

Photocatalytic Degradation of Benzene for Polishing
of
Refinery Wastewater



By

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NUST-2012-61058-M-SCEE-65212-F

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

2014

It is certified that the contents and forms of the thesis entitled

Photocatalytic Degradation of Benzene for Polishing

of

Refinery Wastewater

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DEDICATED TO.....

***MY BELOVED PARENTS & BROTHERS TARIQ AND SAQIB
WITHOUT WHOSE SUPPORT ALL THIS WOULD NOT HAVE BEEN
POSSIBLE***

ACKNOWLEDGEMENTS

This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in planning, executing and finally, presentation, of this study.

First and foremost, I would like to express my sincere gratitude to my thesis supervisor Prof. **Dr. Ishtiaq A. Qazi** (IESE) for his continuous support throughout my stay at IESE, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me through my research and writing of this thesis. I could not have imagined having a better advisor and mentor for my MS studies.

Many thanks also go to **Dr. Zahiruddin Khan** (IESE) and **Dr. Imran Hashmi** (IESE) for their guidance and support.

I am also very thankful to Prof. **Dr. Thomas C. Voice** (MSU, USA) for his unfailing moral support as my external advisor.

I am grateful to the staff of the Wastewater Lab, especially Mr. **Akif Zeb**, for the technical assistance. Last but not least, I would like to express my gratitude to all my friends, for their support during this arduous academic odyssey.

“Abid Hameed”

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LIST OF ABBREVIATIONS

Ag-TiO ₂	Silver doped Titanium Dioxide
e ⁻	Electron
EDS	Energy Dispersive Spectroscopy
eV	Electron Volt
FWHM	Full width of a diffraction line at half of maximum intensity
GPR	General Purpose Reagent
h ⁺	Hole
[•] O ₂	Oxygen Radical
[•] OH	Hydroxyl Radical
OH ⁻	Hydroxyl Ion
ROS	Reactive Oxygen Species
SEM	Scanning Electron Microscopy
TiO ₂	Titanium Dioxide
UV	Ultra Violet
XRD	X - Ray Diffraction
λ	Wavelength
WHO	World Health Organization
EPA	Environmental Protection Agency

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ABSTRACT

Aromatic organic compounds such as benzene, toluene, ethyl-benzene, and xylene (BTEX) are essential ingredient of refinery wastewater. Their presence in wastewater is a major environmental concern because these compounds are flammable, toxic, carcinogenic, and mutagenic. In this study, benzene was selected as a representative pollutant due to its intensive health impacts and more solubility in water among other BTEX compounds, for investigation of a sequential process, whereby, post-GAC adsorption effluent is exposed to photocatalysis, using titania, for polishing. The concentration of benzene was reduced from 1000 ppm to below 0.140 ppm, which is the permissible limit for wastewater. Photocatalytic degradation of benzene may follow a close chain (phenolic) or open chain (muconaldehyde) pathway which has been under debatable for over three decades. In order to clarify this confusion, the photocatalytic degradation pathway of benzene has been carefully investigated. Based on the results of High Performance Liquid Chromatography (HPLC), it is confirmed that benzene follows both closed chain (phenolic) and open chain routes (muconaldehyde).

INTRODUCTION

1.1 Background

“BTEX” represents a group of volatile organic compounds (VOCs) comprising of Benzene, Toluene, Ethyl-benzene and Xylenes, also called monoaromatic hydrocarbons, that are an important class of environmental pollutants because of their recognized toxicity to different organisms (Anneser *et al.*, 2008; Jo *et al.*, 2008). The BTEX contamination occurs as a result of incomplete combustion of fossil fuels, leakage from oil pipelines and underground storage tank, oil spills, petroleum refining, and other industrial processing (Nadarajah *et al.*, 2002).

1.2 Oil Refinery Wastewater

Petroleum is formed from organic matter such as plants, animals and diatoms that were buried deep below the Earth’s surface. Organic matter, covered by layers of sand and silt, over millions of years, due to heat and pressure, was converted into the liquid known as crude oil (Carlson *et al.*, 2011). This crude oil is a mixture of different hydrocarbons and other constituents and has to go through the process of desalting, distillation and thermal cracking collectively known as “refining” to produce useful products such as Gasoline, Kerosene and Gas Oil. With the process of petroleum refining utilize large quantities of water, up to 1.6 times the oil processed (Ishak *et al.*, 2012), resulting into a large volume of wastewater. The discharged Petroleum Refining Wastewater (PRW) consists of many hazardous and toxic compounds including Benzene, Toluene, Ethyl-benzene, Xylenes (BTEX), Phenols and Heavy Metals (Nadarajah *et al.*, 2002; ATSDR, 2004; Anneser *et al.*, 2008; Jo *et al.*, 2008). Eventually, when this wastewater becomes a part of a water body it

creates many environmental and human health problems. An effective treatment of the Petroleum Refining Wastewater (PRW) is, therefore, required before its disposal to a water body. Composition of a typical petroleum refinery wastewater is given in Table 1.1.

Parameters mg/L	Dold <i>et al.</i> , 1989	Ma <i>et al.</i> , 2009	Khaing <i>et al.</i> , 2010	PAK. NEQS mg/L
BOD	150 - 350	150 - 350	-	80
COD	300 - 800	300 - 600	330 - 556	150
Phenol	20 - 200	-	-	0.1
Oil	3000	50	40 - 91	10
TSS	100	150	130 - 250	150
BTEX	1 - 100	-	20-200	-
Heavy Metal	0.1 - 100	-	-	-
Chrome	0.2 - 10	-	-	-
Ammonia	-	10 - 30	4.1 - 33.4	-
pH	-	7-9	7.5 - 10.3	6 - 10

Table: 1.1 Characterization of Petroleum Refinery Wastewater (PRW)

In a typical refinery wastewater the benzene level is 1 to 200 mg/L (Dold *et al.*, 1989; Worrall *et al.*, 1998; Al- Zarooni and Elshorbagy, 2006; Ishak *et al.*, 2012).

1.3 Treatment Technologies

Over the past several decades, many techniques have been investigated for the removal of VOCs from wastewater. Such methodologies include Volatilization, Bioaccumulation, Biodegradation, Adsorption on Activated Carbon, Air and Gas Stripping, Oxidation, and Photocatalytic Degradation.

For this study Benzene was selected as a representative pollutant for adsorption and photocatalytic degradation because it is carcinogenic and mutagenic to humans and other

animals (Das *et al.*, 2004; WHO 2008; Jiang *et al.*, 2011) and has more solubility as compared to other BTEX compounds.

Exposure to even 1 ppm of benzene has been reported to reduce blood cell count leading to hematotoxicity in factory workers (Xie *et al.*, 2011).

1.4 Regulations for Benzene

In the US Environmental Protection Agency (EPA) National Priority Pollutants list, Benzene appears at number '4' (Hazdat, 2006). Stringent regulations have, therefore, been imposed on the concentration levels of the compound in drinking water and wastewater discharge. Benzene is designated as the priority chemical that needs to be reduced to a very low level. The guidelines and regulations for benzene in water are summarized in Table 1.2.

Agency	Description	Guidelines
Environmental Protection Agency (EPA)	Hazardous substance Section 311 (b) (2)(a) of Clean Water Act	
	Drinking Water Standard	
	Maximum contaminant level goal (MCLG)	Zero
	Maximum contaminant level (MCL)	0.005 mg/L
	Wastewater Stream Standard	
	Universal treatment standard (UTS)	0.14 mg/L
	Non-Wastewater Stream Standard	
	Universal treatment standard (UTS)	10.0 mg/L
Health Canada	Maximum acceptable concentration (MAC)	0.005 mg/L
WHO	Drinking Water	0.01 mg/L

Table 1.2 Regulations and Guidelines Applicable to Benzene

According to the U S EPA, 2012 guideline, the maximum contaminant level goal (MCLG) of benzene in water should be zero but the maximum contaminant level (MLC) in drinking water should not be more than 0.005 mg/L (Nollet, 2007), whereas it is 0.14 ppm and 10 ppm for the wastewater stream Standard and Non-wastewater stream Standard respectively (EPA, 1994).

1.5 Proposed Treatment Method

In order to meet the regulatory guidelines, therefore, effective treatment of such wastewater is required which is generally done by a physical processes (adsorption), or chemical processes (advanced oxidation) or biological processes (anaerobically) or a combination thereof. Conventional treatment methods for petroleum refinery wastewater (PRW) for removing BTEX face some limitations at very low concentrations (Mazzeo *et al.*, 2010; Daifullah and Girgis, 2003) and their traces are left behind, demanding further polishing of the treated wastewater.

In this study, therefore, an investigation of a sequential process, whereby, post Granular Activated Carbon (GAC) adsorption effluent is exposed to photocatalysis, using titania, has been carried out. The aim here is to establish a process, where the bulk pollutant load is removed by adsorption, the resultant low concentration water then being polished by photocatalysis.

1.6 Objectives

The primary objectives of this study were to:

- Establish a process, whereby bulk pollutant load is removed by adsorption on Granular Activated Carbon (GAC), the resultant low concentration water the being polished by Titania photocatalysis.
- Confirming the intermediate products and pathway for the benzene photocatalysis.

REVIEW OF LITERATURE

Volatile organic compounds (VOCs) are among the most commonly found contaminants in groundwater and wastewater. These contaminants are released into the environment during their production, distribution, storage, handling and use, and can enter both surface water and groundwater.

The term 'Volatile Organic Compound' refers to the characteristic evaporative abilities of these compounds (Letterman, 1999). Volatile organic compounds are organic compounds which have a boiling point ≤ 100 °C and/or a vapor pressure > 1 mm Hg at 25 °C (Golfinopoulos *et al.*, 2001).

Three broad groups of VOCs have been found in wastewater. One group includes compounds found in petroleum products, especially aromatics released from leaking fuel oil and underground gasoline tanks. Another group is the halogenated VOCs, used as solvents and degreasers. The third group includes some of the chlorinated organic disinfection by-products, particularly trihalomethanes (Letterman, 1999).

2.1 Benzene

Benzene is the simplest aromatic compound with C_6H_6 molecular formula and contains three pi bonds, arranged in alternate manner, in a hexagonal ring.

Benzene is produced from both natural and anthropogenic processes (Lin *et al.*, 2010; Adachi *et al.*, 2008). It is also part of crude oil (4 g/L), gasoline, and cigarette smoke (Leusch and Bartkow, 2010; ATSDR, 2004). It is used in the production of rubbers, lubricants, dyes, detergents, drugs, pesticides and other chemicals which are used to make plastics, resins, nylon and other synthetic fibers (ATSDR, 2004; Mohamed and Ouki, 2011).

2.2 Physical and Chemical Properties of Benzene

Benzene is a colorless liquid with a characteristic sweet odor and is both volatile and flammable. Benzene solubility in water is 1785.5 mg/L at 25 °C (Gitipour *et al.*, 1997; Mohamed and Ouki, 2011). Some major physical and chemical properties of benzene are given in Table 2.1.


Property	Info/Value
Structure	
Molecular weight	78.11 g/mol
CAS. number	71-43-2
Color	Clear, colorless
Physical state	Liquid
Melting point	5.5 °C
Boiling point	80.1 °C
Solubility in water	1.785 g/L (25 °C)
Density/specific gravity	0.8787 g/mL (15 °C)
Henry's law constant	5.5 X 10 ⁻³ atm-m ³ /mol

Table 2.1: Physical and Chemical Properties of Benzene

2.3 Industrial Application of Benzene

Historically, benzene had been used widely as a solvent (Hindarso *et al.*, 2001) and as a synthetic intermediate for several chemicals such as paint strippers, carburetor cleaners, denatured alcohol, rubber cement, glue, liquid soap and polish for furniture.

Because of its adverse health effects the use of benzene has decreased significantly, in recent years, with many of the above mentioned formulations being replaced by other chemicals.

Fig. 2.1 illustrates the major commodity and chemicals that are generated from benzene (Adachi *et al.*, 2008; Mohamed and Ouki, 2011).

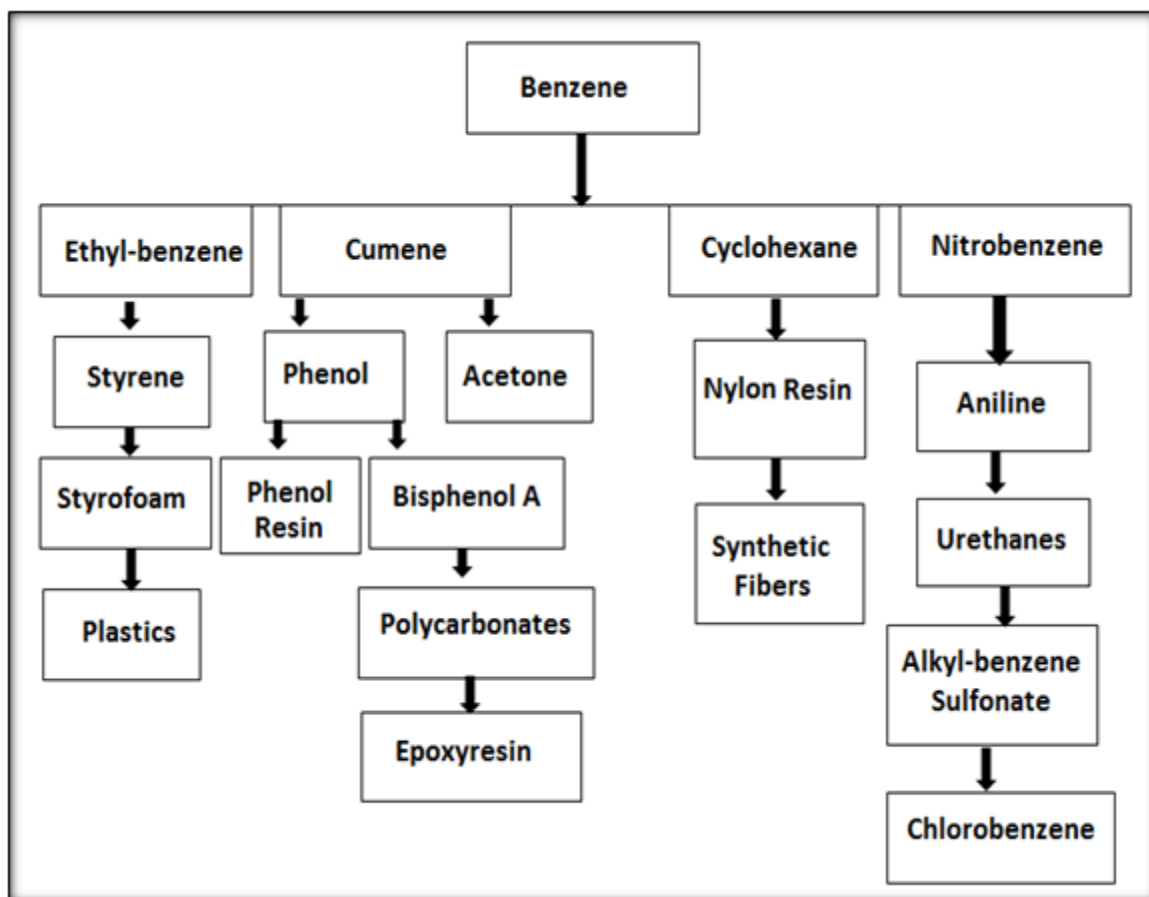


Fig. 2.1: Major Chemicals and Polymers Derived from Benzene

Styrene, produced from ethyl benzene, is used to make plastics and rubber. Generally, phenol and acetone are produced from cumene derived from benzene. Phenols are widely used in making of pharmaceuticals, nylon and rubber production. Mostly acetone is used as a solvent. The cyclohexane generated from benzene is used to produce nylon. Nitro-benzene is used in the production of aniline, urethanes, linear alkyl-benzene sulfonates, chlorobenzene, and maleic anhydride. Benzene is also used for the manufacturing of rubbers, lubricants, dyes, detergents, drugs and pesticides.

2.4 Sources of Benzene in the Environment

Benzene is a naturally occurring compound found in crude oil, forest fires, and gas emissions from volcanoes and can be found in sea water (0.8 ppb) in the vicinity of petroleum deposits and natural gas (ATSDR 2004). Anthropogenic benzene emission can result from burning coal and oil, auto exhaust, chemical production, destructive distillation of coal and consumer products such as paints and lacquers, thinners, rubber products, adhesives, inks, cosmetics, and pharmaceutical products, are some major sources of benzene release to the environment during their production, distribution, storage, and handling (Gallego *et al.*, 2001; Daifullah and Girgis, 2003). Benzene is also released from hazardous waste sites which may have been contaminated by the chemical.

2.5 Benzene as a Pollutant

BTEX are very important materials for the chemical industry especially benzene which is used as a solvent in a number of processes. (Wibowo *et al.*, 2006). It is classified as a flammable, toxic and carcinogenic material (Das *et al.*, 2004; WHO 2008; Jiang *et al.*, 2011,) so its presence in the environment, usually in air and wastewater, even at low concentrations, is a major problem (Xie *et al.*, 2011). Stringent regulations, therefore, have been imposed on the concentration levels of these compounds in wastewater discharge.

2.6 Benzene Exposure and Health Effects

Benzene is highly toxic, carcinogenic and mutagenic to humans and other animals (Das *et al.*, 2004; WHO 2008; Jiang *et al.*, 2011). Exposure to even 1 ppm of benzene can reduce blood cell count leading to hematotoxicity in factory workers (Xie *et al.*, 2011). The main sources of benzene exposure are industrial emissions, automobile stations, tobacco smoke, wastewater and vapors from products that comprise benzene like glues, paints and

furniture polish.

Brief exposure (five to ten minutes) at very high levels i.e. 10,000 – 20,000 ppm, of benzene in air can result in death. Lower level exposure i.e. 700 – 3,000 ppm, can cause headaches, dizziness, joint pain, drowsiness rapid heartbeat, confusion, tremors, and unconsciousness (Daifullah *et al.*, 2003; ATSDR 2004). Other than inhalation, people can be exposed to benzene through food, beverages, or drinking water. The major chronic effects of benzene exposure occur through the blood. It causes harmful effects on the bone-marrow leading to a decrease in red blood cells and finally resulting in anemia. It can also cause excessive bleeding and depress the immune system, increasing the chance of infection (Lan *et al.*, 2004).

Exposure to benzene may also be harmful to the reproductive organs, therefore, women who had inhaled high levels of benzene for many months had irregular menstrual periods and a decrease in the size of their ovaries. Exposure effects on the developing fetus in pregnant women, or fertility in men, however, are not confirmed (ATSDR 2007).

2.7 Conventional Wastewater Treatment Methods

In general, wastewater treatment plants rely on conventional treatment methods such as physical processes (adsorption), or chemical processes (advanced oxidation) or biological processes (aerobic/ anaerobic) or a combination thereof. The common treatment methods reported for the reduction of VOCs in water are adsorption on granular activated carbon (GAC), air stripping, photo and chemical oxidation, Ozonation, Reverse Osmosis, and Biological treatment (bioremediation) (Health Canada, 2009). Studies, however, indicate that these methods are ineffective in reducing benzene concentration to the acceptable limit (Love *et al.*, 1983; Daifullah and Girgis 2003; Mazzeo *et al.*, 2010).

2.7.1 Adsorption Method

For many decades adsorption has been used for removing volatile organic

contaminants from wastewater employing a variety of adsorbents (Wang *et al.*, 2004). Of these, activated carbon, generally in the granular form – hence, Granular Activated Carbon (GAC) – has emerged as the most important commercial adsorbent. The adsorption efficiency depends on the presence of other contaminants in the waste stream, empty bed contact time (EBCT), flow rate, filter runtime, adsorptive competition, influent concentrations, preloading of natural dissolved organic matter, humic interactions, microbial growth, pH, physical and chemical properties of the chemical in question and the type of carbon used (Speth *et al.*, 1990).

GAC is widely used to reduce VOC concentration in water and a number of studies have been conducted on the removal of BTEX compounds using activated carbon (Benkhedda *et al.*, 2000; Chiang *et al.*, 2001; Hindarso *et al.*, 2001; Huang *et al.*, 2003; Das *et al.*, 2004; Wibowo *et al.*, 2007; Bunyakan *et al.*, 2008; Negrea *et al.*, 2008; Bouhamra *et al.*, 2009; Zhang *et al.*, 2009; Dobre *et al.*, 2010). GAC is a carbonaceous material with a large surface area and high porosity.

Studies by Koffskey and Brodtmann have demonstrated that a GAC filter having a bed volume of 23.8 m³, with a flow rate of 1.5 ML/day and an empty bed contact time(EBCT) of 23.7 minutes was successful in reducing the influent benzene concentration of 10 µg/L to the finish water concentration of 0.1 µg/L. During the 180 days study period, no breakthrough of benzene was observed (Health Canada, 2009). Another study reported by the American Water Works Association (AWWA, Report No. 0033986) demonstrated that three parallel GAC adsorbing columns, with a flow rate of 5 ML/day, empty bed contact time (EBCT) of 21 minutes, bed life of 12 months were capable in achieving 99% removal efficiency (reduction of benzene concentrations from 20 to 0.2 µg/L). Similarly Yue *et al.*, 2001 demonstrated that fiberglass supported activated carbon filters have a higher BTEX adsorption capacity than conventional the activated carbon process. Synthetic carbonaceous resins also have shown better removal efficiency than activated

carbon (Shih *et al.*, 2005).

Negrea *et al.*, (2008) reported the removal from wastewater of benzene, toluene and o-xylene, by adsorption on active charcoal using a column containing 4 g of granular activated charcoal. The efficiency of the adsorption process was studied for different water flow rates, and it was found that BTEX removal degree decreases as the waste water flow rate increases. Benzene, toluene and o-xylene, dissolved in the aqueous solutions, were analyzed by UV-VIS spectrophotometry.

A combination of photocatalysis, using platinum and titanium dioxide catalyst, and adsorption processes have shown higher removal efficiency and prolonged adsorbent bed life (Crittenden *et al.*, 1997).

One of the major drawbacks of adsorption methods is that they do not actually treat benzene but simply shift it from the aqueous phase to the solid phase. The benzene remains unaltered in the process but gets more concentrated in the solid. The adsorption process depends on several factors, which include the nature of the adsorbent, adsorbate and adsorption conditions i.e. time and pH (Salame and Bandosz, 2003; Ania *et al.*, 2002; Koh and Dixon, 2001).

2.8 Photocatalysis

2.8.1 Introduction

The term photocatalysis consists of the combination of photochemistry and catalysis. Photocatalysis can be defined as a process that accelerates the rate of a chemical reaction in the presence of a substance (photocatalyst) that absorbs UV, visible or infrared light (Braslavsky, 2007; Al-Bastaki, 2003).

The interest in semiconductor Photocatalytic reactions was initiated, almost three decades ago, when researchers suggested it as a potential way to promote the dissociation of water to produce molecular hydrogen and molecular oxygen using solar illumination.

Subsequently, additional applications were also discovered and these applications could be classified into following areas as shown in Fig. 2.2.

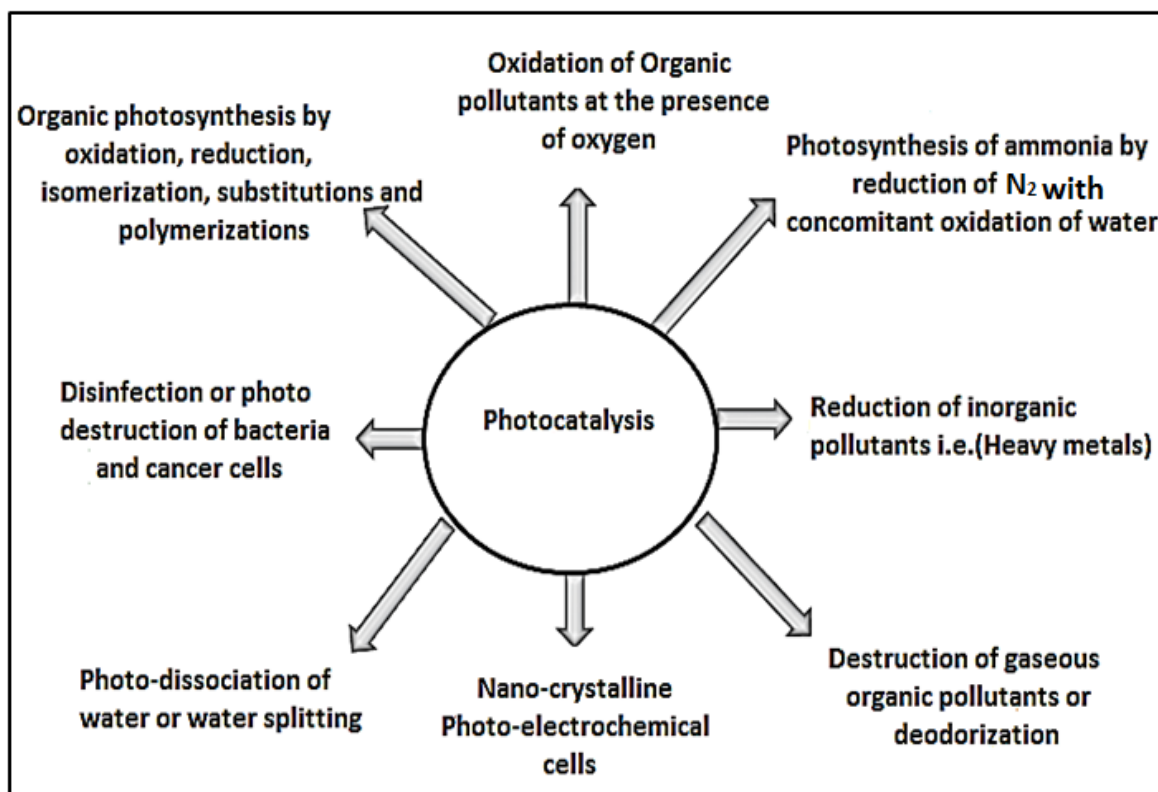


Fig. 2.2: Applications of Photocatalysis

The most significant applications of photocatalysis is photooxidation of organic pollutants in air and water, attempted by many researchers (Zuo *et al.*, 2006; Braslavsky *et al.*, 2007; Zhang *et al.*, 2011; Laokiat *et al.*, 2012; Lin *et al.*, 2013; Younas *et al.*, 2014;).

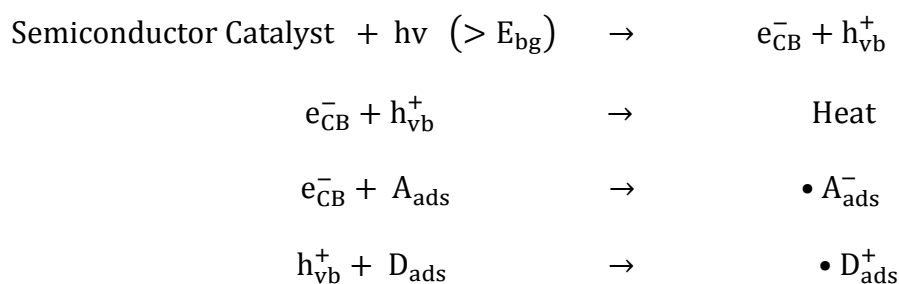
Today, photocatalysis exhibits a considerable potential for wastewater treatment as an Advanced Oxidation Processes (AOPs) technology. All AOP technologies are based on the generation of highly reactive free radicals like hydroxyl radical, to act as an initiator that converts the pollutants into harmless compounds (Tan *et al.*, 2011). Primarily, there are four major methods of AOPs: homogeneous oxidation, homogeneous photolysis, heterogeneous photocatalysis, and radiolysis. Among these, photocatalysis is the most discussed method in the destruction of harmful pollutants.

2.8.2 Mechanisms of Photocatalysis

The process of photocatalysis comprises of some basic chemical and physical steps, initiated by light, that have been discussed, in detail, by many researchers (Konstantinou and Albanis, 2003; Adesina, 2004; Tan *et al.*, 2011). When the energy delivered by a photon equals, or exceeds, the band-gap of the semiconductor photocatalyst, a photo excited electron shifts from the filled valence band (VB) into the empty conduction band (CB) resulting in a hole in the VB. As a result, an electron-hole pair is generated. The energized electron and hole can either recombine and dissipate the energy, as heat, or dissociate other molecular species which then become available for the REDOX reactions

Mostly metals have a widely extended conduction band whereas insulators have large separation between the valence and conduction band.

When a semiconductor photocatalyst is irradiated with photons, whose energy is equal to or greater than the catalyst's band gap energy E_{bg} an electron is promoted from the valence band to the conduction band producing an electron hole pair. In the absence of either electron or hole scavengers, the excited conduction band electron (e_{CB}^-) will recombine with the valence band hole (h_{vb}^+) and dissipate the input energy as heat. If a suitable scavenger is available to trap the electron or hole, recombination is prevented and subsequent redox reaction may occur. Such scavengers, namely donor (D_{ads}) and acceptor (A_{ads}) molecules react by adsorption onto catalyst surface, to facilitate the electron transfer, wherever the reaction is thermodynamically feasible. Figure 2.3 is a pictorial representation of the process.



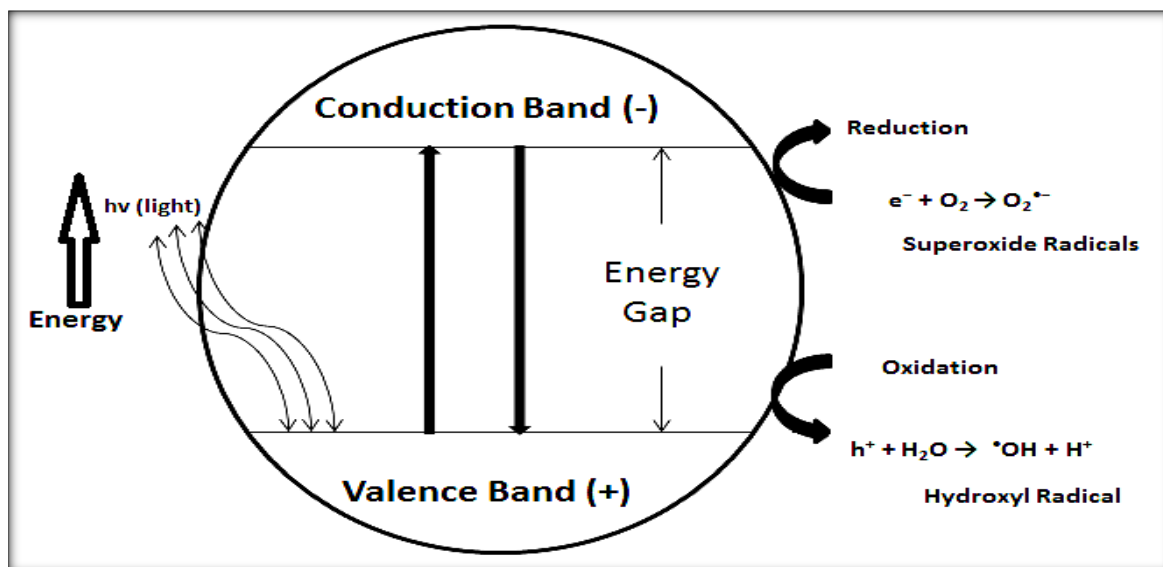


Fig. 2.3: Photocatalytic Activity Mechanism in Semiconductor Catalyst

2.8.3 Factors Affecting the Photo-catalysis

Photo-catalytic reactions generally depend upon several factors which affect the kinetics and performance of photo-catalysis. Some of these factors are:

- Catalyst loading
- Physical and chemical properties of Photo-catalyst (Herrmann, 2005)
- Oxygen pressure
- Type of light (UV or visible)
- Concentration and type of organic material
- pH
- Temperature (Rincon and Pulgarin, 2003).

2.8.4 Properties of an Ideal Photocatalyst

According to Bhatkhande and coworkers (2001), an ideal photo-catalyst should be

- Photoactive under visible light
- Bearing low band gap energy
- Inert (biologically and chemically)

- Stable under light
- Nontoxic to humans and environment

2.8.5 Examples of photo-catalysts

Photo-catalysts are usually solid and not consumed or used during a reaction. They only tend to enhance the reaction kinetics. Photo-catalysts are semiconductor in nature for example CeO₂, Fe₂O₃, TiO₂, WO₃, ZrO₂, and ZnO etc. (Benabbou *et al.*, 2007; Herrmann, 2005).

2.9 TiO₂ as a Photocatalyst

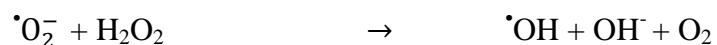
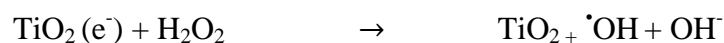
Photocatalytic activity of TiO₂ was first discovered by Fujishima and Honda in 1972 (Fujishima *et al.*, 1972). Redox process is induced on the surface of titania, commonly used as a photo catalyst due to generation of charge carriers (Kim *et al.*, 2007). TiO₂ is renowned in the world of photo - catalysis due to unique properties like

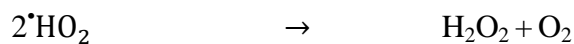
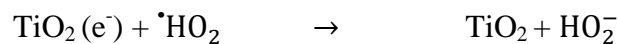
- High photo excitation
- Nontoxic in nature
- Very stable
- Cost effective (Benabbou *et al.*, 2007; Kumar and Raza, 2009)

2.9.1 TiO₂ Photocatalytic Mechanism

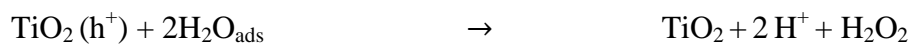
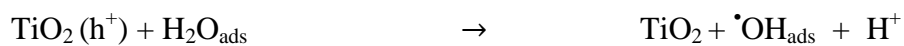


Reaction involving conduction band





Reaction involving valance band h^+



2.9.2 Polymorphs of TiO₂

Three polymorphs of TiO₂ are:

- 1) Anatase
- 2) Rutile, and
- 3) Brookite

Almost all studies have used Anatase and Rutile phase of TiO₂ in photocatalytic degradation processes. Of the two, the Anatase phase is the preferred polymorph having highest photo-catalytic activity (Beydoun *et al.*, 1999; Carp *et al.*, 2004).

Crystal structure of polymorphs of TiO₂, Rutile, Anatase, Brookite are shown in Fig. 2.3

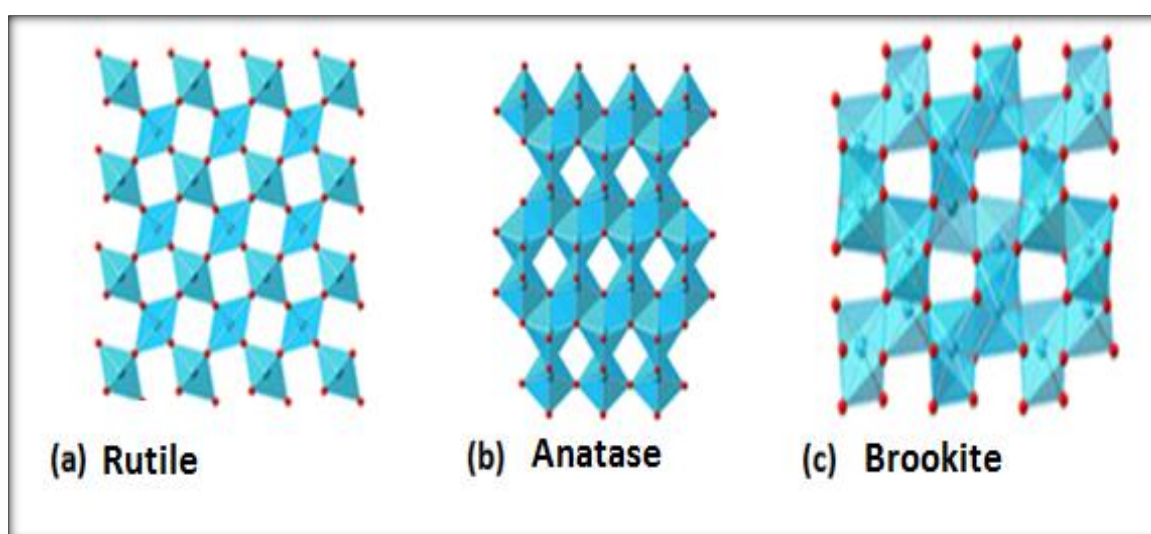


Fig. 2.4: Crystal Structures of Polymorphs of TiO₂

Some studies have claimed that mixtures of Anatase and Rutile phase give better results in term of photo-catalytic degradation of organic material (Giolli *et al.*, 2007; Sun *et al.*, 2008).

Polymorph	Band Gap Value	λ Photo-excitation (nm)
Rutile	3.2 eV	Upto 385
Anatase	3.02 eV	Upto 385
Brookite	2.96 eV	Upto 375

Table 2.2: Required Wavelengths for Activation of Polymorphs of TiO₂

2.9.3 Technical Drawback of TiO₂ and its Solution

TiO₂ is the best among many photo-catalysts but its band gap energy requirements restrict its use. TiO₂ requires 3.2 eV of energy (equivalent to a wavelength of 388 nm) in order to act as a photo-catalyst; this energy can only be provided by UV light source making the process of photo-catalysis slightly inconvenient (Linsebigler *et al.*, 1995). This difficulty has been overcome by inducing low energy levels within the band gap of TiO₂ with the help of doping (Gaya and Abdullah, 2008).

2.9.4 TiO₂ Doping

Various elements can be used as dopants for TiO₂, including metals like Iron, Silver, Manganese and Copper, or non-metallic dopants such as Carbon, Boron and Nitrogen etc. (Arana *et al.*, 2004; Wu *et al.*, 2004; Hamal and Klabunde, 2007). Doping must be controlled carefully as high dopant concentrations may result in electron and hole recombination (Coleman *et al.*, 2005; Carp *et al.*, 2004).

2.9.5 TiO₂ Application for Organic Compound Removal from Water

Water purification has been one of the main applications of photocatalysis (Younas,

et al., 2014). In the current practice of water and wastewater treatment, conventional methods of chlorination, ozonation, air stripping, solidification and landfill, granulated activated carbon adsorption and biodegradation, are used meanwhile newer technologies like membrane bioreactor and advanced oxidation processes (AOPs), including photolysis and photocatalysis, are under extensive research and development. This latter has the advantage that it completely removes, or mineralizes, the organic pollutants in a single step and subsequent treatment, or disposal of the byproducts, is not required. TiO₂ photocatalysis is therefore very suitable for removing many pollutants in both aqueous and gaseous waste stream (Bockelmann *et al.*, 1995; Alfano *et al.*, 2000; Zuo *et al.*, 2006; Xie *et al.*, 2011; Laokiat *et al.*, 2012). There are several advantages associated with photocatalysis process (Matthews, 1992) which make it a good alternative to other treatment technologies:

- The photocatalyst is non-hazardous
- No consumption of expensive and hazardous oxidizing chemicals
- Complete mineralization of the majority of organic pollutants, and
- The effluent is environmentally benign

Table 2.3 shows the range of applications using TiO₂ photo-oxidation of organic pollutants.

Class of Organics	Examples
Alkanes	Methane, Isobutane, Pentane, Heptane,
Alkenes	Propene, Cyclohexene
Aromatics	Benzene, Naphthalene
Phenolic-compounds	Phenol, 4-Chlorophenol, 4-Fluorophenol,
Polymers	Polyethylene, PVC
Pesticides	Parathion, Lindane, DDT, Tetrachlovinphos
Dyes	Methylene Blue, Methyl Orange

Table 2.3: Examples of Organic Compounds Studied in TiO₂ Photo-oxidation

2.10 Benzene in a Photocatalytic Medium

Photocatalytic degradation of benzene has been extensively discussed in the literature. It results in the formation of various oxidations intermediates due to the attack of hydroxyl radical on carbon atoms of the ring (Sobczynski *et al.*, 2004; Bui *et al.*, 2010).

2.10.1 Benzene Photocatalytic Intermediate Products and Pathway

As shown in Figure 2.5 benzene follow two routes for photocatalysis. One is the Close Chain (Phenol) pathway while the other is the Open Chain (Muconaldehyde) pathway. Consensus between researchers, regarding which pathway is actually followed is, however, lacking. For example in 1984, Hashimoto and coworkers reported that benzene adopts an open chain pathway during photocatalysis. Subsequently d’Hennezel *et al.*, (1998), Einaga *et al.*, (2002), Park *et al.*, (2005) and Yoshida *at al.*, (2008) reported that benzene photolysis occurs through the close chain compounds. More recently, however Bui *et al.*, (2010, 2011) have reported that benzene is photo-catalyzed through both Close Chain and Open Chain routes, in parallel, with the former being the dominant process. They mentioned that the amount of muconaldehyde produced during the photocatalysis reaction is much smaller than phenolic compounds, and is thermodynamically unstable and thus is very difficult to detect. This may be the reason that others have ignored concentrating only on the Close Chain pathway.

This issue has been investigated in this study, in detail.

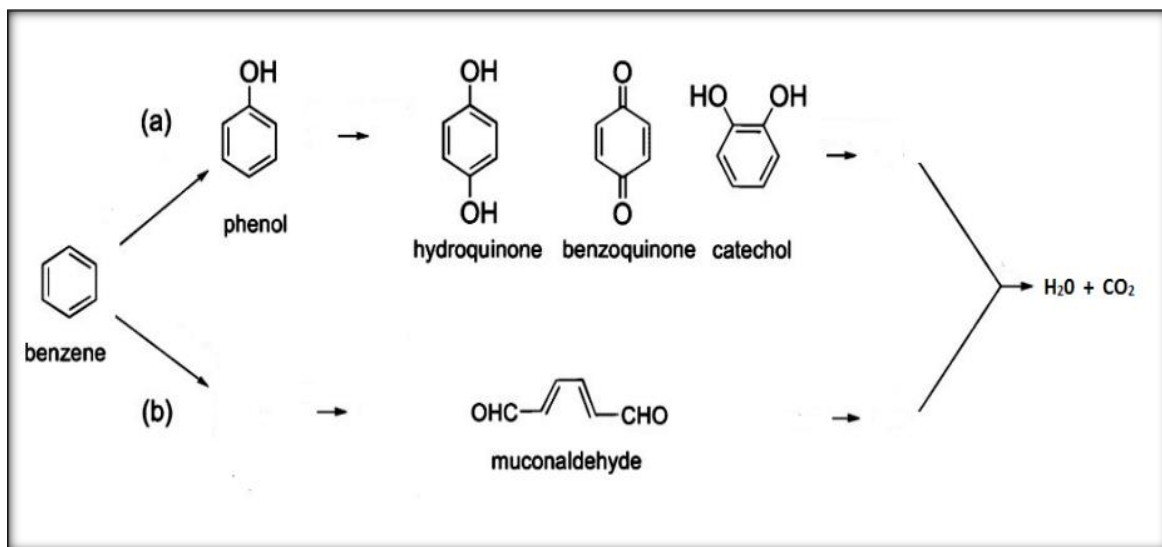


Fig.2.5: Possible Pathways of Benzene Photocatalysis (a) Close chain (b) Open chain

MATERIALS AND METHODS

3.1 Materials and Chemicals

Titanium dioxide, silver nitrate, hydrochloric acid, sodium hydroxide and benzene (analytical grade) were obtained from Sigma Aldrich.

Hydroquinone, para-benzoquinone, catechol, phenol, and muconic acid (HPLC grade) were obtained from International Laboratory USA.

GAC was purchased from the local market.

3.2 Benzene Stock Solution

Benzene stock solution of 100 and 1000 ppm were prepared by dissolving 113 and 1130 μL of benzene in 1.0 L De-Ionized water respectively. These solutions were mixed well and then stored in the dark. The pH of the solution was adjusted to 4.0, 7.0 and 10.0 (± 0.1), using Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), as and when required.

3.3 Instrumentation

For the experimental work, a UV Lamp (6W), a Fluorescent Lamp, quartz cell (20849 Hach), UV-Vis Spectrometer (SQ-2800 Unico), pH-meter (CyberScan 500 Eutech), centrifuge (D3752O Sigma), HPLC (Agilent 1200 Waldbronn) and orbital shaker were used.

3.3.1 UV/Vis Spectrophotometer

Spectrophotometry was used as a quantitative analytical technique by measuring the absorbance of benzene solution before and after degradation reaction with TiO_2 . For this

purpose, the benzene UV spectrum, in water, was recorded to check the wavelength of maximum absorbance (λ_{max}) and a calibration curve was developed.

3.3.1.2 Principle of Working

Spectrophotometry technique is widely used for the quantitative analysis of organic compounds. The molecules after exposure to UV-light absorb it. Due to absorption of light, electrons become excited and move to high energy orbitals. The instrument basically measures transmitted light which is commonly known as transmittance. The absorbance is recorded by taking the difference of light transmitted before and after the sample solution is being exposed to light (Thomas and Burgess, 2007).

3.3.1.3 Beer-Lambert law

According to Beer-Lambert law, absorbance is directly proportional to the concentration of the sample and path length of the cell in which sample is taken.

$$A = \epsilon \cdot c \cdot L$$

Where,

A = absorbance

ϵ = absorption coefficient, specific to sample solution

c = concentration of sample solution

L = path length of cell

Spectrophotometer (SQ-2800 Unico) was used to record the benzene spectra and then measure the absorbance of benzene at 254 nm.

3.3.2 High Performance Liquid Chromatography (HPLC)

3.3.2.1 Introduction

HPLC is a standard qualitative and quantitative analysis technique for the analysis of organic molecules and ions and based on the mechanisms of adsorption, partition and ion exchange, depending on the type of stationary phase used. HPLC can be used to assess the purity and/or determine the content of many pharmaceutical substances. It can also be used to determine enantiomeric composition, using suitably modified mobile phases or chiral stationary phases.

3.3.2.2 Principle of Working

HPLC works on the same principle as other chromatographic techniques: to separate the components of a mixture on the basis of their relative affinities for the stationary phase (normally packed inside a stainless-steel column), under the influence of an appropriate mobile phase, under high pressure. Separation of the components of a solution results from the difference in the relative distribution ratios of the solutes between the stationary phase and the mobile phase.

3.3.2.3 How HPLC Works

The main procedure of HPLC is outlined below, and the basic components of a HPLC system are shown in Fig 3.1.

(i) Creating Pressurized Solvent Stream

- Solvent (mobile phase) from a solvent reservoir is pulled up the solvent inlet line into the pump head through a one-way check valve.

- The pressurized mobile phase passes through the injector and into the column, where it equilibrates with the stationary phase.
- It then exits into the detector flow cell and out to the waste collector.

(ii) Sample injection

The sample, dissolved into the mobile phase or a similar solvent, is first loaded into a sample loop then injected by turning a handle swinging the sample loop into the pressurized mobile phase stream. Fresh solvent, pumped through the injector sample loop, washes the sample onto the column head and down the column.

(iii) Getting a Chromatogram

The separated bands in the effluent from the column pass through the column and exit into the detector flow cell. The detector reads the concentration changes and converts it into a signal voltage. This change in voltage, with time, is passed on to the recorder or computer, over the signal cable, and is traced on paper as a chromatogram, allowing fractions to be detected as rising and falling peaks

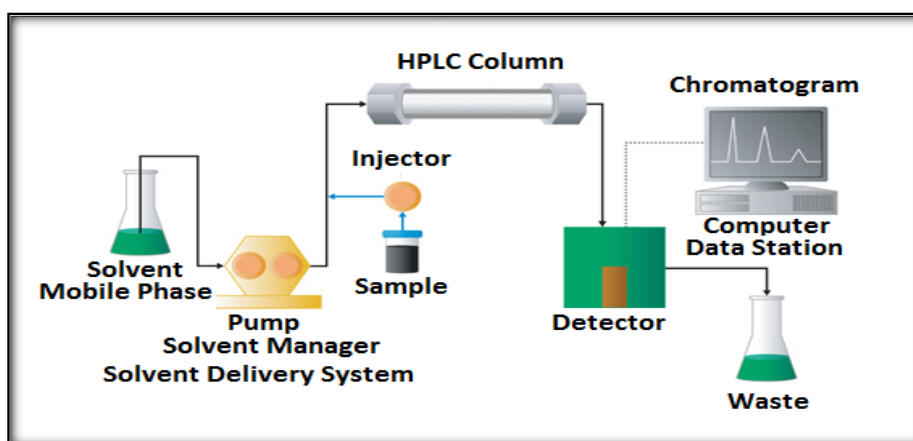


Fig. 3.1: Basic components of a High Performance Liquid Chromatography (HPLC)

3.4 Methodology

3.4.1 Adsorption Studies

3.4.1.1 Determination of Benzene Concentration

UV-Spectrophotometry technique was used for the quantitative measurement of benzene. For this purpose, benzene UV spectrum in water was recorded to check the wavelength of maximum absorbance (λ_{max}) and a calibration curve (Fig. 4.2) was developed using serial dilutions of 1000 ppm stock solution.

3.4.1.2 Effect of pH on Adsorption

Experiments were performed to check the effect of pH on adsorption. For this purpose 100 mL benzene solution of 1000 ppm was taken in glass flask with 1 g GAC, the flask being placed on a shaker for 6 hours. Adsorption was observed over 4, 7 and 10 pH [Fig. 3.2].

In order to adjust the pH of the solution HCl and NaOH (0.1 Normal) were used. Since the added amounts of these solutions were insignificant, compared to the total volume of the sample, it was assumed that the concentration of solutes was not affected by these additions.



Fig. 3.2: Effect of pH on Adsorption

3.4.1.3 Column Studies

Ordinary 100 mL burette was used for the preparation of columns, with a diameter of 1.5 cm and height of 60 cm. A small plug of glass-wool was pushed into the bottom of the burette with a wooden dowel. The column was packed with the 15 g of GAC [Fig. 3.3]. Benzene solution was then poured into the column with different flow rates (1, 3, 5, and 20 mL/min), each time new column was used against each flow rate. Benzene adsorption efficiency on GAC for each flow rate was calculated.



Fig. 3.3: Column for Adsorption Study

3.4.2 Photocatalysis Studies

3.4.2.1 Synthesis of Pure and Ag-TiO₂ Nanoparticles

Liquid Impregnation method (Khan *et al.*, 2013; Younas *et al.*, 2014) was used for the synthesis of pure and silver doped TiO₂ nanoparticles as described below [Fig. 3.4].

(i) Mixing

Slurry of TiO₂ nanoparticles was prepared in water by mixing 50 g of TiO₂ in a beaker and continuous stirring for 24 hours.

(ii) Settling

This solution was allowed to settle, for 24 hours so that proper settling of the solids could take place.

(iii) Drying

After decanting the supernatant, the solid material was placed in oven for 12 hours at 105 °C so that water could evaporate.

(iv) Calcination

After drying, the material was crushed properly using a pestle and mortar and placed in china dishes. The china dishes were placed in a muffle furnace for 6 hours at 400 °C to obtain the pure TiO₂ nanoparticles.

Silver (Ag) doped TiO₂ nanoparticles were prepared using the same steps, with 1% molar ratio of the metal salt (AgNO₃) being added to the solution, before adding TiO₂.

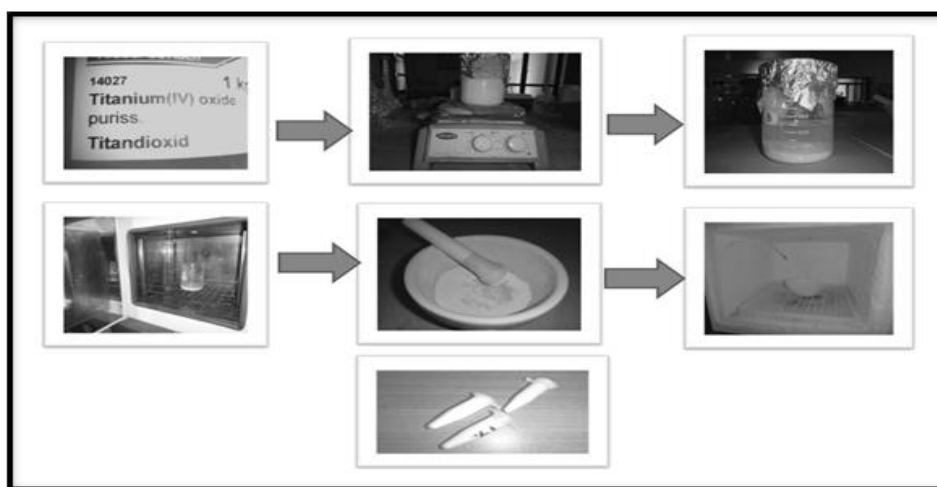


Fig. 3.4: Steps Involved for the Synthesis of Nanoparticles

3.4.2.2 Characterization of Nanoparticles

The nanoparticles synthesized were characterized using the following techniques.

(i) X-Ray Diffraction (XRD)

X-ray powder diffraction is a very rapid nondestructive analytical technique primarily used for phase identification of a crystalline material. It can provide information on unit cell dimensions. The material to be analyzed is finely ground, homogenized, and average bulk composition is determined.

XRD studies of pure and metal doped TiO₂ were carried out using JEOL JDX-II XRD equipment. Average crystalline size of nanoparticles was determined by using the Scherer formula (Younas *et al.*, 2014).

$$L = K \lambda / \beta \cos \theta$$

Where,

L = Average particle size

K = 0.891, $\lambda = 0.1542$

θ = the diffraction angle of crystal phase

β = Full width of a diffraction line at one half of maximum intensity (FWHM)
radian

(ii) Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a powerful technique that uses a focused beam of electrons to obtain largely magnified image.

The high-resolution, three-dimensional images produced by SEM provides information like

- Topography
- Morphology
- Chemistry
- Crystallography

- Orientation of grains

SEM images were obtained using JEOL JSM-6460 scanning electron microscope at 10,000 magnifications.

(iii) Energy Dispersive X-Ray Spectroscopy (EDS)

Energy dispersive X-ray spectroscopy (EDS) is a simple but very powerful analytical technique used to know elemental composition of very small samples.

EDS system embedded with JEOL JSM-6460 was used in this study for the characterization of synthesized nanoparticles by assessing the elemental composition.

3.5 Photocatalysis Experiments

3.5.1 Photo-catalysis at room Temperature with pure TNPs

Photocatalytic reactions were carried out at room temperature in quartz cell containing 10 mL sample of 100 ppm benzene solution. The reaction solution was an aqueous suspension with 25 mg pure TiO₂ nanoparticles. The suspension was continuously shaken while exposed to UV light. Samples were collected after every 30 min.

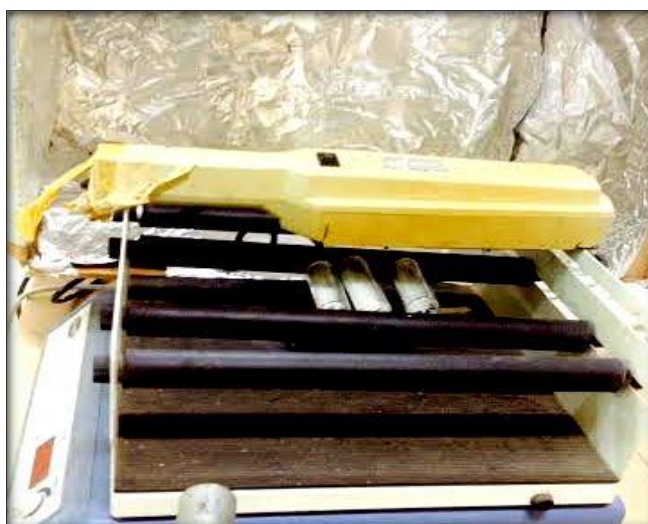


Fig. 3.5: Photocatalysis at Room Temperature with Pure TNPs

3.5.2 Photocatalysis at 40 °C with Pure TNPs

Photocatalytic reactions were carried out at 40 °C in quartz cell containing 10 mL sample of 100 ppm benzene solution. The reaction solution was an aqueous suspension with 25 mg pure TiO₂ nanoparticles. The suspension was continuously shaken and irradiated with UV light and samples were collected after every 30 min. Incubator was used to control the temperature.



Fig. 3.6: Photocatalysis at 40 °C Temperature with Pure TNPs

3.5.3 Photocatalysis with Silver Doped TNPs

Photocatalytic reactions were again performed at room temperature and at 40 °C with silver doped TiO₂ nanoparticles under visible light rather than UV light and samples were collected after every 30 min. Incubator was used to control the temperature.



Fig. 3.7: Photocatalysis with silver doped TNPs at Room Temperature and 40 °C

3.6 Combined Adsorption and Photocatalysis Process

After performing both experiments separately, a bench-scale experimental system was designed and constructed for the sequential application of adsorption and photocatalysis in a continuous-flow system. The system was fed with a 1000 ppm benzene solution at 20 mL/min through a fixed-bed adsorption column as described above with the column effluent flowing, under gravity, through four 500 mL flasks, connected in series and placed on an orbital shaker with continuous exposure to UV light at 40 °C. Each flask contained 0.5 g TNPs.

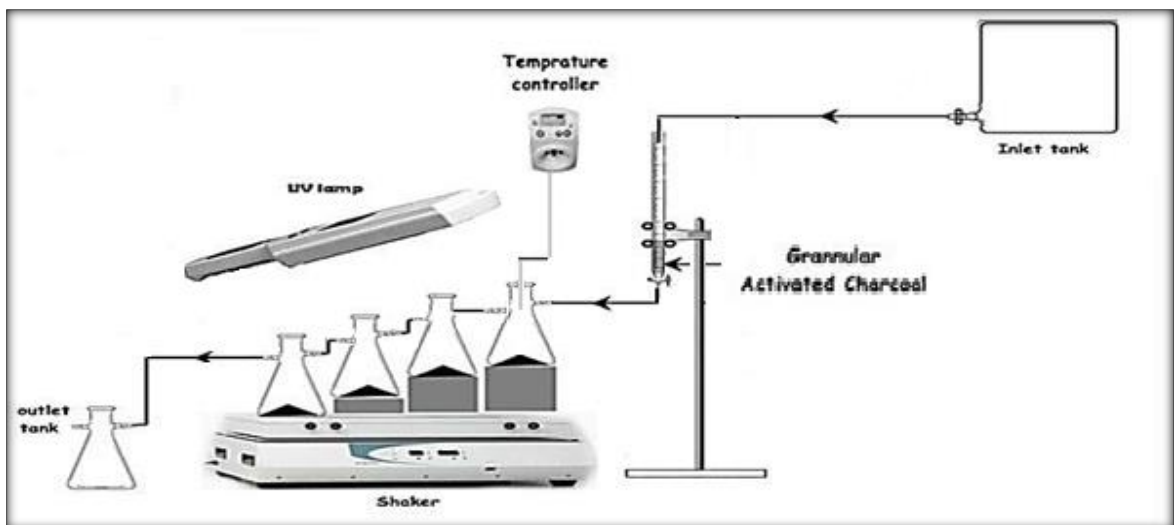


Fig. 3.8: Experimental System for Combined Adsorption and Photocatalysis

3.7 Photocatalytic Degradation of Benzene: Intermediate Products and Pathway

During the photocatalysis experiments, samples of the solution were periodically analyzed by using high performance liquid chromatography with diode-array UV–Vis detection (HPLC, 1200 Series Agilent) to identify the intermediates of benzene degradation. C18 reverse phase 100 Å column (5µm particle size, 150 mm × 2 mm, Phenomenex Luna W) was used. The mobile phase consisted of water and acetonitrile (1:1 v/v), at a flow rate of 1.0 mL/min. The injection volume was 20 µL and the spectrum of the eluting substances being recorded at 270 nm.

3.8 Photocatalytic Degradation of Phenol

Photocatalytic reaction of phenol with pure-TNPs was conducted in aqueous solution under UV light at room temperature. For this purpose 10 mL sample of 1000 ppm solution was taken in quartz cell and exposed to UV light for 3 hours to find the intermediate products of phenol during the photocatalysis reaction.



Fig. 3.9: Photocatalysis of Phenol

RESULTS AND DISCUSSION

4.1 Benzene Determination (λ_{max})

The UV spectrum of benzene in water is shown in Figure 4.1. The wavelength of maximum absorption (λ_{max}) as 254 nm is in conformity with earlier reports (Hindarso *et al.*, 2001; Pirajan *et al.*, 2013). Calibration curves were developed using serial dilutions of the benzene stock solution of the 1000 ppm [Fig. 4.2].

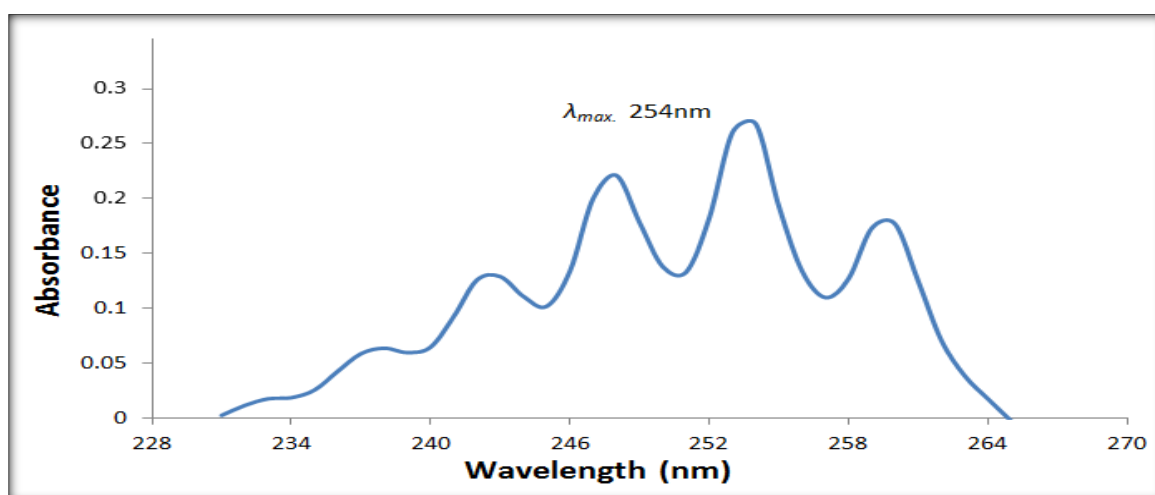


Fig. 4.1: UV Absorbance Spectra of Benzene

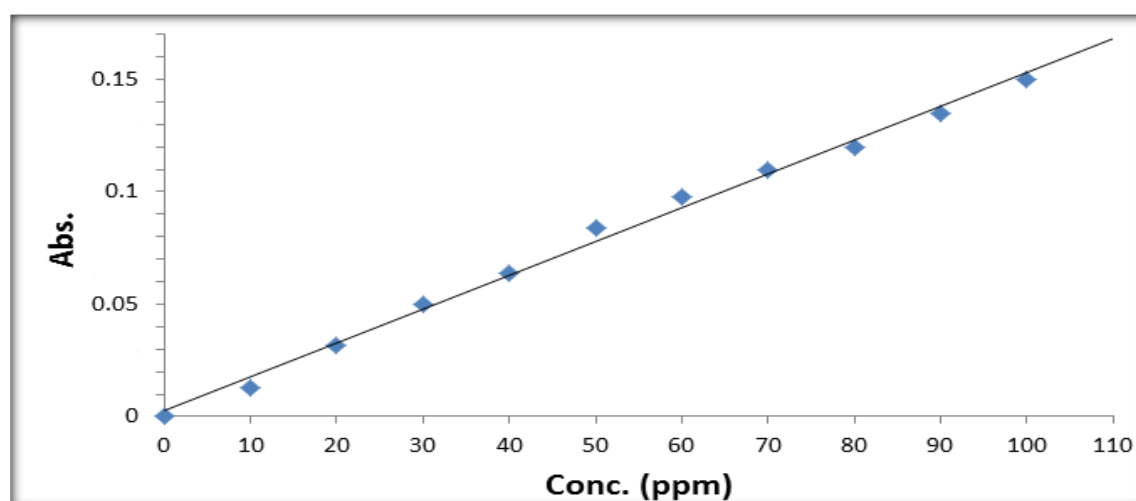


Fig. 4.2a: Calibration Curve (10-100 ppm) for Benzene in Water

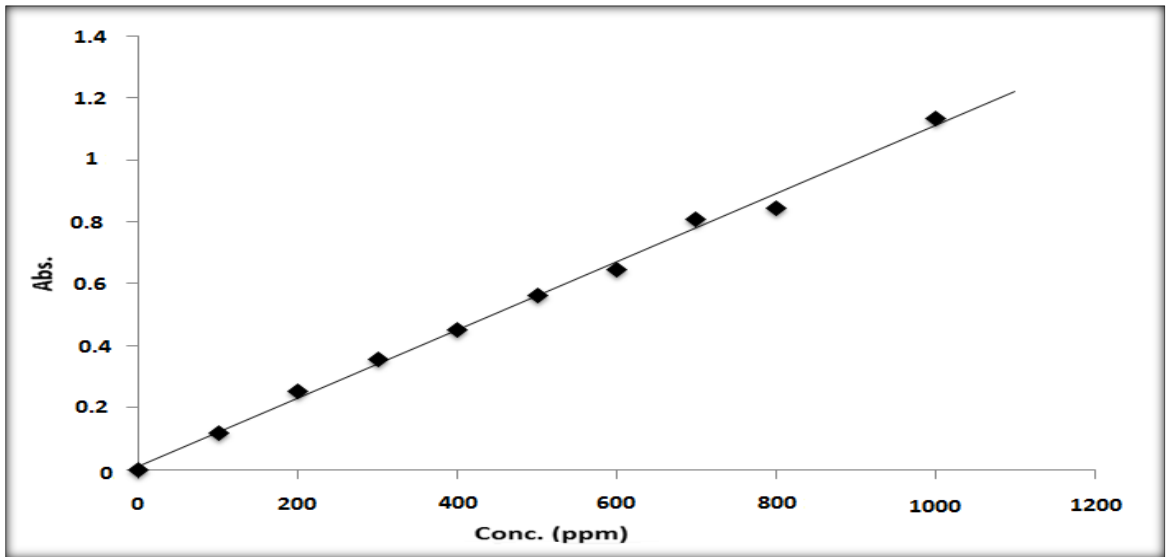


Fig. 4.2 b: Calibration Curve (100-1000 ppm) for Benzene in Water

4.2 Effect of pH on Adsorption

Adsorption of benzene on GAC over 4, 7, and 10 pH was almost the same, so pH was found not to have any effect in this process [Fig. 4.3].

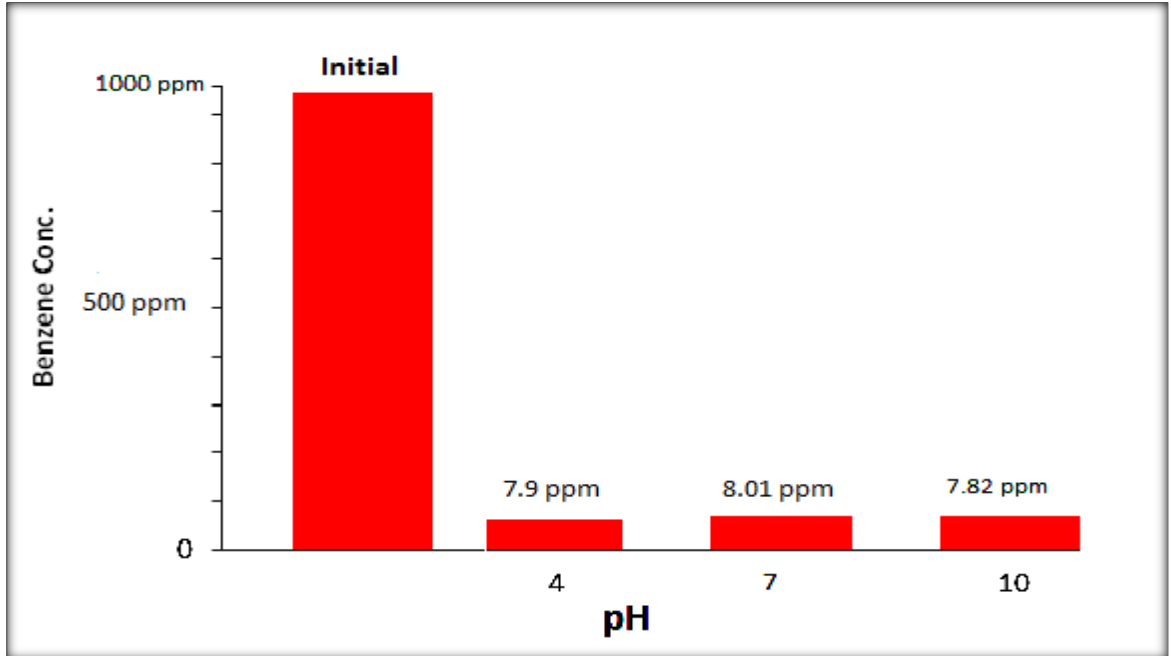


Fig. 4.3: Effect of pH on Benzene Adsorption

4.3 Column Studies

The column experimental data for the benzene removal against the flow rates of 1, 3, 5, and 20 mL/min is presented in Figure 4.4. It was observed that the extent of benzene removal degree decreases as the flow rate increases. When benzene solution was passed through column with a flow rate of 20 mL/min, over 80 % reduction in benzene concentration was observed in continuous flow in slightly over one hour.

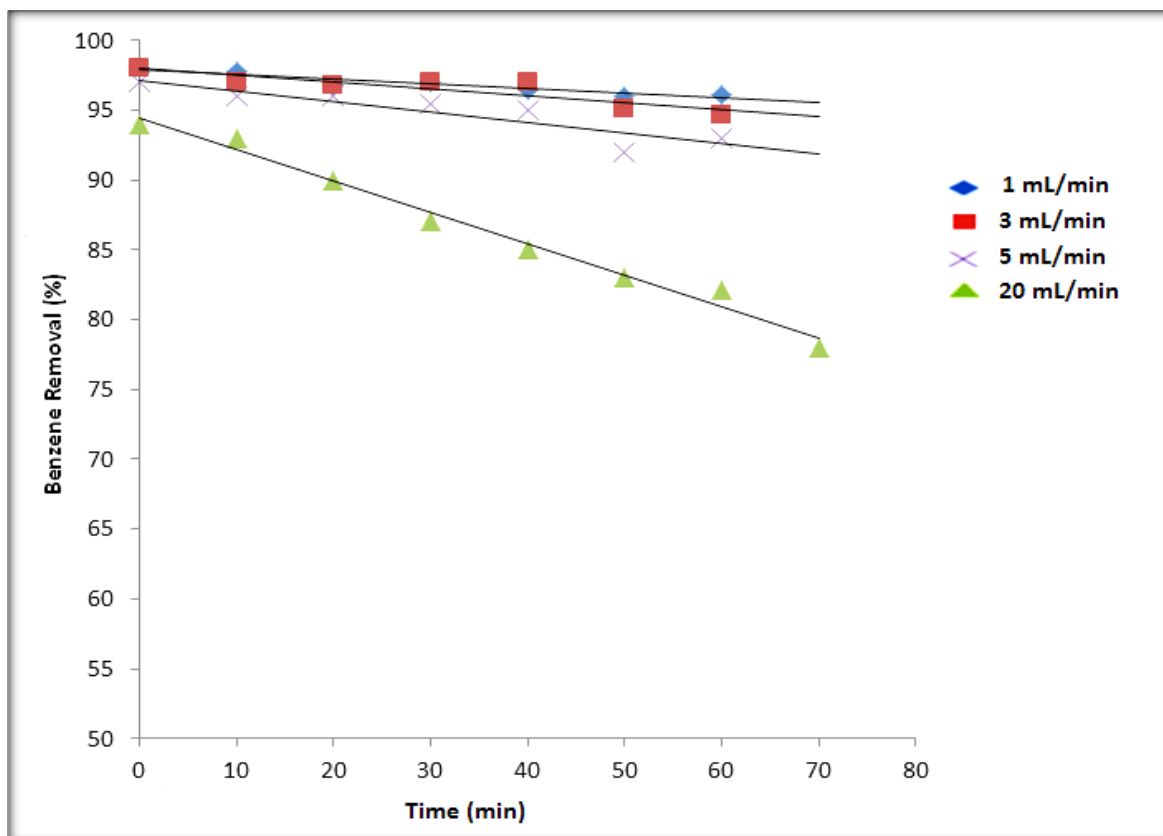


Fig. 4.4: Effect of Flow Rate on Benzene Removal via Adsorption

4.4 Characterization of Nanoparticles

4.4.1 X - Ray Diffraction (XRD) Analysis

The crystal structure and the crystallite size of the prepared nanoparticles were analyzed by XRD. Average particle size of each category of nanoparticles (TiO₂ and Ag-

TiO₂) was found to be 67 and 74 nm respectively as shown in Table 4.1. XRD Pattern of Pure TiO₂ and Ag-TiO₂ Nanoparticles are shown in Figures 4.5 and 4.6 respectively.

Nanoparticles	Average particle size
Pure TiO ₂	67
Ag-TiO ₂	74

Table 4.1: Average Particle Size of Nanoparticles

Average crystalline size of nanoparticles was determined by using the Scherrer formula (Younas *et al.*, 2014).

$$L = K \lambda / \beta \cos \theta$$

Where,

L = Average particle size

K = 0.891

λ = 0.1542

β = Full width of a diffraction line at one half of maximum intensity (FWHM)

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θ = the diffraction angle of crystal phase.

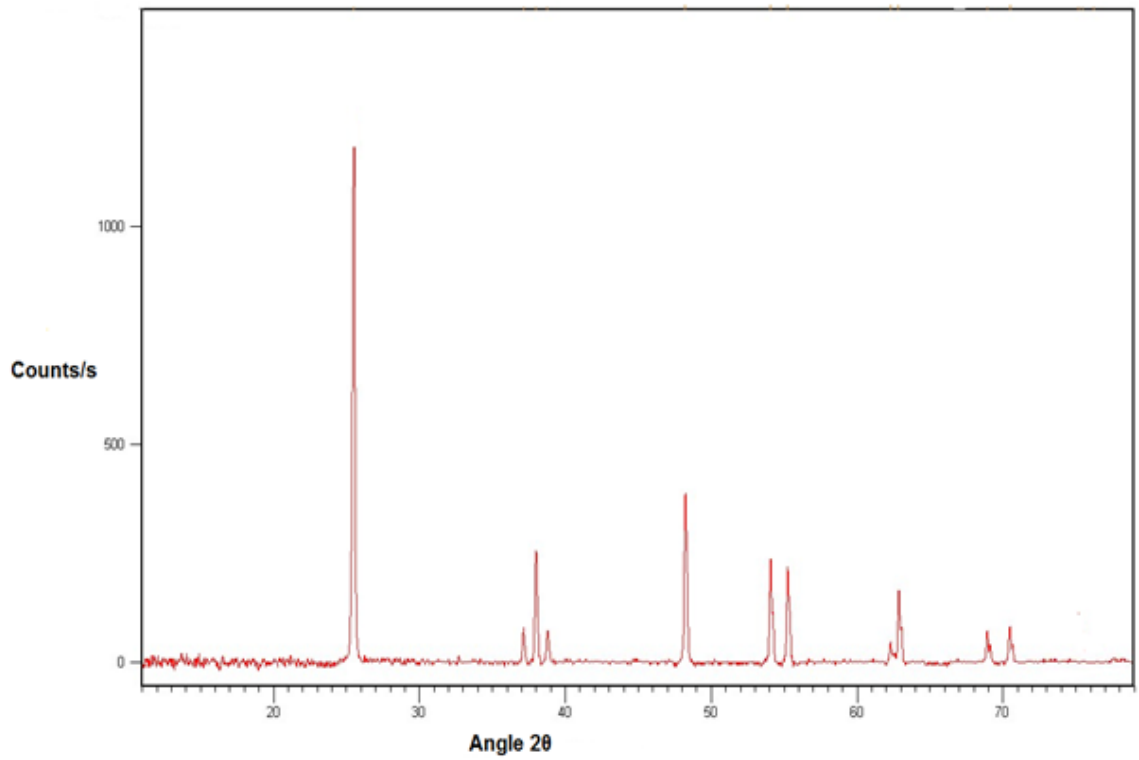


Fig. 4.5: XRD Pattern of Pure TiO₂ Nanoparticles

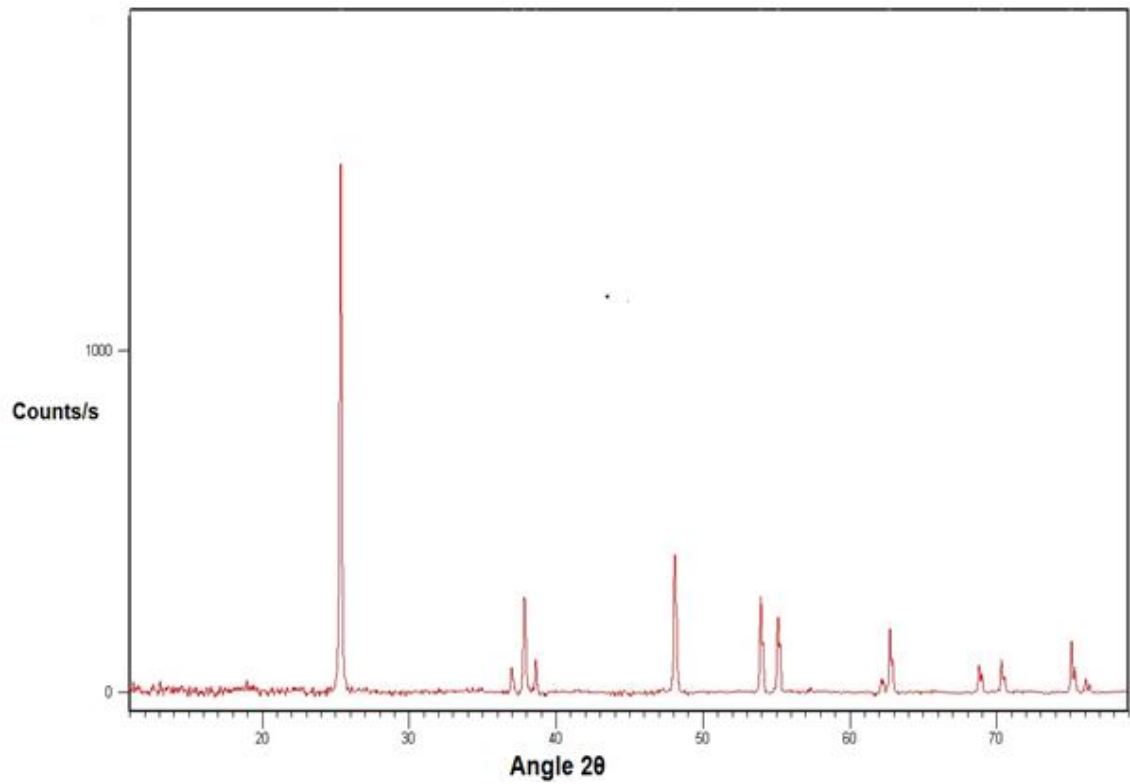


Fig. 4.6: XRD Pattern of Ag-TiO₂ Nanoparticles

Peaks of XRD results reveal that nanoparticles have Anatase TiO₂ crystalline structure.

4.4.2 Scanning Electron Microscopy (SEM)

The SEM images of pure and Ag-TiO₂ nanoparticles were obtained, at the magnification of 10,000, and are shown in Figures 4.7 and 4.8. Images of pure and Ag-TiO₂ nanoparticles confirmed the presence of porous, sponge like structure, of high roughness and complexity. Such structure indicates the high surface area which has been proven to be efficient for photo catalytic degradation purposes.

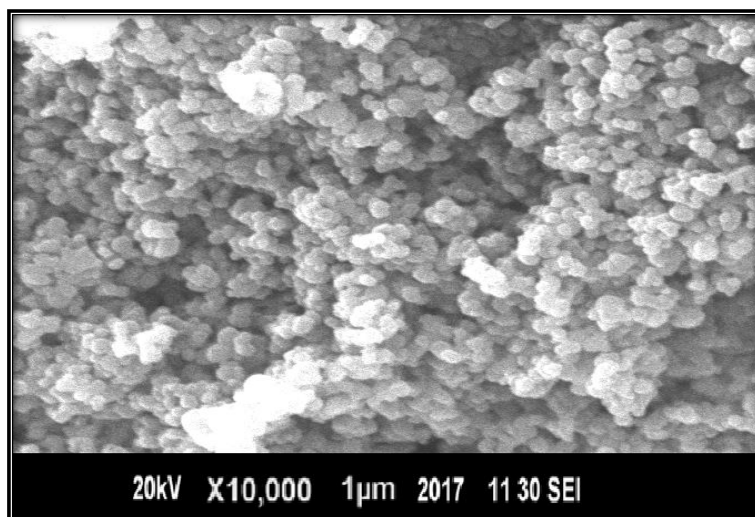


Fig. 4.7: SEM Image of Pure TiO₂ Nanoparticles at X 10, 000

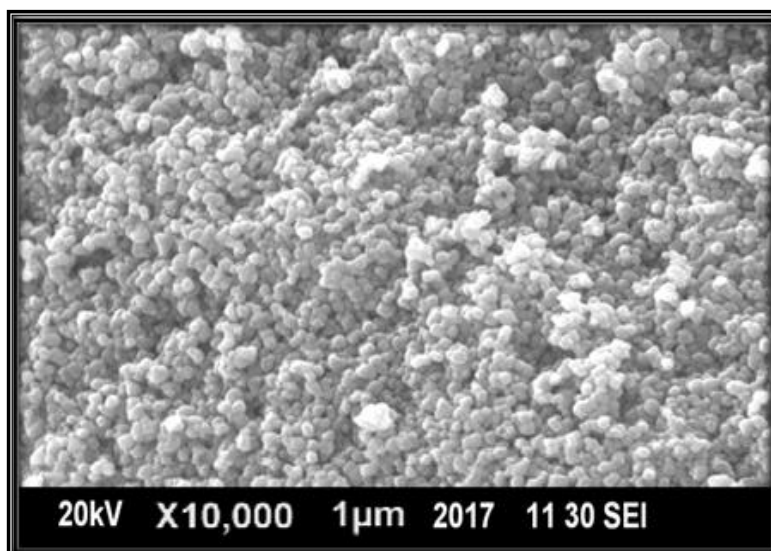


Fig. 4.8: SEM Image of Ag-TiO₂ Nanoparticles at X 10, 000

4.4.3 Energy Dispersive Spectroscopy (EDS) Analysis

The chemical composition of the synthesized nanoparticles was analyzed by Energy Dispersive Spectroscopy (EDS) analysis. It is evident from the spectrum that TiO₂ nanoparticles contain only Ti and O and Ag-TiO₂ nanoparticles contain only Ti, O and Ag so no impurity was present in the nanoparticles.

Nanoparticles	Relative Elemental Mass Ratios		
	Ti	O	Ag
Pure TiO ₂	58.73	41.27	0
Ag- TiO ₂	52.45	46.05	1.50

Table 4.2: EDS Results of Nanoparticles

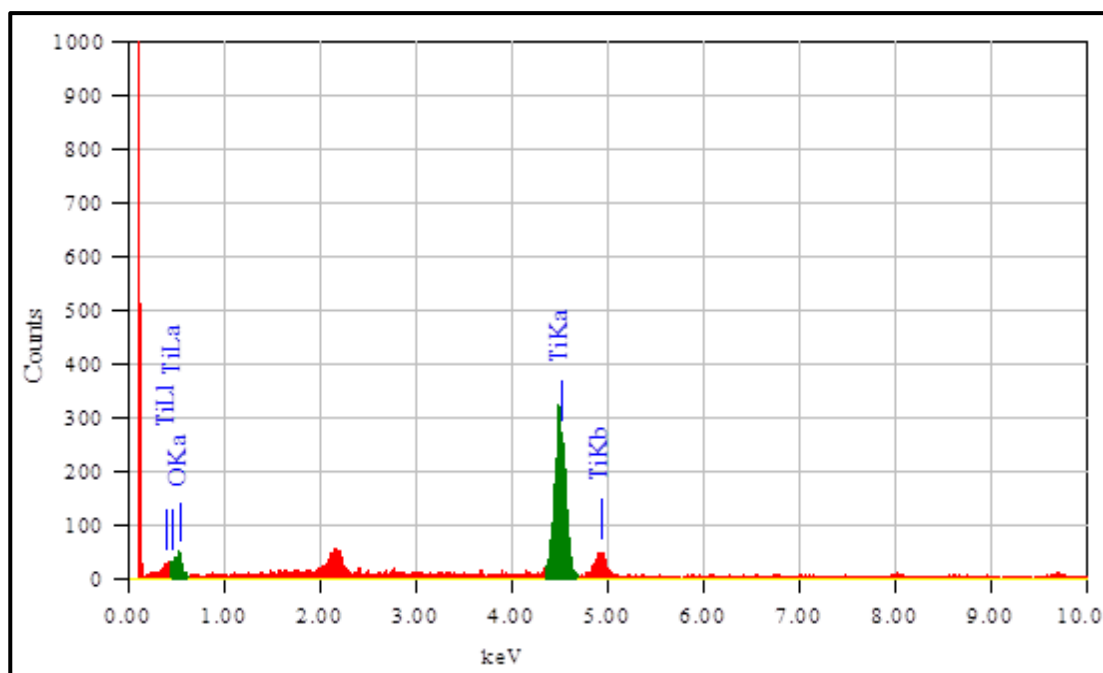


Fig. 4.9: EDS spectra of Pure TiO₂ Nanoparticles

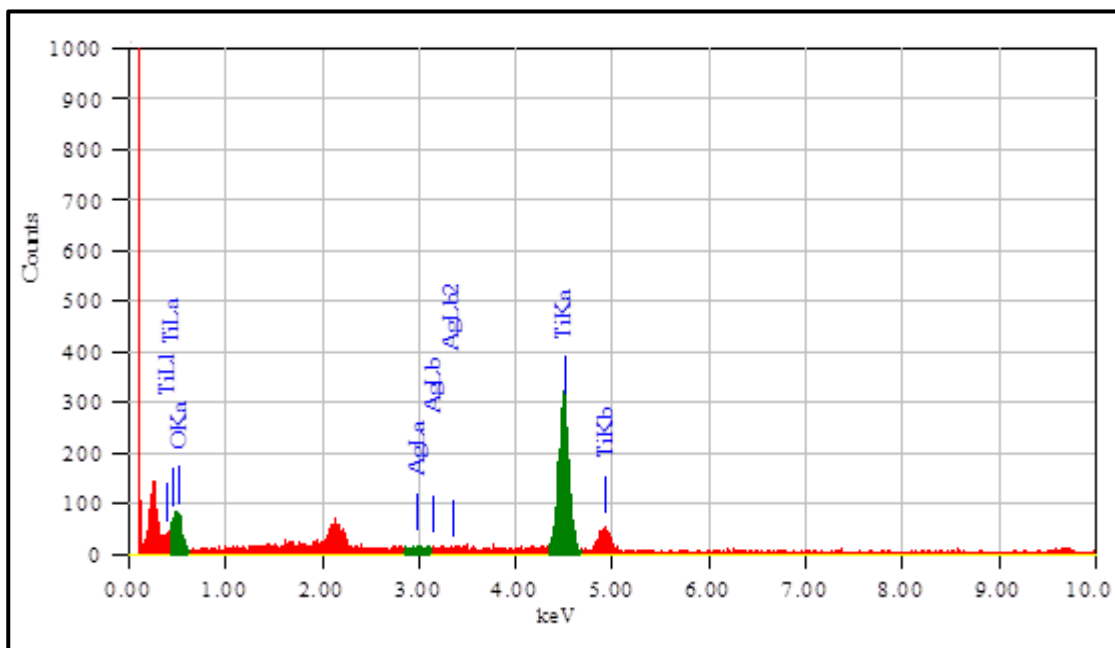


Fig. 4.10: EDS spectra of Ag-TiO₂ Nanoparticles

4.5 Photocatalysis Experiments

Photocatalysis was carried out with both, pure and silver doped TiO₂ at room temperature and 40 °C. Benzene concentration was checked after every 30 minutes by measuring the absorbance of the solution, at 254 nm, and comparing the absorbance with the calibration curve. The best results were obtained when experiments were performed with pure TNPs under UV light at room temperature and 40 °C, after 180 and 120 min, benzene concentration was found to be below 0.14 ppm respectively.

Although photocatalysis of benzene was also observed under visible light at both, room temperature and at 40 °C but the rate of degradation was too slow as shown in results [Fig. 4.11].

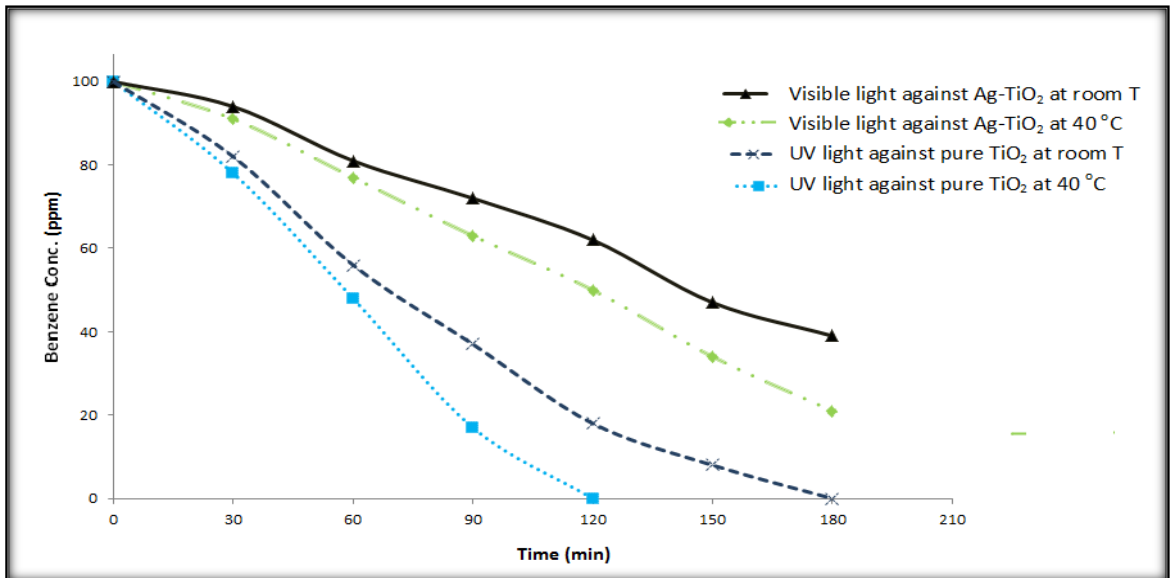


Fig. 4.11: Effect of Light and Temperature on Benzene Removal

4.6 Removal of Benzene by the Combination of Adsorption and Photocatalysis

From the reservoir tank benzene solution of 1000 ppm was allowed to flow continuously through the GAC column, at a flow rate of 20 mL/min. It was observed that over 80 % benzene concentration had been adsorbed on GAC. This water was then passed through four flasks connected in series for photocatalysis. The outflow from the last flask was analyzed and found to have benzene concentration below 0.14 ppm [Fig. 4.12].

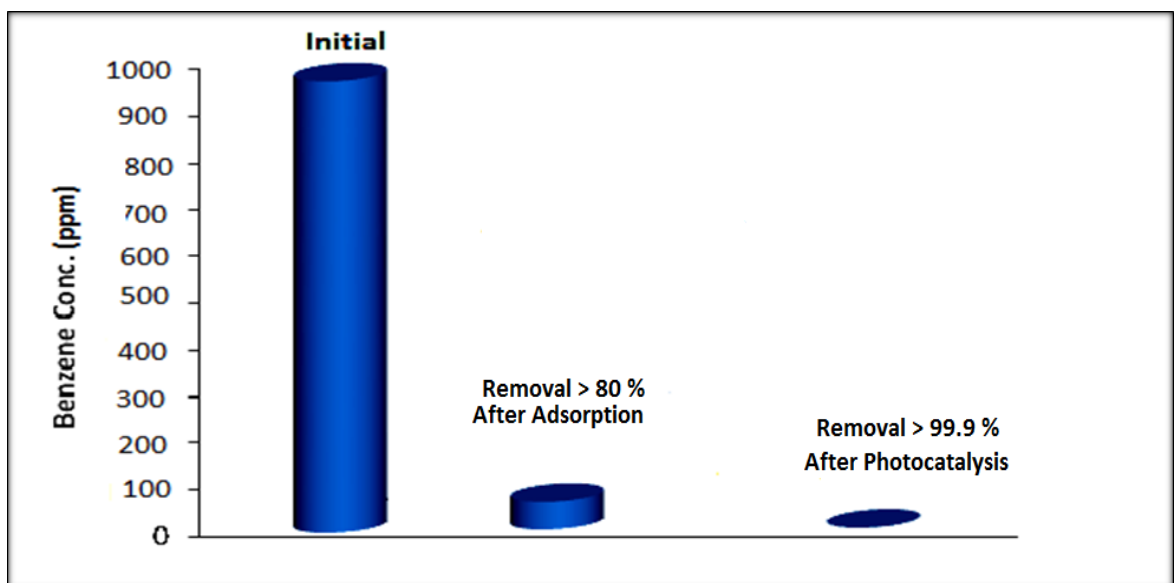


Fig.4.12: Benzene Removal by the Combination of Adsorption and Photocatalysis

4.7 Benzene Intermediate Products and Pathway

During photocatalytic experiments, samples were periodically analyzed using HPLC. The products were identified by comparing retention times and UV-Vis absorption spectra of the products with those of corresponding authentic compounds and revealed that muconaldehyde, phenol, p- benzoquinone and catechol were formed during the photocatalysis of benzene Figure 4.13.

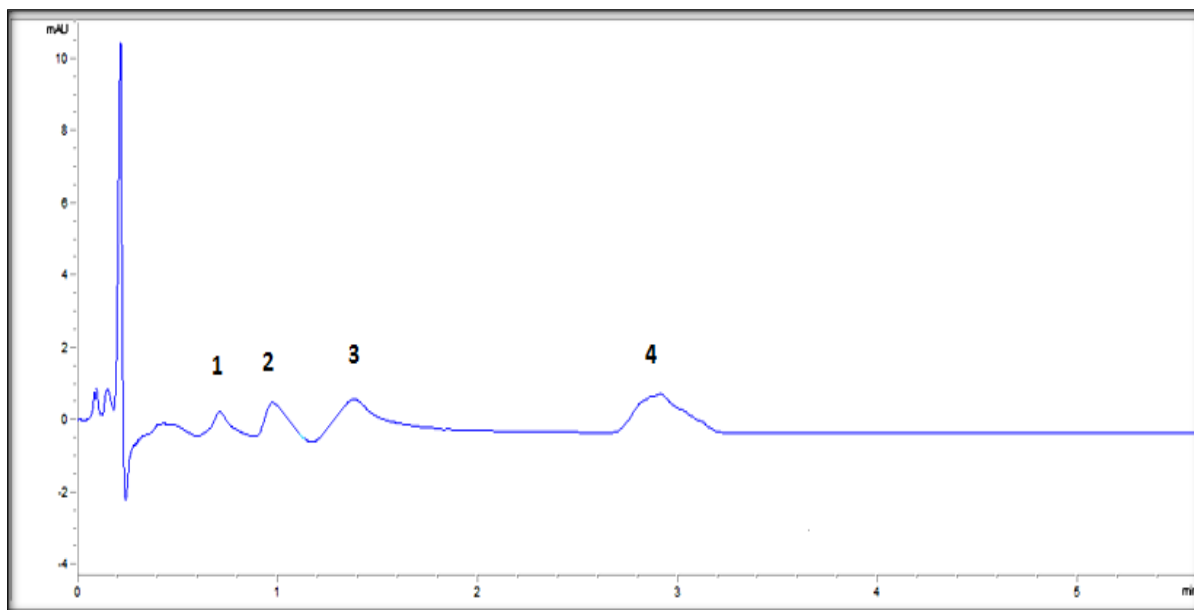


Fig. 4.13: Reversed phase HPLC Elution Profile of Benzene Photocatalysis, Recorded at 270 nm. The Products are, (1) Muconaldehyde, (2) p-Benzoquinone, (3) Catechol and (4) Phenol

4.8 Photocatalysis of Phenol

All compounds formed during the photocatalysis of benzene were phenolic compounds except muconaldehyde so a question rises whether muconaldehyde is produced from benzene directly, or by the phenolic precursors.

To solve this confusion, photocatalytic reaction of phenol was carried out, independently, in aqueous solution containing TiO₂ nanoparticles. The result showed that

no muconaldehyde was produced in this case, although other phenolic compounds (p-Benzoquinone, Catechol and Phenol) were formed [Fig. 4.14]. It was, therefore, concluded that muconaldehyde was formed from benzene directly.

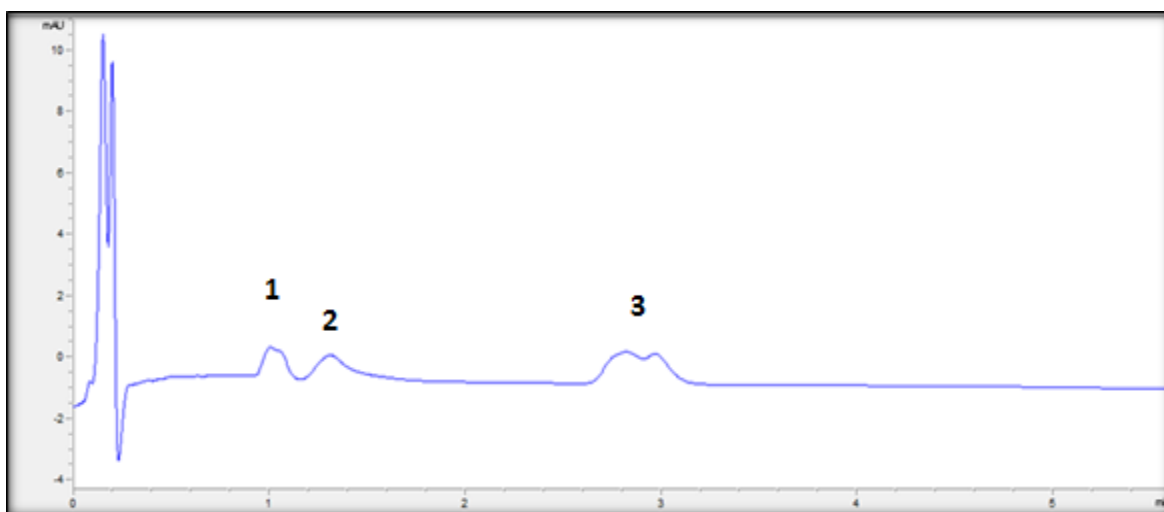


Fig. 4.14: Reversed Phase HPLC Elution Profile of Phenol Photocatalysis, Recorded at 270 nm. The Products are, (1) p-Benzoquinone, (2) Catechol and (3) Phenol

4.8.1. Benzene Photocatalysis: Conclusion

Through these experiments, therefore, it was confirmed that Benzene Photocatalysis proceeds through two independent pathways: The Close Chain (Phenolic) and the Open Chain (Muconaldehyde) routes, with the former being the dominant process, as indicated by Bui *et al.*, 2010 [Fig. 4.15].

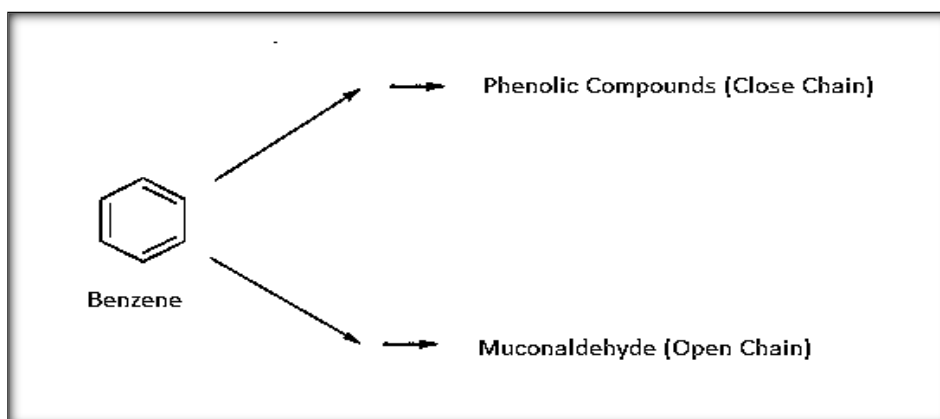


Fig. 4.15: Two Pathways of Benzene Photocatalysis

4.9. Treatment of Refinery Effluent

After optimizing the procedure for removal of benzene from synthetic wastewater, it was applied to an actual sample. In this context an effluent sample was collected from a local refinery (Figure 4.16) and the UV spectrum scanned from 220 to 280 nm. The spectrum, shown by the upper curve in Figure 4.17, displays the characteristic peaks for benzene, with a baseline absorbance due to other impurities in the effluent. In order to find the concentration of benzene in the refinery sample the method of Standard Addition, which involved spiking the sample with different concentrations of benzene, was used by measuring the absorbance at 254 nm. The resulting Absorbance vs. Spiked Concentration results are shown in Figure 4.18. Intercept of the straight line on the horizontal axis shows that the concentration of benzene in the refinery wastewater sample is around 620 ppm. The sample was allowed to flow through the GAC column and then through the photocatalysis set-up, described above. The spectrum of the treated wastewater is shown by the lower curve in Figure 4.17 showing the absence of any peak due to benzene. This confirms that the methodology developed in this study could be effectively applied to actual refinery effluent.

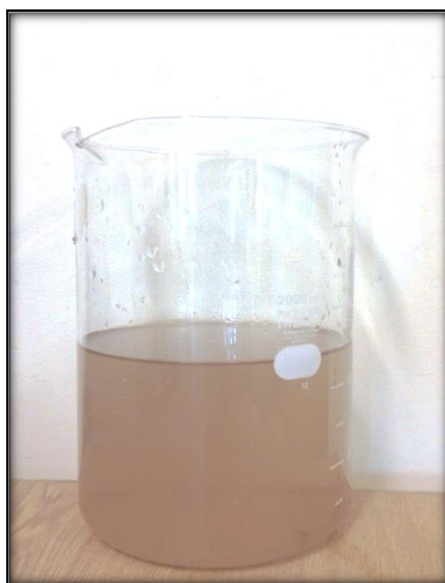


Fig. 4.16: Actual Sample of Local Refinery

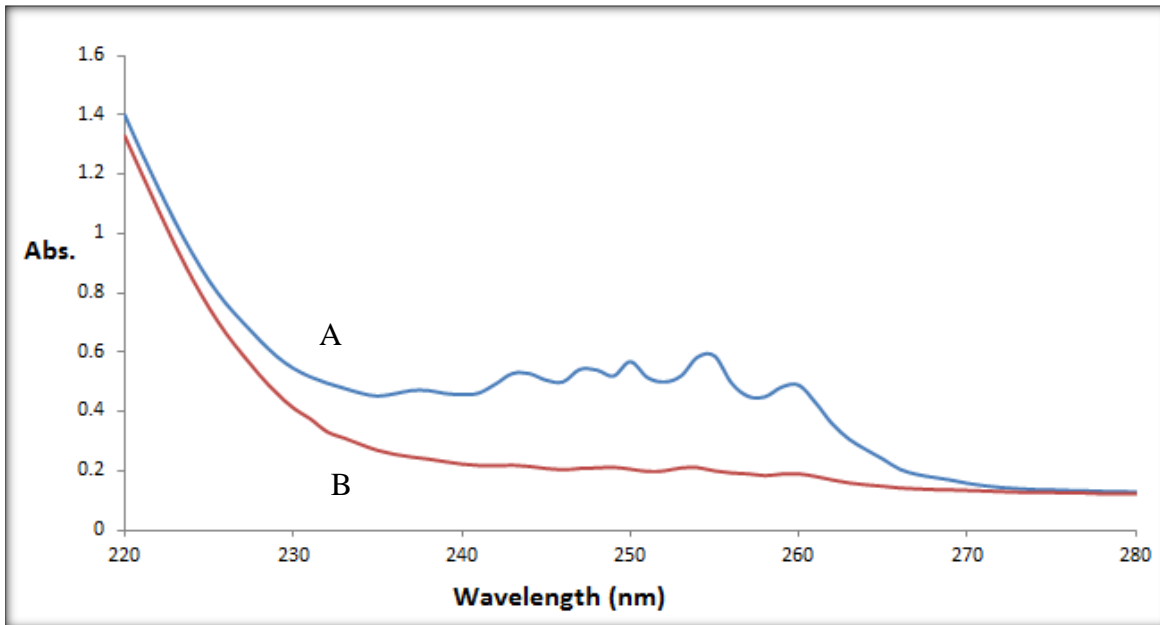


Fig. 4.17: UV Spectrum (A) Actual Sample, (B) Treated Wastewater

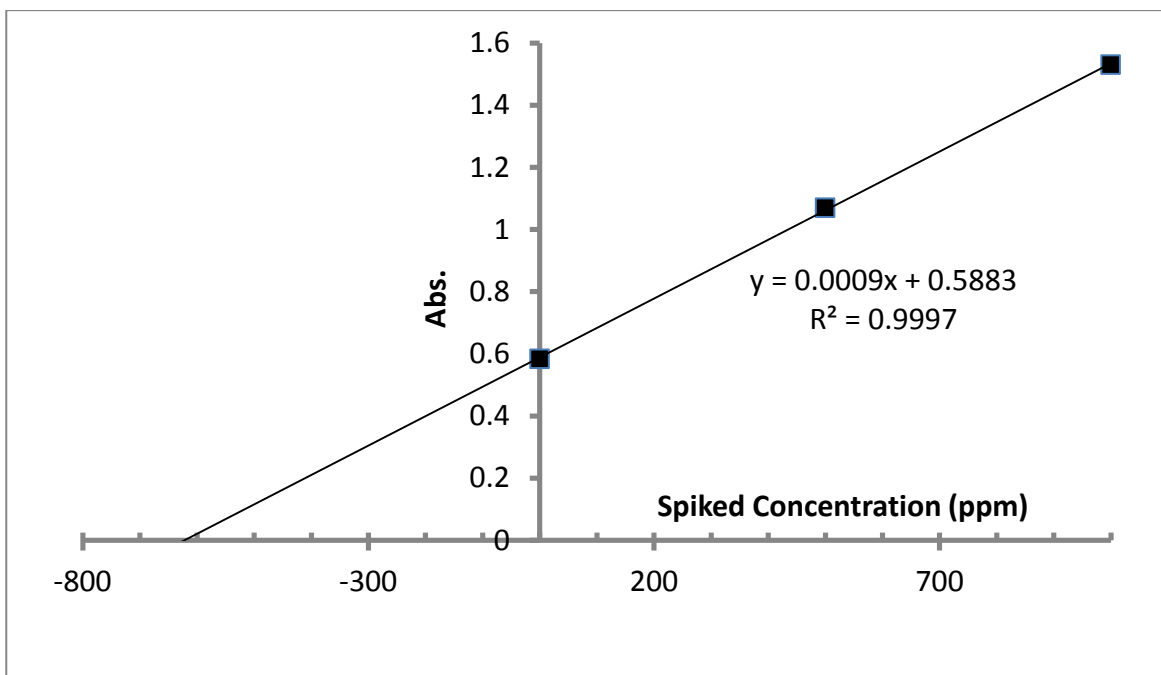


Fig. 4.18: Absorbance vs Spiked Benzene Concentration in Refinery Wastewater

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Following conclusions are drawn from this study:

1. Combination of adsorption and photocatalysis is an effective treatment for benzene removal, from wastewater, down to trace levels.
2. The results showed that the pH has no effect during adsorption.
3. During adsorption benzene removal degree decreases as the flow rate increases.
4. The benzene photocatalysis pathway, under debate since 1984, has been addressed; benzene follows both the close chain (phenolic) and open chain (muconaldehyde) pathways, in parallel.

5.2 Recommendations

Following are some of the suggestions for carrying forward the work reported in this thesis:

1. Photocatalytic degradation of other BTEX compounds i.e. Toluene, Ethylbenzene, and Xylenes may be studied.
2. A photocatalytic reactor may be built to work, continuously, in conjunction with the GAC adsorption column.
3. Based on the data from the GAC adsorption dependence of Benzene, on the flow rate, and the subsequent photocatalytic efficiency of reactor, modeling may be done for maximum throughput.

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