 catalyst view stability over 120 hours with varying toluene concentrations and rest untouched by 5 vol.% water vapor at 155°C. Roy et al. (2023), examined novel catalyst, Ru-Fe_3O_4/CeOx-SiO_2, was synthesized using excess solution impregnation method, mixed with Ru and Fe_3O_4 nanoparticles on ceria-loaded mesoporous SiO_2. The catalyst definite effective conversion of phenol, obtaining 95% conversion for an aqueous solution and 92% for industrial effluent containing phenol. The nearest interaction between ruthenium and Fe_3O_4 nanoparticles working at low-temperature phenol oxidation characteristic, using ceria nanoparticles promotors for the oxidation reaction. The kinetics of the oxidation reaction were discussed, and the catalysts were thoroughly characterized using several techniques. The optimal process conditions yielded significantly higher phenol

conversion ability to compared for previous scientific searching. Makatsa et al. (2021), reviews an improved oxidation method for refractory organic compounds is catalytic wet air oxidation (CWAO), which has been observed to work on phenol in wastewater. Acetic acid is recognized as a stable intermediate in the several chemical pathways for phenol oxidation that researchers have solved, whether direct or indirect. According to Power law and Langmuir-Hinshelwood models states for reactant adsorption/desorption on the catalyst surface. Phenol is degradation impacted by temperature, pressure, gas velocity, and liquid space velocity. The investigated displayed to hot spots formation, catalyst deactivation, and reactor thermal runaway, observation of liquid maldistribution is enhanced by using computational fluid dynamics (CFD) modeling, that is express liquid channeling conduct to hot spots and catalyst deactivation. Quintanilla et al. (2006), explained catalytic wet air oxidation (CWAO) of phenol was investigated by using Fe/activated carbon catalyst at easy conditions (Temp:100-127°C; Pressure: 8 atm) in a trickle-bed reactor. Intermediate oxidation products containing ring compounds (hydroquinone, p-benzoquinone, p-hydroxybenzoic acid) and short-chain organic acids. According to experiments with these intermediates as starting mixture demonstrate two oxidation pathways for phenol: para-hydroxylation leading to p-benzoquinone or para-carboxylation resulting in p-hydroxybenzoic acid. The catalyst opposed the formed of ring-condensation products in the reactor effluent, an ecotoxicity concern. considerably, acetic acid verified refractory to CWAO under the remarkable conditions. Wang et al. (2015., performed wet air catalytic oxidation (CWAO) of fomesafen wastewater by using CeO_2-TiO_2 catalyst ready by coprecipitation method and characterized by BET surface area, X-ray diffraction, and X-ray photoelectron spectroscopy. I researched, the catalyst with Ti/Ce ratio of 3:1 had the maximum BET surface area. Under the required conditions (temp:250°C, 3 MPa oxygen partial pressure, pH 5.0, and 3 h reaction time), a chemical oxygen demand (COD) removal

rate of 78% was obtained. After 3 h, the BOD_5/COD ratio enhanced from 0.03 to 0.32, indicating developed biodegradability. The second-order kinetic model describe perfectly the experimental data with correlation coefficients greater than 0.90. This study is the first to investigate the CWAO of real fomesafen production wastewater by using CeO_2-TiO_2 catalysts and give valuable insights into the understanding and applicability of these catalysts in such processes. Gizaw et al. (2022), Catalytic Wet Air Oxidation (CWAO) by using copper oxide loaded activated carbon (CuO/AC) practically degraded reactive red 2 mono azo dye. Activated carbon (AC) from water hyacinth root and CuO/AC catalyst were prepared through physical-chemical activation and wet impregnation methods, respectively. Characterization working on FTIR, SEM, XRD, and TGA analyses. Required conditions (6 g/L catalyst dose, 120°C reaction temperature, 3 bar oxygen partial pressure, 120 min reaction time) obtained complete dye decolorization (100%) and 88.57% chemical oxygen demand (COD) conversion. Dye decolorization percentages reduced in the presence of free radical scavengers, and the performance of the reused catalyst declined. After treatment dye solution showed lower phytotoxicity (62.67%) than the untreated solution (34.80%) based on the germination index of Lepidium sativum seeds. Gupta et al. (2021) investigated the effective petrification of pesticide glyphosate (PMG) in wastewater by preparing iron nanoparticles (Fe NPs) and dispersing carbon nanofibers (CNFs) on activated carbon beads (ACBs). It has been done using catalytic moist air oxidation (CWAO). Effective CWAO was demonstrated by the Fe-CNF/ACB catalyst, which also showed high BET specific surface area, good Fe loading, thermal stability, higher exposure of Fe NPs, and graphitic properties. Complete decomposition of 100 mg/L PMG is obtained within 6 h using a catalyst dosage of 0.75 g/L maintained at 220°C and 25 bar. The turnover frequency indicates the efficient role of the active Fe metal center. Additionally, 80% of the chemical oxygen demand is removed within 6 hours and the treated water is non-toxic. The preparation method and CWAO

technique are scalable and offer the possibility to treat other recalcitrant organic compounds. Rocha et al. (2020), review emphasizes the potential of metal-free carbon materials such as carbon nanofibers, nanotubes, graphene-based materials, and nanoporous carbon gels as alternatives to traditional metal-based catalysts synthesized by wet air catalytic oxidation (CWAO). The synthesis of novel carbon allotropes has inspired research on their ability to catalyze the oxidation of organic compounds by CWAO. This review gave an overview of the advances in the use of these nanocarbons as catalysts in CWAO and underlined the importance of nanocarbons in promoting environmentally friendly oxidation processes. Feng et al. (2023), research addresses challenges in wet catalytic oxidation (CWAO), where catalyst stability is checked at high temperatures and pressures. Here using TiO_2 as a stable support and a copper-based catalyst where excellent hydrothermal stability was developed. The sol-gel method use for synthesis, it ensures that the copper nanoparticles are evenly distributed on the support and more active centers are retained for a long time. The result showed catalyst stability and catalytic activity with maximum degradation even after 10 cycles of use. In oxidative degradation experiments, the catalyst effectively degraded m-cresol, with complete COD removal rate of 79.15% in 2 hours at 140°C and 2 MPa. Achieved decomposition. The developed catalyst system improves the analysis of CWAO in the treatment of refractory wastewaters such as coal chemical wastewaters. Hammedi et al. (2023), investigated Wet air catalytic oxidation (CWAO) of p-hydroxybenzoic acid (p-HBA) was working on Ru-based catalysts where four mesoporous supports (TiO_2, CeO_2-TiO_2, ZrO_2-TiO_2, La_2O_3-TiO_2) was performed at 140°C and 50 bar air pressure. The supported based catalyst synthesized by using sol-gel method was saturated with loading 3wt.% Ru precursor. Characterization methods expressed effective surface area, abundant surface active oxygen, and Lewis acid sites on the cerium-containing catalyst (Ru/Ce-Ti). The fresh Ru/Ce-Ti catalyst displayed superior activity than its cerium-free counterpart. This is attributed to

the enhanced interaction between Ru particles and surface oxygen via the cerium redox process (Ce^{3+}/Ce^{4+}). The presence of cerium increased surface active oxygen and prevented carbon deposition on the Ru catalyst surface. The pseudo-second-order model effectively described the oxidation of p-HBA kinetic data by using Ru catalyst. Yang et al. (2023), states A carbon-supported Ru/Cu bimetallic catalyst was developed to effectively ammonia-containing wastewater treatment in industrial production by catalytic wet air oxidation (CWAO). The above catalyst performed by a simple impregnation method, it showed high activity and hydrothermal stability. Ru and Cu bimetallic ions were loaded into micro-mesoporous carbon, and the morphology of the carbon which was controlled by the calcination temperature. The preparation demonstrated excellent performance, give 99.6% ammonia water conversion and 99.1% nitrogen selectivity in 4 h at 200°C and 2 MPa O_2. The Ru/Cu@C-700 catalyst displayed low ammonia nitrogen emission and shows no deactivation after 5 cycles, and has low loading (‹1%). Ding et al. (2023), was synthesized melamine which comes from a nitrogen source and used in catalytic wet air oxidation (CWAO) to promote simulated wastewater with high concentrations of phenol. N-LCO(M) showed efficiency of phenol degradation, and wastewater containing 8000 mg/L phenol displayed, the COD degradation rate reached 87.9%, while it was only 43.8% in undoped LCO prepared by citric acid. Density functional theory (DFT) characterization and calculations confirmed that N doping increases oxygen vacancies and promotes charge transfer between Cu and O. This promoted the formation of reactive oxygen species and more extensive phenol degradation through the Cu redox cycle. The promised CWAO technology demonstrated a wastewater treatment with environmental friendliness and reduced intermediate toxicity. Kilgore et al. (2023), used hydrothermal liquefaction (HTL) to reduce the amount of wet waste and produce biofuels such as SAF and sustainable diesel. They reported that molecular weight of a significant portion (20-30%) of the carbon in wet waste feed became low, water-

soluble organic compounds resulting in aqueous products that require processing before disposal. The authors used humid air oxidation treatment to reduce the complexity and catalyst screening and subsequent batch reactor studies showed that metal catalysts such as WO_3 and ZrO_2 increased acetic acid concentration by 10-20%. They reported that the acetic acid concentration increased by 72% when using WO_3 at 225°C under more severe conditions. The authors also reported that a continuous trickle bed reactor with Ce-Zr catalyst reduced COD by 50% and increased acetic acid concentration by 40%. Gopakumar et al. (2023), used silver-promoted manganese on zirconia as catalyst for catalytic oxidation of NO to NO_2, under circumstances that are applicable to industrial settings (10% NO, 6% O_2, and 15% H_2O). The authors reported that presence of silver enhanced the low-temperature activity of manganese catalysts in both dry and humid conditions when contrast to manganese without the promotional addition. Chai et al. (2023), employed Simapro 9.0 software to construct a life cycle assessment model for the treatment of high-concentration organic wastewater using CWAO and provided a comprehensive analysis of the environmental impact, considering three key phases: construction, operation, and demolition. The authors reported that marine ecotoxicity, mineral resource consumption, and global warming were the primary factors affecting the environment adversely. The study reported the operational phase, the primary driver of global warming to have most significant environmental effects and sensitivity analysis to have the most substantial influence on abiotic depletion and freshwater aquatic ecotoxicity, associated with electricity consumption. Yang et al. (2023), prepared of N-tert-butyl-2-benzothiazolesulfenamide (TBBS) wastewater using a catalytic wet air oxidation (CWAO) process in a microchannel reactor. This reactor permit for continuous reaction operation with effective mixing of oxygen and pollutants. The author focused parameters-pressure, temperature, time, and mass ratio of feed oxygen and wastewater COD was performed using response surface methodology (RSM) and

backpropagation artificial neural network (BP-ANN). The result prediction based on correlation coefficient BP-ANN better working than RSM in simulation. The analysis shows the importance of parameters, with temperature having the highest influence (35.61%), followed by pressure (29.74%), time (19.53%), and ROC (15.12%). Zhang et al. (2023), research used of high salinity treatment, high-organic wastewater where organic matter was removed and salt separation was limited. Combining catalytic wet air oxidation (CWAO) with desalination technologies (membrane distillation, membrane bioreactors, ultrafiltration, and nanofiltration) decomposed high-salinity and high-organic substances in wastewater. The experiments of RuO_2/TiO_2 catalysts were prepared of malic acid organic solvents by CWAO process at various calcination temperatures. The result showed 20000 mg/L of COD value, much 80% TOC removal rate in a CWAO system containing 5 wt.% Na_2SO_4. RuO_2/TiO_2-350 shows optimal performance in both non-salt and Na_2SO_4 conditions. Calcination temperature directly affects specific surface area, pore volume, oxygen vacancies, acid centers and catalytic activity. Moreover, the RuO_2/TiO_2-350 catalyst exhibits good versatility and good salt tolerance in the treatment of various organic compounds in saline wastewater. Li et al. (2022), study, Cu-Ce/AC catalyst was prepared by impregnation method, walnut shell used as a carbon precursor where source as Cu and modifier as Ce. The decomposition of Phenol wastewater worked on a fixed bed reactor by CWAO methods. The experiment investigate, Cu-Ce/AC catalyst stability was verified under different pH conditions. The result observed complete phenol conversion and intermediate product of acid produced that was not easy for complete conversion. Another result showed decreased in COD conversion. The alkaline environment reduces Cu leaching and maintains the catalytic activity. This study explains the reaction mechanism and highlights the redox cycle between Cu^{+}, Cu^{2+}, Ce^{3+}, and Ce^{4+} during phenol conversion. Redox cycles promote the formation of oxygen vacancies, improve oxygen storage capacity, and gives reaction sites for the decomposition of phenols and

intermediates. However, incomplete decomposition products can block active sites and reduce catalytic activity. Sun et al. (2022), Catalytic wet air oxidation (CWAO) combined with desalination offers a promising solution for the decomposition of high-salt, high-organic wastewater, but chloride occur by used advanced oxidation processes (AOP) which contained high content jeopardizes. B-site Ru-doped $LaFe_{1-x}Ru_xO_{3-\delta}$ catalyst was studied for his CWAO treatment of chloride ion wastewater, and $LaFe_{0.85}Ru_{0.15}O_{3-\delta}$ was 45.5% greater than of 6 % RuO_2@TiO_2 obtained supports and $LaFe_{0.85}Ru_{0.15}O_{3-\delta}$ exhibited remarkable chloride ion stability, and it was confirmed by various characterization techniques that Ru did not dissolve after the reaction. Kinetic data and density functional theory (DFT) suggest that Fe sites promote acetic acid oxidation and chloride ion adsorption, thereby protecting Ru sites and pretend catalytic activity of reactive oxygen species. The CWAO used for the enhanced chloride-resistant of catalysts. Santos et al. (2021), used the two process to produced carbon coated ceramic monoliths by wash-coating with nitrogen-doped carbon nanotubes (CNTs) and chemical vapor deposition (CVD) to increased carbon nanofibers (CNFs). The above both compounds were performed by catalytic wet air oxidation of oxalic acid (1000 mg L^{-1}). In the wet catalytic oxidation of oxalic acid, the addition of N-doped CNTs did not increase the removal rate due to binder coverage, but the high heat treatment temperature (900 °C) condition, not increased the conversion rate of oxalic acid (>55%) and only improved stability. The result achieved 55% conversion of oxalic acid, (48h required time at temp. 140^0C and pressure 8 bar) used by wash-coating without N-doped CNTs. Feng et al. (2022), investigated Ammonia-nitrogen wastewater used that was risks to the environment and human living and requires effective treatment methods. A new Pt@Ti-Si catalyst prepared in a one-pot process exhibits high efficiency in wet air catalytic oxidation (CWAO) of high concentrations of ammonia (>2000 ppm) where Pt used as a support combined with TiO_2 and SiO_2 catalyst. The bimetallic catalyst provide increased surface area and acid-base resistance,

ensuring excellent catalytic performance and stability. Under the optimal conditions (200°C, 2 MPa O_2 pressure, 2 h), the 1% Pt@Ti10-Si1 catalyst showed 96.32% conversion of 2470 ppm ammonia with 97.15% N_2 selectivity after 5 cycles. The result displayed the catalyst was good resistance to chloride ions, which facilitates the subsequent biochemical processes of the treated ammonia-nitrogen wastewater, offering potential industrial applications. Scelfo et al. (2022), focused on D-glucose into value-added chemicals by the converting of biomass which had highest attention. For this purpose, catalytic wet air oxidation (CWAO) using a noble metal-based heterogeneous catalyst system was performed. Similar catalysts on biomass are currently investigated by redox effect. In this work, the author discovered perovskite-type oxides ($LaBO_3$; B: Fe, Co, Mn) for the conversion of D-glucose to C_6-aldaric acid, lactic acid, and levulinic acid. $LaCoO_3$ and $LaMnO_3$ produced 50.3 mol% and 69.5 mol% lactic acid and levulinic acid, respectively, under optimal conditions. $LaMnO_3$ is the most easily oxidized/reduced catalyst at low temperatures and exhibits the highest catalytic activity, achieved the hydroxymethyl furfural to levulinic acid conversion. Fu et al. (2022), This study focused on an effective Pt/TiO_2 catalyst was prepared for wet air catalytic oxidation (CWAO) of phenol, a hazardous compound in industrial wastewater. Pt was supported on TiO_2 occurred excess strong hydrogen during hydrogen reduction without TiO_2 migrating onto Pt as confirmed by XPS, first reduced then increased support promoted electron transfer from TiO_2 to Pt and the proportion of negative Pt ($Pt\delta^-$) partially increased proportion. The catalyst exhibits enhanced activity due to strong electron-metal support interactions (EMSI), with a total organic carbon (TOC) conversion of 88.8% and a turnover frequency (TOF) of 149 h^{-1} at 100 °C and 2 MPa Achieved O_2. The CWAO of phenol used conventional method of Pt/TiO_2 TOC conversion of 39.5% and TOF 41 h^{-1} was achieved. This approach demonstrates the effectiveness of his EMSI enhancement in developing highly active catalysts for phenol processing. Zhang et al. (2022), research focused on catalytic wet

air oxidation (CWAO), which was harmless and cost-effective method to decompose toxic compounds into CO_2 and H_2O. g-C_3N_4 (Cux-g-C_3N_4) was performed by used CWAO of phenols, antibiotics, and vitamins obtained highly dispersed Cu(II)/Cu(I)-N. The formation of g-C_3N_4 Characterization results was displayed with chemical coordination of copper and N, remove copper aggregation inhibition. Cu(II) or Cu(I) in g-C_3N_4 showed superior efficiency in phenol degradation compared to Cu(0) and CuO and degraded more than 23 toxic compounds under mild conditions . The remarkable performance of $Cu_{0.1}$-g-C_3N_4 was attributed to the in situ formed H_2O_2, which enhanced the activity of the CWAO reaction. Ali et al. (2021), studied supported CeO_2 on multi-wall carbon nanotube (CNTs) were prepared of noble metal-free catalyst, and acid treatment of CNTs improves the catalytic performance. CeO_2 loaded on acid-treated CNTs (CNTs-M) displayed significantly higher TOC conversion and stability compared to CeO_2 loaded on raw CNTs (CNTs-Raw). Kinetic analysis showed decreased in DMF (N,N-dimethylformamide) oxidation activation after acid treatment. Detailed characterization worked by acid treatment to generates surface functional groups on CNTs that enable strong interaction with CeO_2, the result showed in better dispersion, increased surface oxygen, and superior performance of the catalyst. Bouabdellah et al. (2021), was synthesized by using precipitation, sol-gel, and hydrothermal methods produced W-La/CexZr_1-xO_2 catalysts with different Ce/Zr molar ratios and comprehensively characterized. Evaluation of wet air catalytic oxidation (CWAO) of phenol at 160 °C and 25 bar O_2 pressure showed that a Ce/Zr molar ratio equal to 1 provides optimal performance. Catalysts synthesized displayed good mineralization (M) and good total organic carbon by using precipitation or hydrothermal routes. This study highlights the importance of synthesis method and Ce/Zr ratio in improving catalyst efficiency for CWAO applications and provides insights for catalyst design and performance optimization. Bensouilah et al. (2020), was used sol gel and impregnation methods studied bisphenol-A of catalytic wet air oxidation for

prepared ZrO_2 catalysts. The author reviewed Characterization techniques such as N_2 physisorption, XRD, TEM, TGA/TDA, FTIR spectroscopy, XPS, and H_2-TPR were used on the solids. The result showed at 100°C and 20 bar, a 10 mg/L BPA solution ZrO_2 achieved 49% conversion in 5 h. The noble metals increased the catalytic activity at 3%, Ru/ZrO_2 90% BPA conversion was obtained within 3 h, and observed no catalyst deactivation. Parvulescu et al. (2021), used conventional methods to mineralize water contaminants of refractory substances which is not effective but catalytic processes was performed that be an alternative. As industrial scale, the advantages in kinetics transformation, selectivity, and energy efficiency was not implemented. The author resulted to solve the gap of bridge between fundamentals and practical experiments at various range followed by controversies and limitations. New processes such as photovoltaic catalytic technologies, microwave-assisted catalysis, plasma catalytic processes, and biocatalytic remediation was receiving particular attention given their advantages and disadvantages. Challenges include understanding the system complexity and interactions between solid, liquid, and gas interfaces. Wu et al. (2021), investigated Sulfites used as a precursor which was produced high active pores to remove water pollutants. This review advantages of their abundance, low cost and environmental friendliness. According to redox features the advanced oxidation process (AOP) and advanced Reduction Process (ARP) used to prepared sulfite activation. classify sulfite-based systems and extend their applicability to water purification. The author review investigates sulfite-based AOPs/ARPs and details the activation mechanism using homogeneous or heterogeneous transition metals and UV irradiation. Factors such as dissolved oxygen, pH, sulfite concentration, and water content affect performed of sulfite based AOPs/ARPs removal. Quantitative and qualitative analysis of reactive species express their role in pollutant degradation, identified important research gaps and future directions for improving sulfite-based AOP/ARP in water treatment suggests gender. Xiaoxia Ou et al.

(2022), explores catalytic wet oxidation (CWO) of phenol in high-ionic-strength wastewater (HISWW) using a Mn-Ce-Ox catalyst and discovered the effect of high NaCl concentrations. The mixture of Mn-Ce-Ox and NaCl increase phenol and total organic carbon (TOC) conversions, that is- 98% and 85%respectively, and it changes after 24 hours with 200 g L^{-1} NaCl and 1.0 g L^{-1} Mn-Ce-Ox. However, without using NaCl, conversions are reduced at ~41% for phenol and 27% for TOC under the same conditions. The approach of NaCl decreases carbon deposition, promoting surface oxidation and catalyst reoxidation, guided to raised mineralization. Additionally, the Mn-Ce-Ox catalyst can be efficiently regenerated in the saltwater system, demonstrating its potential for practical HISWW treatment. Kumari et al. (2018), founded rapid industrialization and urbanization around the world have led to source of reduction, underlined the necessity for environmental sustainability. Eco-friendly and cost-effective methods are severe for wastewater and gas depollution or a zero-emission access. Wastewater treatment and reuse are environmentally favorable due to freshwater deficit. Catalytic wet air oxidation (CWAO) originated as a undertaking technology for treating toxic and non-biodegradable organic pollutants in industrial wastewater. The observation emphasis on the acting of several noble and non-noble metal catalysts in CWAO for treating pollutants, enhancing biodegradability, addressing catalyst deactivation and mitigation, and exploring factors influencing CWAO reactions. Makatsa et al. (2021), reviews catalytic wet air oxidation (CWAO) as an advanced oxidation process for acts refractory organic compounds, observing on phenol in wastewater. Various researchers resolve different reaction mechanisms for phenol oxidation, either direct or indirect, with acetic acid identified as a stable intermediate. According to Power law and Langmuir-Hinshelwood models states for reactant adsorption/desorption on the catalyst surface. Phenol is degradation impacted by temperature, pressure, gas velocity, and liquid space velocity. The investigated displayed to hot spots formation, catalyst deactivation, and reactor thermal

runaway, observation of liquid maldistribution is enhanced by using computational fluid dynamics (CFD) modeling, that is express liquid channeling conduct to hot spots and catalyst deactivation. Yu et al. (2016), investigated Sewage sludge-formed with carbonaceous materials (SW) were acid-behave and used as catalysts in catalytic wet air oxidation (CWAO) of m-cresol. Various types of Characterization using XRF, XRD, FTIR, XPS, and TPD-MS appearing HNO_3-acts SW (HNO_3-SW) as the most effective catalyst. The experiment is maintained temperature at 160°C and Pressure at 0.66 MPa oxygen for 90 min, HNO_3-SW obtained 99.0% conversion of m-cresol at an initial concentration of 5000 mg L^{-1}. Continuous 8-day experiments shows that durability and sustained catalytic performance of HNO_3-SW. Balanced between m-cresol conversion and carboxyl group content revealed the key role of carboxyl groups in SW catalysts' CWAO activity. Oxidation ways for m-cresol in CWAO were accepted depends on intermediate product analyses. De mora et al. (2024), examined Hydrothermal carbonization (HTC) of anaerobic cycle sludge produced from activated carbon by using KOH, $FeCl_3$, $ZnCl_2$, $CuCl_2$ to enhance the surface area and conduct metal active substances. Activation of KOH obtained in a surface area of approximately 1000 m^2/g. Activation of $CuCl_2$ and $FeCl_3$prepared by numerous Cu^- and Fe^-doped materials with significant surface area (metal content 49.1% and 42.5%, respectively). The synthesized carbon-based materials, both metal-free and doped, were assess as catalysts in the wet air catalytic oxidation (CWAO) of HTC aqueous solutions of animal compost, which increasing the biochemical methane potential in anaerobic digestion. Did. CWAO treatment enhanced the proportion of carboxylic acids in the wastewater and developed the anaerobic digestion rate, but the reduced TOC concentration in the treated stream limited methane production. This exploration will foster a sustainable HTC spirits processing strategy and complete the circular economy. Gutiérrez-Sánchez et al. (2023), Activated carbon supported with iron nanoparticles describe from sewage sludge (FeSAC) showed highly effective catalytic

activity in the conversion of ciprofloxacin by using catalytic wet air oxidation (CWAO). The FeSAC catalyst was characterized and the CWAO parameters (temperature, pressure, catalyst amount) were performed in a batch reactor. At 140°C, 20 bar, and catalyst dosage of 0.7 g/L, the conversion of ciprofloxacin and CO_2 selectivity obtained within 2 h were over 99% and 60%, respectively. The FeSAC catalyst pretend high stability with negligible loss of active phase (Fe). The resolved equation accurately described the conversion rate of ciprofloxacin and gave maximum activation energy of 53.8 kJ/mol. Density functional theory (DFT) calculations demonstrate the conversion mechanism and identified compounds that are difficult to degrade by CWAO. A proof of concept by using environmentally relevant matrices confirmed the technical analysis of the catalyst for complex matrices, sequential reaction cycles, and low processing costs. Yang et al. (2008), CeO_2-TiO_2 catalysts, produced through coprecipitation, was examined for their efficacy in catalytic wet air oxidation (CWAO) of phenol in both batch and packed-bed reactors. Mixed CeO_2-TiO_2 oxides demonstrate better activity than pure CeO_2 and TiO_2, with the 1/1 catalyst displaying the maximum efficiency. COD and TOC removal rates showed nearly 100% and 77% respectively after 120 minutes at 150°C, 3 MPa pressure, 1000 mg/L phenol concentration, and 4 g/L catalyst dose in a batch reactor. In a packed-bed reactor, employing the same catalyst, over 91% COD and 80% TOC removal are sustained for 100 hours at 140°C, 3.5 MPa air pressure, and 1000 mg/L phenol concentration. Minimal metal ion leaching is detected during continuous reaction, supporting the remarkable activity and stability of the CeO_2-TiO_2 catalyst. Olgun et al. (2021), studied pharmaceutical wastewater treatment by using photocatalytic oxidation and catalytic wet air oxidation (CWAO). The effect of reaction parameters was design using a Box-Behnken. The review shows Fe/AC catalyst was more effective in both photocatalytic and wet air catalytic oxidation. In the photocatalytic oxidation process, 72.7% COD removal was obtained at pH = 4.5, 2.0 g/L, and [H_2O_2]O = 0.32 MM.

CWAO determined as catalyst loading of 3 g/L, pH = 3, and 50°C, a COD removal efficiency of 83.1% was achieved. The CWAO method was found to be more suitable as it achieved higher COD removal efficiency with shorter reaction time. The toxicity in terms of growth inhibition of L. sativum was calculated to be 4.82% after the treatment of CWAO. First-order kinetics showed the best result with the experimental CWAO data. The activation energies displayed of the fast and slow steps were 25,661.16 and 28,327.46 J/mol, respectively. Christophliemk et al (2023), investigated A porous, long-lasting alkali-activated material (MK-AAM) based on metakaolin contained active metals (CuO, MnO_2) was working on catalytic wet air oxidation (CWAO) to bisphenol A (BPA). Two processes was produced porous He CuO, MnO_2, and $Cu(OH)_2$ composites. The $Cu(OH)_2$ composite was displayed the maximum specific surface area (89 m^2/g) and compressive strength (3.6 MPa). In CWAO methods were performed the condition at 150 °C and 1 MPa using $Cu(OH)_2$ composite, the degradation of BPA andorganic carbon (TOC) was 100% and 53%, respectively. Decomposition occurred during 5 h of oxidation due to erosion (1.5 wt.%) and active metal leaching (Cu, Mn) (1.1 wt.%, 3.6 wt.%), the remark that energy This suggests that efficient BPA degradation does not affect energy efficiency. Properties of composite materials. The authors proposed that under mild reaction conditions BPA can be degraded energy-efficiently via CWAO into less harmful compounds without losing the desired properties of the composites. Tekin et al. (2023), synthesized lanthanum cobalt oxide ($LaCoO_3$) as catalyst to efficiently handle synthetic sugar industry wastewater in a single process using catalytic wet air oxidation. The authors emphasized the vital roles of reaction temperature and ideal air percentage and reported that sugar derivatives were almost fully removed with 91% TOC and 87% COD removals, thus achieving a high level of mineralization-a major purpose of advanced oxidation. The authors investigated the reaction kinetics using pseudo homogeneous and heterogeneous models, considering sucrose and TOC (total organic

carbon) concentrations as parameters and reported that the reaction order of the pseudo homogeneous model was two. The authors reported mass transfer limitations were found only for oxygen as the gaseous reactant in the heterogeneous models and the Mars-van Krevelen model was selected as the most suitable model for the oxidation of sucrose and TOC among the heterogeneous models. Wang et al. (2008), investigated various supports: ZrO_2, CeO_2, TiO_2, ZrO_2-CeO_2, and TiO_2-CeO_2 was prepared by impregnating method with different ruthenium catalyst. Their effectiveness in oxidizing acetic acid in aqueous solution was studied in a stirred reactor at 200°C and 4 MPa pressure. The catalyst activity order observed was RuO_2/ZrO_2-$CeO_2 > RuO_2/CeO_2 > RuO_2/TiO_2$-$CeO_2 > RuO_2/ZrO_2 > RuO_2/TiO_2$, which corresponds to the surface concentration of non-lattice oxygen (defect-oxide or hydroxyl-like group) on these catalysts. Non-lattice oxygen on the catalyst surface significantly influences catalytic activity. Javid et al. (2023), performed wet air oxidation (WAO) of PPE mixture at temperatures between 300°C and 350°C, at initial air pressures of 30 bar and 60 bar, and reported reduction in total suspended solids (TSS) by up to 99% and the total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) to 360 mg/L and 110 mg/L, respectively. The authors reported volatile fatty acids (acetic and propionic acids) and ammonia nitrogen (NH_3-N) with concentrations achieve 1117 mg/L, 975 mg/L, and 18 mg/L, respectively as the main products and nitrogen (72% w/w) and oxygen (14% w/w) as gaseous products. They also performed semi-batch WAO treatments at 300°C and 350°C and got similar waste reduction result and suggested that non-catalytic WAO as a viable solution for PPE waste management. Mondal et al. (2016), examined a fixed bed reactor was used for catalytic wet air oxidation of phenol with noble metal (Ru) supported on silica MCM-41 material. The required amount of ceria used as a promoter for the MCM-41 material enhanced both the activity and selectivity of Ru in this reaction. The reaction conversion at 413 k and 18 bar oxygen pressure was displayed 99%. At 413 K using the ceria promoted

Ru/MCM-41 catalyst the activation energy of the oxidation reaction was determined to be 33 kJ mol^{-1}. The supports and catalysts were characterized using various techniques, including BET surface area analysis, TPR, CO chemisorption, TPD, XRD, SEM, EDX, TEM, and ICP-AES. Isgoren et al. (2023), used automobile catalytic converter (ACC) which in contained huge number of precious metals as catalysts. ACC was expensive process when it used waste recovery and/or activation. Here the researchers was used various chemical treatment methods such as catalytic wet air oxidation. The author investigated CWAO conditions by response surface methodology (RSM). The conversion showed 88% with the condition of temperature 111.5℃ and pressure 20 bar and catalyst recovered 0.41 g. Before and after CWAO was used Malathion-contaminated wastewater to check quality of toxicity. The authors final investigation showed the toxicity of wastewater was eliminated by using CWAO. Gai et al. (2022), discovered hydrothermal method was used to prepared highly dispersed Ru/functionalized CMK-3 of novel decamethonium bromide (DATB)-catalyst for wet air catalytic oxidation (CWAO) of ammonia. This method immobilizes $RuCl_6^{2-}$ on the support of DAT-modified CMK-3-N and result showed high temperature treatment was inhibited due to Ru nanoparticles aggregation. This inhibition can be attributed to the electrostatic interaction between Ru species and CMK-3-N-DTA and the insulating effect of carbon deposits. The final result of DMH-AH catalyst displayed better activity and selectivity in ammonia nitrogen removal compared to the reference catalyst prepared using the conventional impregnation method. Liu et al. (2022), focused on the misuse of chloroquine phosphate (CQP) during the COVID-19 pandemic has raised concerns about water contamination. A high-entropy oxide catalyst (HEO), (Mg-Cu-Mn-Co-Fe) Ox, synthesized by coprecipitation method was effective for wet air catalytic oxidation (CWAO) to treat CQP wastewater. Electron spin resonance (ESR) analysis revealed the role of HEO in accelerating superoxide and hydroxyl radical generation and CQP degradation. Reactive surface method

(RSM) optimization identifies ideal CWAO conditions: initial oxygen pressure of 15 bar, catalyst dosage of 1.4 g/L, and temperature of 230^0C. Principal component analysis (PCA) confirms the benefits of HEO in CWAO, elucidates the degradation mechanism, and opens new avenues for environmental catalysis. Wang et al. (2021), focused Integrated pollutant removal techniques was used for their simplicity and low operating cost and important for coal-fired power plants and industrial boilers. They had discussed recent advances in advanced oxidative integrated gas removal, including methods such as nonthermal plasma, chlorine-based, sulfur-based, ozone oxidation absorption and Fenton-based approaches. Multiple air pollutant removal processes were discussed and endorsed, highlighting the author's conclusion that the Fenton-based method is best. These processes include metal element doping catalysts that improve the reaction through catalyst optimization, redox pairing, photocatalysis, electrochemical corrosion, and catalytic NO reduction. An analysis was conducted on the suggested Fenton-based industrial design and the potential for industrialization with much lower operating costs than conventional approaches. Prospects for the removal of various air pollutants in the future are illuminated by challenges and recommendations related to oxidizers, catalysts, and economy. Pinter et al. (2008), investigated the catalytic wet-air oxidation (CWAO) of formic acid, acetic acid, and phenol using Ru/TiO_2 catalysts in a trickle-bed reactor at temperatures ranging from 328 to 523 K and pressures up to 50 bar. Complete oxidation of formic acid was achieved under mild conditions, with no catalyst deactivation attributed to material dissolution. Thermal decomposition contributed significantly to formic acid removal. Acetic acid oxidation was structure-sensitive, with the highest activity observed when the Ru phase on the catalyst surface was predominantly zero-valent. However, oxidation of metallic Ru to RuO_2 during the reaction reduced acetic acid conversion. Phenol and total organic carbon (TOC) removal were achieved above 483 K without carbonaceous deposits on the catalyst surface.

Deactivation at lower temperatures was linked to strong adsorption of partially oxidized intermediates, mitigated by higher operating temperatures. The oxidative treatment over Ru/TiO_2 catalysts reduced the acute toxicity of end-product solutions to Daphnia magna and Vibrio fischeri compared to feed solutions.

CHAPTER 3

EXPERIMENTAL PROCEDURES

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1. Chemicals for synthesis

3.1.1. Titanium oxide

Titanium oxide (TiO_2) is a versatile metal salt compound derived from titanium and oxygen. Here are various forms such as rutile, anatase, and brookite, each with different properties. It is mainly used in catalyst synthesis whose molecular weight 79.87 g/mol. Nanotechnology synthetic routes, noble material processing processes, and innovative reactor designs provide solutions to improve TiO_2 photocatalysis. These advances address challenges such as improving catalytic activity, controlling structural properties, immobilization for membranes and membrane formation, reducing bandgap energy, and selectively degrading impurities. TiO_2 is mainly supplied by Merek specialities private limited which situated at Shiv sagar estate 'A', Mumbai-400018, it is store in our laboratory for using experiment purpose. Its specifications are assay (TiO_2) substances ($\geq$ 98.5%), soluble in water substances ($\leq$ 0.5%), soluble in diluted hydrochloric acid ($\leq$ 0.5%), heavy metals (as Pb) ($\leq$0.003%), loss on drying at 105^0C, 3h ($\leq$ 0.5%).



Fig 26: Titanium oxide (TiO_2)

3.1.2. Aluminium oxide

Aluminium oxide is a composition of aluminium and oxygen whose chemical formula Al_2O_3. Aluminium oxide is using as a support material which increases activity of catalyst. Molecular weight of this material is 101.96 g/mol. It is supplied by Merek specialities private limited which situated at Shiv Sagar estate 'A', Mumbai-400018. Its specifications contain pH-value in 10% aqueous suspension (6.8-7.8), portion elutable with water (≤ 0.2%), chloride (Cl) (≤ 0.05%), calcium (Ca) (≤ 0.15%) respectively. Al_2O_3 has three phases like that α-alumina, alumina and γ-alumina. It is also used as a catalyst. Its density, boiling point and melting point are 3.95 g/cm^3, 2977^{0}C and 2072^{0}C respectively. Al_2O_3 is using for catalyst synthesis gives larger surface area, aluminium oxide (Al_2O_3), available in diverse forms like nanoparticles, offers a substantial surface area. Enhanced surface area boosts catalyst efficiency by enabling greater contact between reactant molecules and the catalyst, thereby improving catalytic performance. Aluminium oxide (Al_2O_3) exhibits chemical stability across diverse conditions, including high temperatures and acidic or basic environments. This stability preserves catalyst activity, preventing rapid degradation during catalytic processes.



Fig 27: Al_2O_3 support

3.2. Supporting equipment for catalyst synthesis

3.2.1. Magnetic stirrer bar

Magnetic stir bars are coated magnets designed to stir liquids within a sealed container, eliminating the need for an opening. They are commonly used in chemistry and biology research, particularly in medicine, for stirring fluids in modestly sized containers. A magnetic stir bar is placed inside a container and rotated using an external magnetic field, often generated by a stir plate with a rotating magnet underneath. This setup allows stirring without inserting anything into



Fig 28: Magnetic stirrer bar

the container, enabling complete sealing and eliminating concerns about leaks or contaminating the fluid with lubricants. Magnetic stir bars come in various shapes, typically octagonal or circular, with some designed specifically for round-bottom flasks. Special shapes cater to different stirring needs or vessel shapes, with pivot rings aiding rotation. Sizes range from a few millimeters to several centimeters, with smaller ones often called "fleas." Magnetic stir bars typically contain magnetic materials like alnico or samarium cobalt, which maintain strength at high temperatures. Neodymium may be used for low temperatures, and

ferrite stir bars are also available. Due to their small size facilitates easy cleaning and sterilization, and they don't need lubricants that might contaminate the vessel or product.

3.2.2. Magnetic hot plate

A magnetic stirrer with a hot plate is a laboratory device used for both mixing and heating solutions. It features a flat heating surface, often aluminum or ceramic, coupled with a built-in magnetic stirrer. Magnetic stirrers with hot plates find widespread use in chemistry, biology, and medical labs for tasks like dissolving solids, mixing reagents, and sample preparation. They help maintain consistent temperature and agitation levels, crucial for



Fig 29: Magnetic hot plate (Medilab excellence in labware)

chemical reactions. Magnetic stirrers with hot plates ensure thorough and consistent mixing of reactants and catalysts, promoting uniformity in the reaction mixture. The hot plate enables precise control of reaction temperature, critical for catalyst synthesis, as temperature influences reaction kinetics and product yields.

3.2.3. Hot air oven

A hot air oven utilizes forced convection to heat and sustain a steady temperature within a sealed chamber. Hot air ovens contain a heating element, typically electric, positioned either at the top, bottom, or both, depending on the oven's design, to generate heat within the chamber. A fan inside the oven circulates hot air evenly throughout the chamber, preventing hot spots and ensuring consistent heating of the contents. Hot air ovens are utilized in catalyst preparation for tasks like drying or calcination, crucial for removing solvents and activating chemical reactions. They provide a consistent and controlled heating environment, ensuring the formation and stability of catalyst materials. It is supplied by G.B. Enterprises company for the laboratory experiment.

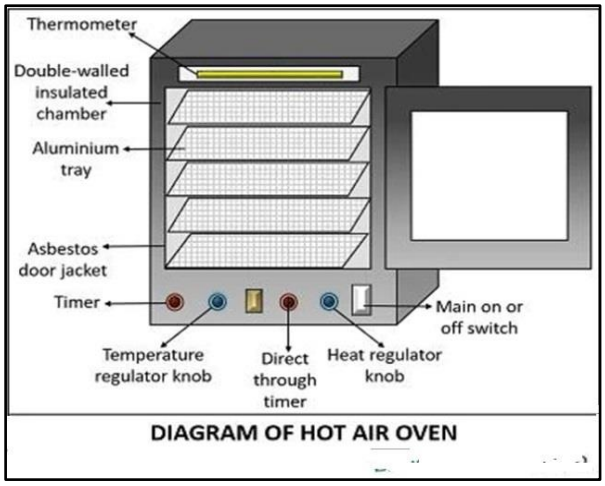


Fig 30: Hot air oven

3.2.4. Calcination chamber

A calcination chamber is a furnace or reactor in industries like chemicals and metallurgy for calcination. Calcination involves heating a substance to high temperatures without slight amount of air, used to remove volatiles, water, or induce decomposition or phase transitions in materials. Calcination chambers use heating elements like electric heaters or gas burners

for heat. They're insulated with refractory materials to prevent heat loss and enhance energy efficiency. The desired reactions occur efficiently due to temperature control that is crucial for calcination, so chambers have monitoring systems like thermocouples and PID controllers. In their initial state, some of precursor catalyst that are not catalytically active. In that case, calcination activates catalyst precursors by removing impurities, solvents, and bound water, initiating chemical transformations to create active catalytic sites. It is manufactured by SICCO.



Fig 31: Calcination chamber

3.3. Excess Solution Impregnation (ESI) Method

It is one of the most widely catalyst synthesis preparation method, solution added in excess of the support pore volume causes the solution transport to change from a capillary action process to a diffusion process which is must slower. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal of the catalyst surface.

3.3.1. Catalyst synthesis (ESI) preparation method

Excess solution Impregnation (ESI) method was used to synthesized of both Ti/γ-Al_2O_3 and Ti-Mn /γ-Al_2O_3 catalyst. Here, metal precursor used as Titanium oxide hydrated salt (TiO_2) and γ-Al_2O_3 was used as a catalyst support to obtain (0.5-2.5wt.%) Ti/γ-Al_2O_3 catalyst. Double distilled water was required for all the syntheses procedure and the amount of Titanium salts necessity to obtain specific catalyst such as, %Ti were determined from stoichiometry. Desired concentration of TiO_2 salt was added to 10gram preheated alumina (γ-Al_2O_3) support (kept at 100^0C for 30 min in hot air oven) and stirred for 4 hours at pH: 8-9. Thereafter, slurry was kept in a hot air oven at 100^0C for 12 hours, and then calcined at 400^0C for 4 hours in an air flow. Thus way, deposition of precursor materials on the γ-Al_2O_3 support was successfully obtained. The calcined catalyst was further reduced using hydrogen flow.

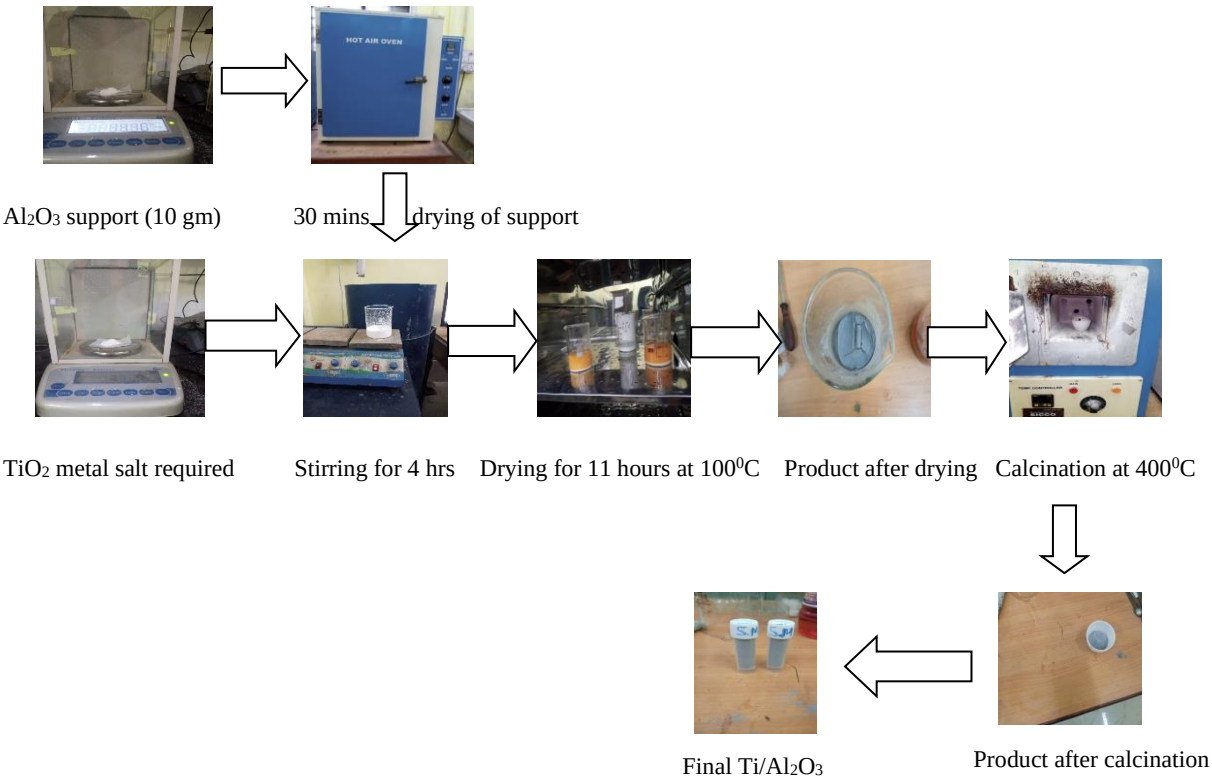


Fig.32. ESI (Excess Solution Impregnation) method of Ti/γ-Al_2O_3 catalyst synthesis (Laboratory experiment)

3.4. Catalyst characterization technique

In this study utilized various techniques were to analyze catalysts. Before and after CWAO (Catalytic Wet Air Oxidation) the researchers examined weight percentage of metal content, specific surface area. These techniques are BET (Brauner-Emmette-Teller) analysis and TGA (Thermogravimetric Analysis) describes below-

3.4.1. BET (Brauner-Emmette-Teller) analysis

BET analysis is a method employed to find out the specific surface area and pore diameter of materials, particularly porous catalysts, adsorbents, and powders. In environmental engineering, for removing pollutants the BET method was plays a crucial role in evaluating the adsorption capacity of materials. It provides insights into the surface properties of materials to facilitates the development of effective environmental remediation approaches. The BET instrument supplied by Quantachrome instrument, model no is autosorb iQ_2.

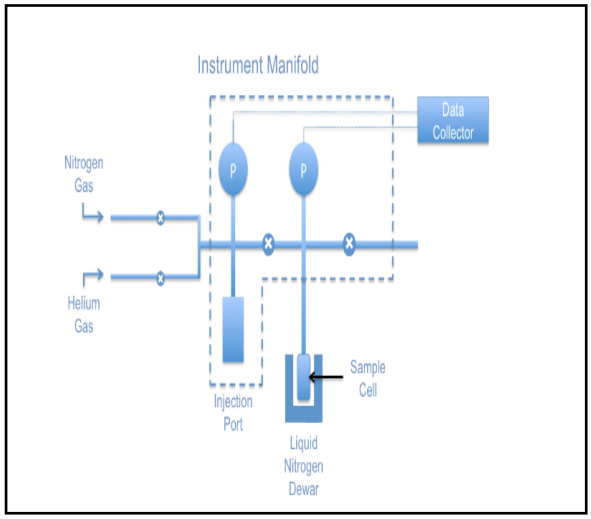


Fig.33. Schematic diagram of BET instrument



Fig.34. BET instrument in laboratory set

3.4.2. TGA (Thermogravimetric Analysis)

Thermogravimetric analysis (TGA) is a system used to determine in thermal analysis to changes in the sample of mass with temperature varies. By notice these changes over time, TGA allows insights into various physical phenomena like phase transitions, absorption, and desorption, as well as chemical processes such as chemisorption, thermal decomposition, and solid-gas reactions (oxidation or reduction). TGA instrument is supplied by PerkinElmer (company) STA 6000 in the laboratory.

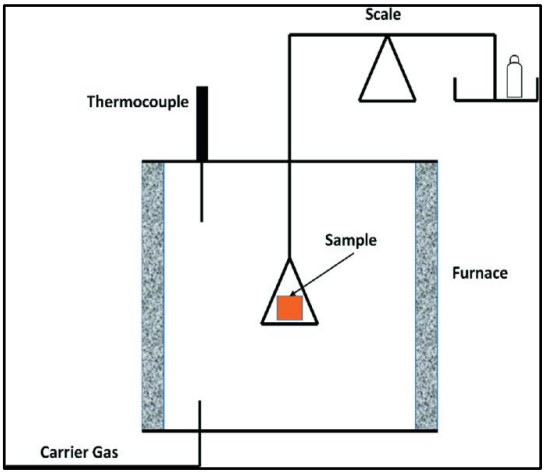


Fig.35. Schematic diagram of TGA



Fig.36. TGA instrument Lab setup

3.5. Oxidation reaction set up

The catalytic oxidation of oxalic acid was performed in a three-neck round bottom glass flask reactor whose 1 L capacity. During the experiment there was a possibility of water vapor escaping out of the flask at high temperature. After that 1000 ml of oxalic acid and distilled water mixture solution and magnetic stirrer is added in the bottom flask reactor. Glass thermometer is introduced in the flask and switch on the heater and compressor. The heat and RPM is controlled increases the temperature, after reaching the temperature up to 50°C,taken 5 ml standard solution of oxalic acid sample for calculating conversion, then 1 gram of TiO_2

catalyst is added to the reactor and air (which was a source of oxygen is passed from a compressor through a rotameter at constant flow rate and oxygen was considered as excess in amount of oxalic acid considered as a limiting reactant) were introduced into the reactor while a magnetic agitator continuously stirred the solution at a certain speed.



Fig.37. Oxidation laboratory setup

After reaching the required temperature then the solution mixture is withdrawing the samples of 5 ml from the flask using a pipette. The taken sample was titrated against 10^{-2} (M) NAOH solution using 1 drop of phenolphthalein as an indicator to calculate of oxalic acid oxidation conversion.

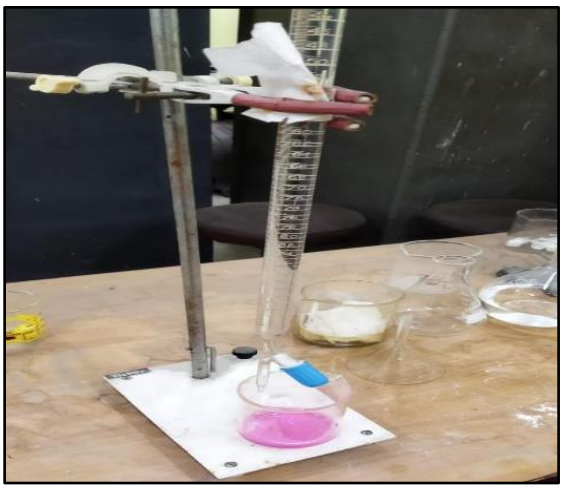


Fig. 38. Titration with Sodium Hydroxide (NaOH)

The percentage conversion of oxalic acid at any time 't', was calculated using the below formula…

$X\ (\%) = [(C_{A0}-C_A)/C_{A0}] \times 100$

Where C_{A0} is the initial concentration of oxalic acid and C_A is the concentration of oxalic acid at any time 't'.

Table 2: Experimental conditions for three neck bubble column catalytic wet air oxidation

Reaction temperature, ^0C	60 / 70 /80 /90
Oxidizing agent	Air
Pressure, atm	1
Catalyst	Ti / Al_2O_3
Air flow rate, L / min	1/ 1.5
Initial concentration of oxalic acid, ppm	500/1000/1500/2000
Catalyst loading, wt. %	0.5/1/1.5/2
Catalyst dosages, g	1

CHAPTER 4

RESULTS & DISCUSSION

CHAPTER 4

RESULTS & DISCUSSION

4.1. Characterization of Ti /γ-Al_2O_3 Catalyst

4.1.1. Brauner-Emmette-Teller (BET) analysis

Ti-Al_2O_3 (1 wt.%) catalyst was degassed at 300^0C for 4 hours under high vacuum conditions (≈10^{-5} mbar) prior to adsorption experiments. Nitrogen adsorption isotherm of Ti/γ-Al_2O_3 catalyst sample was given in below figure. The adsorption isotherm is of type III according to IUPAC classification. The adsorption data were used to determine the BET surface area.

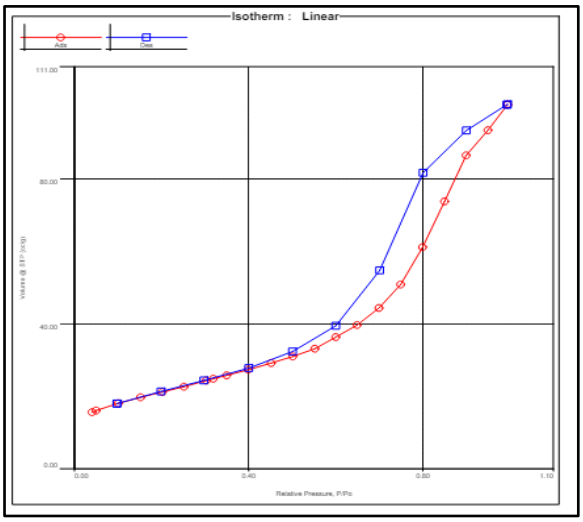


Fig.39. Adsorption and desorption graph

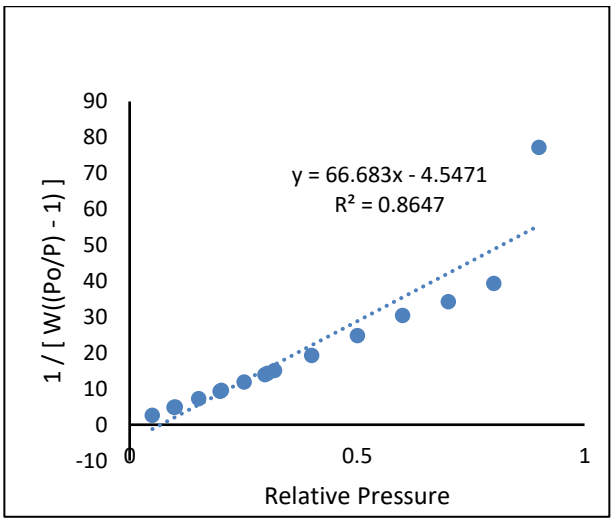


Fig.40. BET graph for surface area calculation

Table 3: Nitrogen adsorption (BET) results of 1 WT.% Ti/ γ-Al_2O_3 catalyst sample [Appendix B.4.]

BET surface area, $S_{BET,}$ m^2/g	81.89
Maximum amount of nitrogen adsorbed, V_{max}, cm^3	0.0160938

Adsorption experiment (Ti/Al_2O_3), the experiments result showed that the adsorption isotherm was a type III isotherm according to IUPAC classification and the BET surface area can be seen 129.57 m^2/g [Gunduz and Dukkanci, 2007].

Table 4. BET surface area table of different catalyst-support [Wang et al, 2008]

Catalyst	**S_{BET} (m^2/g)**
RuO_2/ZrO_2	170
RuO_2/TiO_2	18.1
RuO_2/CeO_2	92.6
$RuO_2/TiO_2–CeO_2$	127.0
$RuO_2/ZrO_2–CeO_2$	114.0

Table 5. Result of BET surface area using $Ti\text{-}Al_2O_3$ catalyst [Ramesh et al, 2021]

Sl. No.	**Catalysts**	**S_{BET} (m^2/g)**
1	$\gamma\text{-}Al_2O_3$	253
2	$Ti\text{-}Al_2O_3$ (10)	221
3	$S\text{-}SO_4^{2-}$ /$Ti\text{-}Al_2O_3$ (10)	198
4	$H\text{-}SO_4^{2-}$ /$Ti\text{-}Al_2O_3$ (10)	193
5	$V\text{-}SO_4^{2-}$ / $Ti\text{-}Al_2O_3$ (10)	190

4.1.2. Thermogravimetric Analysis (TGA)

Thermal stability analysis of synthesized 1.0 wt.% of titanium-alumina catalyst was investigated with TGA measurement in the temperature 30^0C to 800^0C and the result are shown in below Fig. In TGA curve, the loss of weight was observed 1.80% [Appendix B.5.]

in the Temperature between 50^0C to 120^0C. At the temperature between 120^0C to 750^0C, the weight loss is showing 2.08 % [Appendix B.5.] that indicates the thermal decomposition. After 750^0C, the TGA curve is resulting no weight change [Appendix B.5.], because of phase transition of the product.

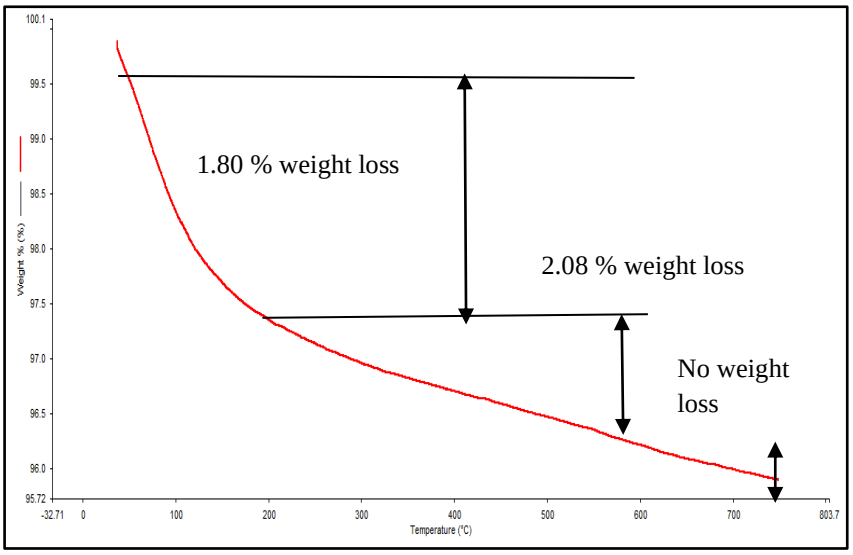


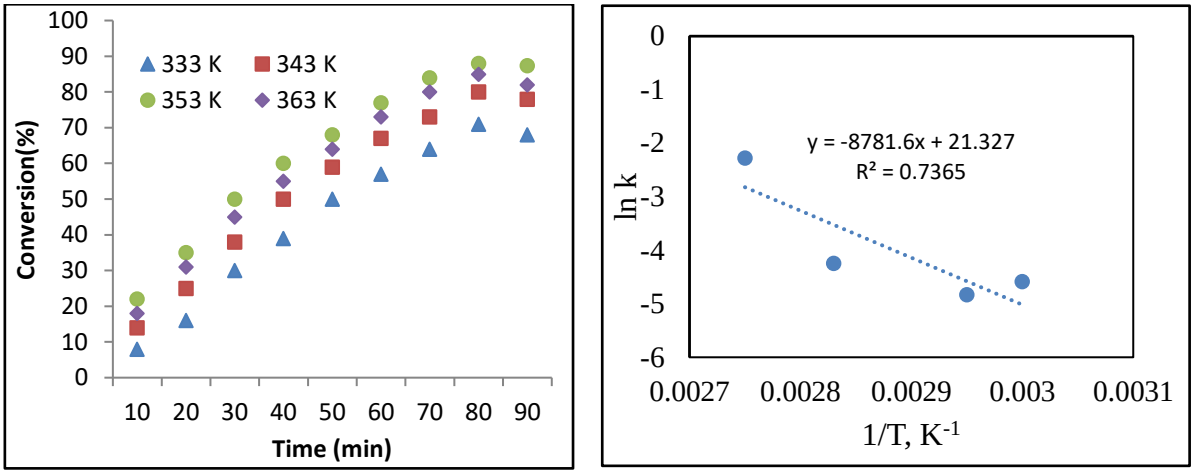
Fig.41. TGA curves of as synthesized 1 wt.% TiO_2/γ-Al_2O_3 catalyst

The H-SO_4^{2-}/Ti-Al_2O_3 (10) catalyst resulted a weight loss in two-step during thermal analysis: the first step (100°C-110°C) was due to moisture, while the second step (400°C–500°C) accounted for a significant weight loss (16.4%) attributed to sulfur decomposition. Beyond 500°C, no further weight loss was observed. The V-SO_4^{2-}/Ti-Al_2O_3 (10) catalyst demonstrated a similar pattern. H-SO_4^{2-}/Ti-Al_2O_3 (10) lost the most weight among the catalysts, indicating more sulfur breakdown than S-SO_4^{2-}/Ti-Al_2O_3 (10) and V-SO_4^{2-}/Ti-Al_2O_3 (10). TGA findings validated the catalysts' thermal stability up to 800°C. S-SO_4^{2-}Ti-Al_2O_3 (10) lost approximately 15.5% of its weight due to sulfur degradation. Below 300°C, V-SO_4^{2-}/Ti-Al_2O_3 (10) shown instability with a notable 19.9% weight loss, suggesting inadequate thermal stability. However, the V-SO_4^{2-}/Ti-Al_2O_3 (10) catalyst did not exhibit any

sulfur degradation. In comparison to the other catalysts, H-SO_4^{2-}/Ti-Al_2O_3 (10) exhibited the highest sulfur decomposition rate [Ramesh et al, 2021].

4.2. Effect of process parameters on oxalic acid oxidation

4.2.1. Effect of reaction temperature on oxalic acid degradation



(a) **(b)**

Fig.42. (a). Effect of temperature on OA degradation. Catalyst: Ti (1.0 wt.%) /Al_2O_3, RPM: 300, Air flow rate: 1.0 LPM, Initial concentration of OA: 1000 ppm, Catalyst dosage: 1 gm/L. (b). Arrhenius plot for activation energy calculation

In the above graph shows that….

An increase in oxalic acid degradation on increase in reaction temperature. It is due to the rate constant increases with increase in the reaction temperature. The increase in the oxalic acid degradation is observed 88.29% at 80^0C [Appendix A, Table-1 & Appendix B,1]. Further increased the reaction temperature resulted in decrease in the oxalic acid degradation & its due to the lower adsorption rate of oxalic acid on the catalyst surface at reaction temperature Higher than 90^0C.

The activation energy using of 1 wt.% Ti/γ-Al_2O_3 catalyst at the temperature of 60-90^{0}C from the Arrhenius plot is shows 73.01 kJ /mol.

For the reaction of activation energy was 47 KJ /mol resulted from the Arrhenius plot using 0.5 wt.% Pt/Al_2O_3 catalyst and used the ceria-promoted 0.5 wt.% Pt/ (10 wt.%) CeO_2-Al_2O_3 catalyst, activation energy showed 42 kJ /mol. The lower activation energy of the ceria-promoted catalyst indicates it had higher activity compared to the Pt/Al_2O_3 catalyst [Modal et al, 2016]. When using a 0.5 weight percent Pt/Al_2O_3 catalyst, the activation energy is 47 kJ/mol; however, when using a 0.5 weight percent Pt/ (10 weight%) CeO_2-Al_2O_3 catalyst that is promoted by ceria, it is 42 kJ/mol. In comparison to the Pt/Al_2O_3 catalyst, the ceria-promoted catalyst exhibits a lower activation energy, suggesting a higher level of activity [Roy et al, 2014].

4.2.2. Effect of rpm on oxidation experiment

In the below graph shows that…

The experiment is conducted under normal atmospheric pressure. The initial concentration of oxalic acid is 1000 parts per million (ppm), and the mixing speed ranges from 100 to 400 parts per million (ppm). The experiment covered a temperature range of 60°C to 90°C in 10°C intervals. A conversion versus time graph was plotted based on data collected over a 90 minute period during the experiment. The optimum conversion obtained at 80^{0}C & 300 RPM is 88.29%.There is no significant conversion obtained at 500 rpm.

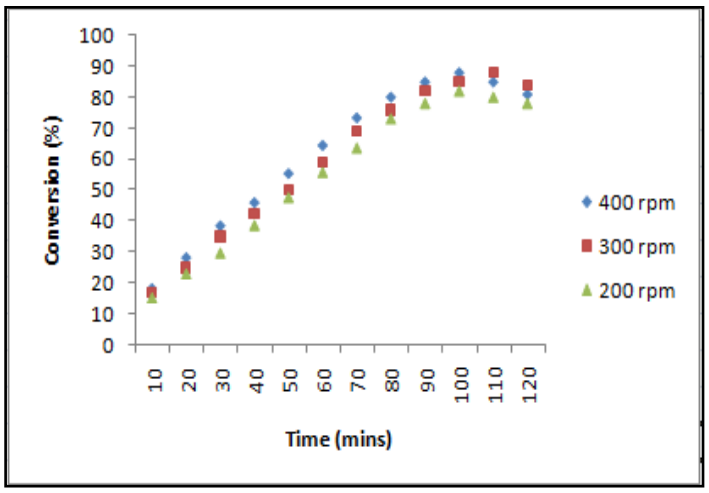


Fig.43. Effect of RPM on OA degradation. Catalyst: Ti (1.0 wt %) /Al_2O_3, RPM: 300, Air flow rate: 1.0 LPM, Initial concentration of OA: 1000 ppm, Catalyst dosage: 1 gm/L.

4.2.3. Effect of loading on oxalic acid conversion

The experiment investigated catalytic wet air oxidation with Titanium loadings ranging from 0.5 to 2.0 wt.%. From the above figure the results, indicating that the highest conversion rate of 88.29% was achieved with 1.0 wt.% Titanium loading. The experiment investigated catalytic wet air oxidation with Titanium loadings ranging from 0.5 to 2.0 wt.%. From the above figure the results, indicating that the highest conversion rate of 88.29% was achieved with 1.0 wt.% Titanium loading. This optimum conversion was attributed to the presence of sufficient active sites on the catalyst at this loading. Increasing the catalyst loading over 0.5 wt.% resulted in smaller active sites but an increase in the reaction rate. Consequently, the oxidation tests revealed that 1.0 wt.% Titanium was the most effective catalyst, resulting in an 88.29% conversion rate for the reaction.

The degradation of phenol rose as Ru dosage increased from 0.2 to 0.5 weight percent. Ru loading of 0.5 weight percent resulted in the maximum conversion, or almost 99%. After this, the rate of phenol decomposition decreased or stopped entirely. This is probably because the

reaction had enough active catalyst sites at 0.5 weight percent Ru, and adding more catalyst loading did not improve the reaction since there might have been less active site availability [Mondal et al., 2016].

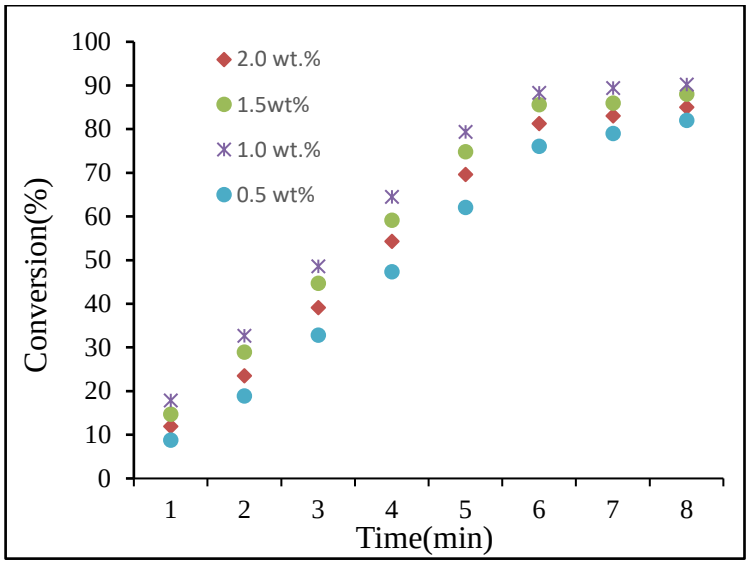


Fig.44. Effect of loading on oxalic acid degradation. Catalyst: Ti (1.0 wt.%)/Al_2O_3, RPM: 300, Air flow rate: 1.0 LPM, Initial concentration of OA: 1000 ppm, Catalyst dosage: 1 gm/L

Oxalic acid degradation experiments were carried out using of various loading of Pt/Al_2O_3 0.2 to 0.7 wt %. The greatest conversion, around 67%, was achieved at 0.5 wt.% Pt loading. Beyond this point, the rate of oxalic acid breakdown remained rather constant. This is most likely because 0.5 wt.% Pt provided enough active catalyst sites for the reaction, and increasing the catalyst loading further did not improve the reaction due to a possible decrease in the availability of active sites [Roy et al 2014].

4.2.4. Effect of initial concentration on oxalic acid

At atmospheric pressure conditions, oxalic acid degradation is calculated by using different four initial concentration of oxalic acid (OA). They maintained a temperature at 60^0C, 70^0C

and 80^0C, flow rate of air at 1L/min and catalyst dosage amount of 1 gram. Results showed that at an initial OA concentration of 1500 ppm, approximately 88.29% degradation occurred within 90 minutes. Interestingly, similar degradation rates of around 60.8%, 88.1% and 84.6% were observed for initial OA concentrations of 500, 1000 and 2000 ppm respectively. Different initial concentrations of oxalic acid (500-3000 ppm) experiments over a 0.5 wt.% Pt/ (10 wt.%) CeO_2-Al_2O_3 catalyst was showed that the initial reaction rate peaks at 1500 ppm. Beyond this concentration, the rate of reaction reduces as the initial concentration of oxalic acid increases [Roy et al, 2014].

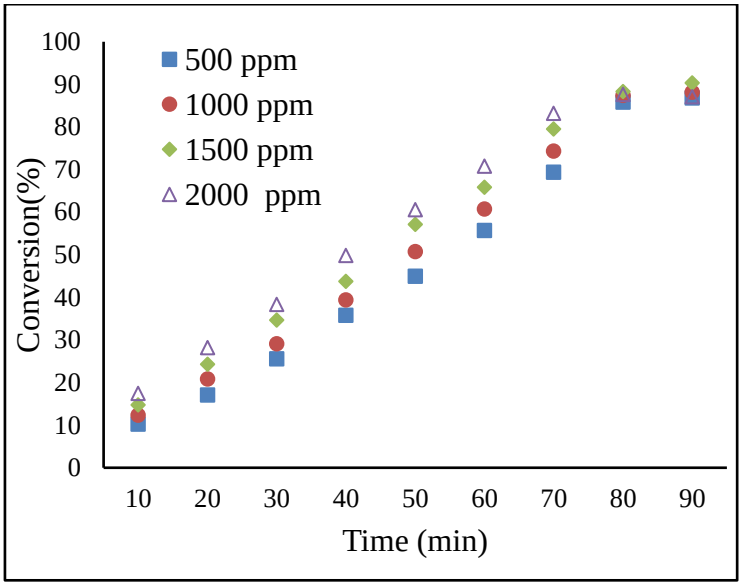


Fig.45. Effect of initial concentration on oxalic acid degradation. Catalyst: Ti (1.0 wt.%) /Al_2O_3, RPM: 300, Air flow rate: 1.0 LPM, Initial concentration of OA: 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm, Catalyst dosage: 1 gm/L.

4.3. Modelling for oxidation reaction

The study concluded that the oxidation of oxalic acid with a titanium catalyst was primarily governed by kinetics. This determination enabled the identification of different heterogeneous catalytic oxidation mechanisms involved in the process.

Power Law Model:

The power law model plays a crucial role in designing catalyst preparation for the Catalytic Wet Air Oxidation (CWAO) process and scaling up reactors from laboratory to industrial scale. This model provides a generalized expression to compute the reaction rate, specifically tailored for three-neck bubble column reactors used in the process. [J. Makatsa et al, 2021].

The general formula of power law model can be expressed as –

$r = k. [OA]^m [O_2]^n$

Where r is rate of reaction, k is the rate constant, m is the order of oxalic acid and n is the order of oxygen.

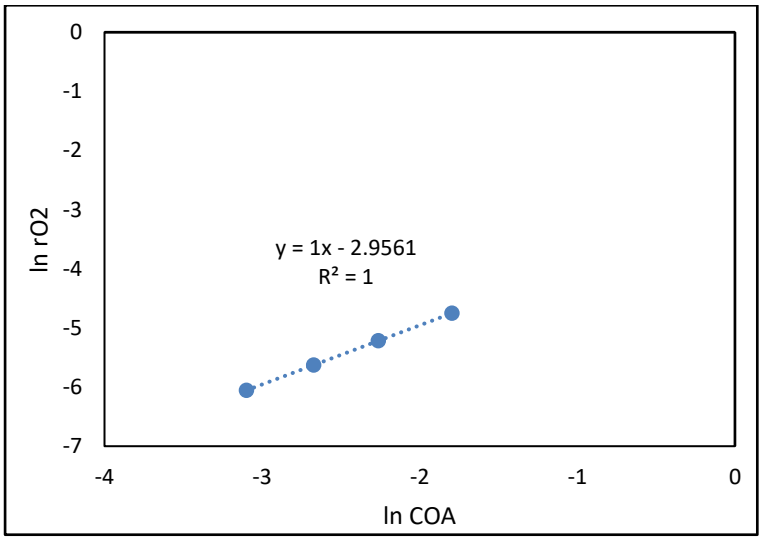


Fig.46. Power law model plot

4.4. Mechanism for oxidation of oxalic acid by using Ti/Al_2O_3 catalyst

The kinetics of the oxidation by using titanium catalyst had been subjected of some studies. In the oxidation with titanium oxide $[TiO_2]^-$ ion the rate of reaction decreased with increase in

$[H]^+$ and $[OH]^-$ ions whose pH range belongs 7-8. The oxidation was described with the following mechanism where $k_2 > k_1$.

$$TiO_2^- + H_2O \xleftrightarrow{Rapidly} TiOH^- + H^+ + O_2^- \text{.....(1)}$$

$$TiO_2^- + HC_2\,O_4^- \xrightarrow{k1} Ti^1 + CO_2$$

$$TiOH^- + HC_2O_4^- \xrightarrow{k2} Ti^1 + CO_2 \text{.....(2)}$$

The formation of between titanium ions and oxalate ions ($H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$) under different conditions. The complex compound was formed $Ti(HC_2O_4)$ and $Ti(C_2O_4)^{2-}$. This process containing a rate limiting step in the formation of a substituted complex. The rate of complex formation was influenced by concentration of oxide ion [O] and the rate decreases as [O] increases.

The empirical rate law governing equation of formation:

$$k = \frac{k_a[O^-] + k_b}{[O^-] + k_c} \text{.....(3)}$$

k represents the second-order rate constant, and the constants k_a, k_b, and k_c are hydrogen ions ($[H^+]$).

$H_2C_2O_4 \overset{k_{a1}}{\longleftrightarrow} HC_2O_4^- + H^+$ .....(4)

$HC_2O_4^- \overset{k_{a2}}{\longleftrightarrow} C_2O_4^- + H^+$ .....(5)

$TiO_2^- + H_2O \overset{k_h}{\leftrightarrow} TiO.H_2O + O^-$ .....(6)

$TiO.H_2O \overset{k_a}{\leftrightarrow} TiOOH^- + H^+$ .....(7)

$TiO_2^- + HC_2O_4^- \overset{k_1}{\leftrightarrow} TiO.C_2O_4^{2-} + O_2^- + H^+$ .....(8)

$TiO(OH)^- + HC_2O_4^- \overset{k_2}{\leftrightarrow} TiOC_2O_4^{2-} + H_2O$ .....(9)

$TiOC_2O_4^{2-} \overset{k}{\rightarrow} TiO_2^- + 2CO_2$ .....(10)

CHAPTER 5

CONCLUSIONS & FUTURE WORK

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CONCLUSIONS & FUTURE WORK

5.1. Conclusions

The alumina supported Titanium (Ti/γ-Al_2O_3) catalyst prepared in the above work are very effective in oxalic acid removal by catalytic wet air oxidation. The objective of this project was to find optimum operating conditions for the catalytic wet air oxidation of oxalic acid within the taken parameters. The reaction temperature being the first parameter was evaluated using experiments and 90°C was set to be the temperature where the maximum conversion of 88.29% was observed for 1.0 wt.% Ti/γ-Al_2O_3. After the temperature, mixing speed was changed at 500 rpm, the degradation of oxalic acid was found to be 87 %, sintering the metal catalyst. Finaly it can be stated that the optimum conditions for achieving the maximum degradation of oxalic acid using catalytic wet air oxidation. The alumina-supported titanium (Ti/γ-Al_2O_3) catalysts proved to be efficient in oxalic acid removal by CWAO. The prepared catalysts were very stable under the reaction conditions, and no significant leaching of the metal phase was observed. The different initial concentration parameter was used during experiments and optimum conversion was showed 88.29 % at 1500 ppm in 90 minutes. The synthesized catalyst is characterized by using the BET and TGA techniques. This technique is used of Ti/γ-Al_2O_3 for fresh catalyst activity check and surface area calculation, loss of weight percent with temperature varies. The BET surface area was observed 81.89 m^2/g. The percentage of weight loss resulted was 1.80% in the temperature between 50^0C to 120^0C and at the temperature between 120^0C to 750^0C, the weight loss is showing 2.08 % that indicates the thermal decomposition. Also, the power law model graph shows that the reaction order is first order reaction for both oxygen and oxalic acid.

5.2. Future work

The complete characterization of catalysts and supports is the main objective of this work, which consists of investigations carried out at atmospheric pressure with higher pressure reactions expected in the future. The synthesis of tri- and bi-metallic catalysts, testing alternative metals as precursors for catalyst synthesis, and using different substances as catalytic supports are important research fields. The impact of feed weight hourly space velocity (WHSV) on oxalic acid conversion, the effect of calcination temperature on oxalic acid degradation, and the effect of oxygen partial pressure on oxalic acid conversion are also examined in this study.

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APPENDIX A

A.1. Calculation of conversion or degradation for catalytic wet air oxidation of oxalic acid:

Ti/γ-Al_2O_3 catalyst taken for oxidation-1 gm, Dosage of catalyst-1.0 wt.%, Oxalic acid (Hydrated salt) solution taken=1 gm.

Data table 1: Conversion table of 1 wt.% Ti/Al_2O_3

Temperature, ^{0}C	**Concentration**	RPM	Air flowrate, L/min	Sample ml	Conversion %
Before 60	18.8	100	1	5	0
60	17.2	100	1	5	8.51
	15.5	100	1	5	17.55
	14.3	100	1	5	23.94
70	13.8	200	1	5	26.59
	12.7	200	1	5	32.45
	11.9	200	1	5	36.70
80	10.8	300	1	5	42.55
	9.6	300	1	5	48.94
	8.4	300	1	5	55.32
90	6.7	400	1	5	64.36
	4.1	400	1	5	78.19
	2.2	400	1	5	88.29

A.2. Data of Arrhenius plot

Table 2: Data of ln k vs 1/T for Arrhenius plot (Temperature range: 60-90^{0}C)

ln k	$\frac{1}{T}(K^{-1})$
-4.5854	0.00300
-4.8308	0.00295
-4.2482	0.00283
-2.2808	0.00275

A.3. Data of power law model

Table 3: Data of ln r_{O2} vs ln C_{OA} for power law model plot

ln r_{O2}	ln C_{OA}
-6.0572	-3.1011
-5.6298	-2.6736
-5.2195	-2.2634
-4.7519	-1.7958

A.4. BET data

Table 4: Data of relative pressure vs 1 / [W((Po/P) - 1)] for BET surface area calculation

Relative Pressure	1 / [W((Po/P) - 1)]
0.040593	2.1732
0.04998	2.6216
0.100892	4.9719
0.152094	7.2833
0.202132	9.5618
0.251979	11.91
0.303104	14.293
0.319036	15.088
0.993161	1156.2
0.900044	77.172
0.800693	39.355
0.700878	34.253
0.600079	30.448
0.501046	24.839
0.400506	19.257
0.297499	13.912
0.198823	9.3255
0.097714	4.8198

APPENDIX B

B.1. Sample Calculation of different weight percentages:

TiO_2 molecular weight (M) =79.87 gm/mol.

Molecular weight of Ti = 47.88 gm/mol

For 0.5 wt.% TiO_2 =79.87 gm/mol

1 gm of Ti = [(79.87/47.88) ×0.5] gm TiO_2 = 0.834 gm TiO_2

Similarly, For 1wt.% of Ti = [(79.87/47.88) ×1] gm TiO_2 =1.67 gm TiO_2

For 1.5 wt.% of Ti = [(79.87/47.88) × 1.5] gm TiO_2 = 2.502 gm TiO_2

For 2.0 wt.% of Ti = [(79.87/47.88) × 2.0] gm TiO_2 = 3.336 gm TiO_2

For 2.5 wt.% of Ti = [(79.87/47.88) × 2.5] gm TiO_2 = 4.170 gm TiO_2

From Table 1 Appendix A

For base,

$V_1 \times S_1 = V_2 \times S_2$

$5 \times S_1 = 18.8 \times 0.1$

$S_1 = (18.8 \times 0.1)/5 = 0.376$

Molarity = normality/ basicity = 0.376/2 = 0.188 (C_{A0})

At 60^0C (1), $V_1 \times S_1 = V_2 \times S_2$

$S_1 = (17.2 \times 0.1)/5 = 0.344$

Molarity = 0.344/2 =0.172 (C_A)

% Conversion = [(0.188-0.172)/0.188] ×100 % =8.51%

(2), $S_1 = (15.5 \times 0.1)/5 = 0.31$

Molarity = 0.31/2 =0.155 (C_A)

% Conversion = [(0.188-0.155)/0.188] ×100% =17.55%

(3), $S_1 = (14.3 \times 0.1)/5 = 0.286$

Molarity = 0.286/2 =0.143(C_A)

% Conversion = [(0.188-0.143)/0.188] ×100% =23.94%

At 70^0C (1),

S_1 = (13.8×0.1)/5 = 0.276

Molarity = 0.276/2 =0.138 (C_A)

% Conversion = [(0.188-0.138)/0.188] ×100% = 26.59%

(2), S_1 = (12.7×0.1)/5 =0.254

Molarity = 0.254/2 = 0.127 (C_A)

% Conversion = [(0.188-0.127)/0.188] × 100% = 32.45%

(3), S_1 = (11.9× 0.1)/5 =0.238

Molarity = 0.238/2 =0.119 (C_A)

% Conversion = [(0.188-0.119)/0.188] ×100% =36.70%

At 80^0C (1),

S_1 = (10.8× 0.1)/5 =0.216

Molarity = 0.216/2 =0.108 (C_A)

% Conversion = [(0.188-0.108)/0.188] ×100% =42.55%

(2), S_1 = (9.6×0.1)/5 =0.192

Molarity = 0.192/2 =0.096 (C_A)

% Conversion = [(0.188-0.096)/0.188] ×100% =48.94%

(3), S_1 = (8.4×0.1)/5 =0.168

Molarity = 0.168/2 =0.084 (C_A)

% Conversion = [(0.188-0.084)/0.188] ×100% =55.32%

At 90^0C (1),

S_1 = (6.7×0.1)/5=0.134

Molarity =0.134/2 =0.067 (C_A)

% Conversion = [(0.188-0.067)/0.188] ×100% = 64.36%

(2), S_1 = (4.1×0.1)/5 = 0.082

Molarity = 0.082/2= 0.041(C_A)

% Conversion = [(0.188-0.041)/0.188] ×100% =78.19%

(3), S_1 = (2.2×0.1)/5 = 0.044

Molarity = 0.044/2 =0.022 (C_A)

% Conversion = [(0.188-0.022)/0.188] ×100% =88.29%

B.2. Calculation for activation energy from Arrhenius plot [Appendix A.2.]

$r_i = -\frac{dC_A}{dt}$ (1st order assumption); $C_A = C_{A_0}.(1 - X_i)$

where, X_i = conversion of oxalic acid (%)

C_{A_0} = initial concentration of oxalic acid (considering 1L/min flow rate volume)

= 0.188

Now, to determine activation energy (E_a), we go for the expression,

$\ln k = \ln A - \frac{E_a}{RT}$

Determination of k_1: $r_i = \left(\frac{0.029}{20}\right) = 0.00145$ and X_i =0.2394

We know that, $r_i = k_1 \times C_{AO} (1-X_i)$

Or, $0.00145 = k_1 \times 0.188 (1- 0.2394)$

Or, $k_1 = 0.0102\ min^{-1}$

Determination of k_2: $r_2 = \left(\frac{0.019}{20}\right) = 0.00095$ and X_i =0.367

Or, $-0.00095 = k_2 \times 0.188 (1-0.367)$

Or, $k_2 = 0.00798\ min^{-1}$

Determination of k_3: $r_3 = \left(\frac{0.024}{20}\right) = 0.0012$ and X_i =0.5532

Or, $0.0012 = k_3 \times 0.188 (1- 0.5532)$

Or, $k_3 = 0.01429\ min^{-1}$

Determination of k_4: $r_4 = \left(\frac{0.045}{20}\right) = 0.00225$ and $X_i = 0.8829$

Or, $0.00225 = k_4 \times 0.188\ (1-0.8829)$

Or, $k_4 = 0.10220\ min^{-1}$

According to Arrhenius equation,

Slope (m)= -8781.6

$\ln k = (-\frac{E_a}{RT}) + \ln A$

$m = -\frac{E_a}{R}$,R= 8.314 J/mol

Or, $-8781.6 = -E_A/8.314$

Or, $E_A = (8.314 \times 8781.6) = 73010.22$ J/K-mol =73.01 KJ/mol.

B.3. Calculation of order for oxgen and oxalic acid using power law [Appendix A.3.]

Considering, T = 90^0C, k = $-0.0501 min^{-1}$ (optimum value is taken, gives the maximum conversion of oxalic acid) and, ln k = 2.9937

To determine r_{OA}, the expression is

$$r = \frac{O_2\ flowrate \times O_2\ density \times Conversion}{O_2\ molar\ weight \times Mass\ of\ catalyst \times \mathrm{Im}\ pregnated\ metal\ mass\ percentage}$$

The general formula of power law model can be expressed as –

$r = k.\ [OA]^m.\ [O_2]^n$

Where r is rate of reaction, k is the rate constant, m is the order of oxalic acid and n is the order of oxygen.

1st data point for r_{O2}:

$(r_{O2})_1 = \frac{0.219 \times 1.429 \times 0.2394}{32 \times 1 \times 1.0}$ = 0.002341mol/g-min

and, $\ln r_{O_2} = n_1 \ln C_{OA} + \ln k$

Or, -6.0572 = n_1 ×-3.1011 -4.5854

Or, n_1 = 0.48

2nd data point for r_{O2}:

$(r_{O2})_2 = \frac{0.219 \times 1.429 \times 0.3670}{32 \times 1 \times 1.0}$ =0.003589 mol/g-min

$\ln (r_{O2})_2 = n_2 \ln C_{OA} + \ln k$

-5.6298= n_2 ×-2.6736 -4.8308

n_2 =0.29

3rd data point for r_{O2}:

$(r_{O2})_3 = \frac{0.219 \times 1.429 \times 0.5532}{32 \times 1 \times 1.0}$ = 0.005410 mol/g-min

$\ln (r_{O2})_2 = n_3 \ln C_{OA} + \ln k$

-5.2195 = n_3 × -2.2634 -4.2482

n_3 =0.43

4th data point for r_{O2}:

$(r_{O2})_4 = \frac{0.219 \times 1.429 \times 0.8829}{32 \times 1 \times 1.0}$ = 0.008635 mol/g-min

$\ln (r_{O2})_4 = n_3 \ln C_{OA} + \ln k$

$-4.7519 = n_3 \times -1.7958 - 2.2808$

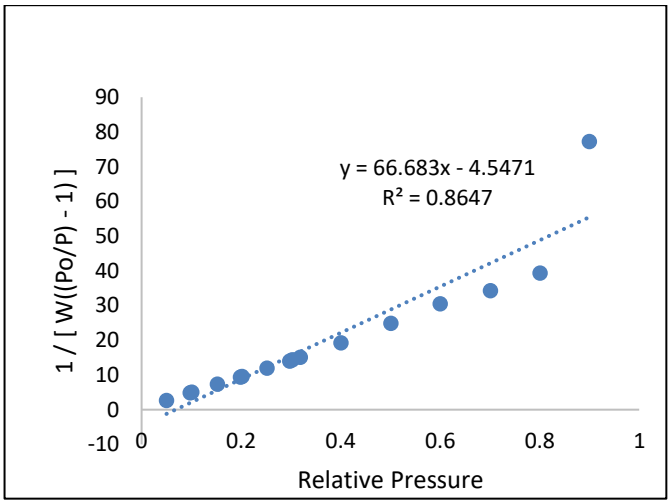
$n_3 = 1.41$

B.4. Surface area calculation using BET equation [Appendix A.4.]

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m.c} + \frac{c-1}{V_m.c}\frac{p}{p_0}$$

represents the form of,

Y = mx + C. where, $Y = \frac{p}{V(p_0 - p)}$, $x = \frac{p}{p_0}$, $m = \frac{c-1}{V_m.c}$ and, $C = \frac{1}{V_m.c}$



From the above linear graph,

Slope (m) = 66.683, and intercept (C) = -4.5471

So,

$$V_m = \frac{1}{(\text{Slope}+\text{Intercept})} = \frac{1}{(66.683-4.5471)} = 0.0160938 \text{ cm}^3$$

and,

$$S_T = \frac{V_m .N .S}{v} \text{ m}^2$$

or, $S_T = \frac{0.0160938 \times 6.023\times10^{23} \times 0.162 \times10^{-18}}{22.4}$ = 70.10329955 m^2

or, $S_{BET} = \frac{70.10329955}{0.856}$= 81.89 m^2/g

where, $S_{BET} = \frac{S_T}{a}$

V_m = monolayer volume in cm^3

N = Avogadro's No. (6.023×10^{23})

S = Cross-sectional area of a N_2 molecule (0.162 nm^2)

v = molar volume of N_2 (22.4 L)

V = amount of liquid N_2 adsorbed in cm^3/g of catalyst

p = vapor pressure of N_2 on the surface of material

p_0 = Pressure at STP 1 atm or 760 mmHg

c = BET constant

S_T = total surface area (m^2)

S_{BET} = BET surface area of the material (m^2/g)

B.5. TGA weight loss calculation

1st stage weight loss calculation

Initial weight from Y-axis of graphical representation =99.8 %

Final weight = 98 %

Change of weight % = (99.8-98) =1.8 %

2nd stage weight loss calculation

Initial weight =98 %

Final weight = 96 %

Change of weight % = (98-96) % = 2%

3rd stage weight loss calculation

Change of weight % = 0 %

APPENDIX C

Images used for instruments and chemicals

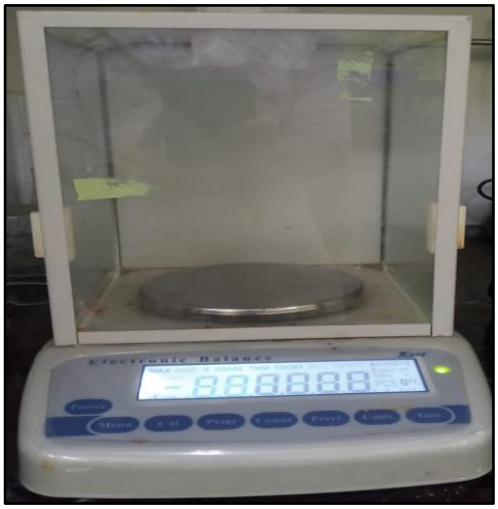


Fig.1. Weight machine for measuring weight of metal and support

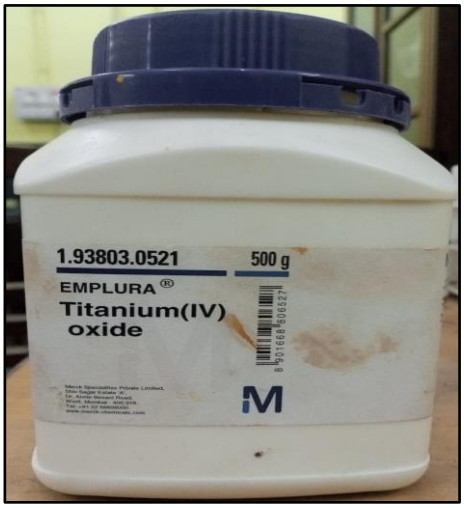


Fig.2. Titanium oxide salt

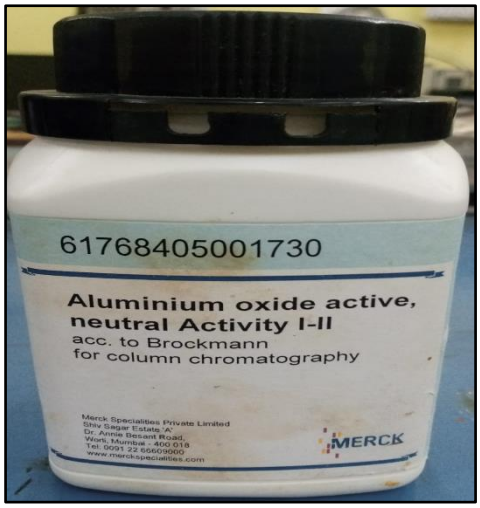


Fig.3. Al_2O_3 support salt



Fig.4. Magnetic hot plate



Fig.5. Hot air oven using for water moisture removed from prepared solution



Fig.6. Calcination chamber using for extra moisture removal, volatile compound extract and oxide form of metal precursor





Fig.7. Three neck bottom glass reactor for catalytic wet air oxidation of oxalic acid

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