PREPARATION OF WASTE-DERIVED COST-EFFECTIVE CATALYSTS AND ITS APPLICATION THEREOF

THESIS

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Declaration of originality and compliance of academic ethics

I hereby declare that this thesis contains literature survey and original research Work by the undersigned candidate, as part of my "***Master of Chemical Engineering***" studies.

All information in this document have been obtained and presented inaccordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited andreferenced all material and results that are not original to this *w*ork.

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CERTIFICATION

This is to certify that Mr. Debnil Bose, final year Master of Chemical Engineering (M.E) examination student of Department of Chemical Engineering, Jadavpur University (Exam Roll: Regd. No.:123135 of 2013-2017), has completed the Project work titled ***"Preparation of waste-derived, cost-effective catalysts and its application thereof"****under the guidance of Dr. Rajat Chakrabortyduring his Masters Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfillment of the course work.*

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DEDICATION

Special Dedication to my parents, friends and my
Respected project supervisor.

For all your care, support and belief in me.

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INTRODUCTION

[1] INTRODUCTION

[1.1] Development of cost-effective catalysts from waste resources

In recent times, technological advances have rendered creation of several useful products, nevertheless, the life cycles of these products are quite limited; thus, leaving no option for disposition. Unworkable Printed Circuit Boards (PCB) are generally waste materials which if normally disposed can have harmful effects on the environment due to the presence of various toxic materials [1]. In developing countries, because of lack of infrastructure, the e-waste is usually dismantled manually; thereby, releasing non- degradable plastics and persistent hazardous chemicals to the environment which contribute to deterioration of air, water and soil quality. Hence, recycling of WPCB for production of valuable materials through green technologies is of utmost importance in order to reduce obnoxious effects on environment [1-3].

Since waste materials can be broadly divided into various categories, this work would primarily focus on valuable treatment of electronic-wastes (e-wastes) which constitutes a major fraction of waste materials being dumped.According to the Global E-Waste Monitor 2017, India generates about 2 million tonnes (MT) of e-waste annually and ranks fifth among e-waste producing countries, after the US, China, Japan and Germany. In 2016-17, India has treated only 0.036 MT of its e-waste [https://www.downtoearth.org.in/blog/ waste/recycling-of-e-waste-in-india-and-its-potential-64034].Every year, 20–50 million tonnes of waste electrical and electronic equipment (WEEE) are generated worldwide, which could bring serious risks to the human health and the environment[4].

[1.2] Current scenario of e-waste recycling

However, dealing with e-wastes for their effective treatment is not at all simple. Effective management of e-wastes requires cooperation between all stakeholders and technological advancements. In most developed counties, the integrated electronic waste management has been well developed and adopted. For instance, countries like Europe have stringent laws and regulations and high customer awareness related to e-waste management[5].Hence the electronics manufacturers are inclined to be in line with the present rules, regulations and customers' culture. Consequently, it is compulsory to manage the discarded products in a friendly and sustainable manner[6]. On the contrary, most developing countries like India, china have not adapted themselves to the concept of e-waste management where the recycling rate of e-waste is still relatively low. There are many obstacles to recycling e-waste in the developing countries,to be precise mainly the lack of proper recycling infrastructure and lack of national regulations besides the export of e-wastes by developed countries to developing countries such as Nigeria, Ghana, and other parts of Africa and Asia.

[1.3] Recycling methodologies of e-wastes

Various extraction and recycling technologies of metallic and non-metallic fractions from WPCBs have been developed by researchers over the years. These mainly include thermal degradation methods (gasification and pyrolysis), techniques related to use of organic solvents (Dimethyl sulfoxide (DMSO) and N-N Dimethylformamide (DMF)), mechanical treatments using ultrafine grinders, hydrometallurgical treatments, bioleaching methodologies etc. Verma et al. [5] reported significant benefits of using DMF as an organic solvent for extracting particularly the non-metallic ingredients because of its low specific heat, low hygroscopicity, and low viscosity as compared to other solvents. On the other hand, extraction of metallic ingredients from WPCBs using strong acids like HCl, H_2SO_4 and HNO_3 etc. has also been significantly investigated by a number of researchers over the past few years. However, recent trends suggest using mild acidic reagents like acetic acid, citric acid etc.to extract the metallic parts [6-7]. Guo et. al reported that use of acetic acid buffer solution rendered higher leaching of copper as compared to strong inorganic acids like

$H_2SO_4$and HNO_3. In addition, application of certain oxidizing agents like H_2O_2 along with mild organic acidic reagents has also been investigated [8]. Moreover, removal of chemical coatings from WPCB also needs to be figured out to further enhance the separation of metallic as well as non-metallic parts [9].

In recent times, preparation of viable cost-effective catalysts has become a challenging and complex research topic that needs to be addressed and investigated in order to bring significant benefits to the society[10]. Production of catalysts from waste materials could indirectly increase the economic progress of a country specifically developing countries like India. These countries would henceforth need not rely on catalysts being exported from other countries at a higher price. Since, in a country like India, large amounts of waste materials are being dumped or land-filled without having any effective and well-accepted recycling technologies [11]. Hence, several technologies need to be thought out to recycle these waste materials into either usable products or which could indirectly help in the preparation of useful products. So, it becomes necessary to effectively treat these waste materials to prevent environmental deterioration.

Due to low costs incurred in terms of its energy consumption and vast categories of applications it possesses, focus has been shifted for the primary development and recycling of heterogeneous photocatalysts. Due to the primary ability of these photocatalysts to work under visible light, it finds extensive applications in areas such as solar water treatment, cleaner sources of hydrogen generation etc.

However, very few investigations and researches has been conducted in the field of effective preparation of photocatalysts primarily due to the lack of knowledge and interest. It is interesting to note that, significant breakthrough researches is being increasingly conducted in this field thus envisaging wider prospects and applications of photocatalysis in other interdisciplinary areas[13]. This thesis work will focus on the preparation of novel photocatalysts from waste materials viz. WPCB for its effective treatment of lignin derived from rice straw for noble production of vanillin and other commercially useful products. But, before delving into the actual research work conducted on effective preparation of TiO_2doped copper supported glass fiber derived from WPCBs, we need to further address the field of photocatalysis , its applications in this chapter. Several researches conducted in this field will be covered in the chapter of literature review[13-15].

[1.4] Photocatalysis: its principles

Photocatalysis is a highly captivating process having multiple applications, mainly in the fields of pollution removal and fuel production [16-17]. Clear evidence corroborating to this technology is that there has been large number of articles published in this area every year, which exceeded to approximately 4600 works in 2012. This growing interest is rooted in the possibility of using sunlight as the natural source, to promote reactions under very light conditions. On the contrary with most industrial catalytic processes, which predominately require high temperature and elevated pressure, photocatalysis mostly operates at basically ambient conditions provided that an abundantsource of irradiation is available. This fact may has an widespread economic impact not only on several processes, but it also opens up new options for autonomous systems such as self-cleaning surfaces, which can operate with almost no maintenance. However, the quantum yield of many photoactivated processes is frequently lower than 5%, and the energy efficiency is further limited due to the reduced overlap of the solar spectrum with thephotocatalytic range of the most popular photocatalytic materials specifically TiO_2[18]. Such drawback is particularly evident in the case of benchmark TiO_2, despite being the mostcommonly utilizedphotocatalyst inspite of its broad bandgap, which in turnrestricts the absorption of photons to the UVA-B range of the solar spectrum. Accordingly, a maximum of 6% of the energy of impinging sunlight can be effectively utilized using this material [19-20]. This clear disadvantage necessitates investigation of new, and more efficient photocatalysts, active under visible-light illumination[21]. Hence, efficient doping with several metals such as copper and/or other transition metals is therefore necessary, to overcome the disadvantages associated without doping.

An analysis of the published scientific literature indicates that several broad-basedresearches on photocatalytic materials and applications experienceawidespread exponential growth. TiO2 is still by far the most used photocatalyst; in fact it isemployed in most research works as benchmark semiconductor for various applications,especially the commercial material Degussa-Evonik P25[21-23]. During the 1990s, the predominance of TiO_2 (mainly as anatase or anatase-rutile mixtures) in research papers devoted to photocatalysis continuously increased, as it can be observed inFig. 1. During the 2000s, however, the ratio of publications related to binary oxides reachedits peak, representing 60% of the materials investigated, with Titania being one of the components in the 80% of the cases. However, employing several dopants derived from waste materials wasn’t investigated to a considerable extent [24]. The interest on semiconductors activated by visible light to develop solar applications led many researchers to explore new materials, but the promising results obtained with doped-TiO_2, the so-called “second-generation photocatalysts”, particularly with non-metals, maintained the expectations of improved TiO_2based photocatalysts [25].

[1.5] Outcomes of doping a semiconductor

In recent times, application of electromagnetic radiation in preparation of catalysts has been explored by several researchers [25-26]. Previous literature reviews has revealed that usage of electromagnetic radiation showed significant beneficial effects in the preparation of nano catalysts [26]. Application of TiO_2 as photocatalyst has been significantly investigatedbecause of its greater chemical stability, and resistance to photo-corrosion. However, generally TiO_2 has higher band gap as compared to a metal (no band gap as they are metal) such as Pt, Cu. which restricts its ability to absorb light in the visible region. On the contrary, semiconductors such as CuO has band gap lower than that of TiO_2[27]. Hence, efficient doping with a semiconductor or metal as well as using an effective support would enhance the performance of the prepared catalyst to a significant level [27-28]. A brief literature can be cited mentioning this concept. Recently, Barman et al. [47] reported usage of WPCB derived glass fiber-epoxy resin as an effective support for preparation of supported Mo-Cu doped catalyst in efficient production of glucose from jute fiber. Notably, usage of WPCB derived glass fiber as a support for preparation of TiO_2 nano photocatalyst has not been reported till date. Hence, from the aforementioned discussion, it becomes clear that doping with an appropriate semiconductor can effectively and redundantly reduce the band gap of TiO_2 which in turn can then be used as an effective photocatalyst. In addition, use of electromagnetic radiations can well be used in place of sunlight using a photocatalytic lamp which could also briefly reflect the photocatalytic activity of the photocatalyst. Use of electromagnetic radiations although incurs a slightly high energy consumption as compared to sunlight, it could however reduce the overdependencies as well as uncertainties associated with the use of sunlight as the natural source [28].

Previous literature indicates doping of TiO_2 with any transition metal as well as semiconductor to enhance its absorption spectra to a visible range. Li et al. [29] reported the role of TiO2-CuO catalysts in photocatalytic degradation of methylene blue. A very small amount of CuO doping on the surface of TiO_2 could enhance the resultant catalysts photocatalytic activity due to the presence of Ti-O-Cu linkages.

[1.6] Lignocellulosic biomasses: its perspective

Lignin an important constituent of lignocellulosic biomass can be a promising feedstock for production of various valuable chemicals like vanillin, syringaldehyde etc.Rice straw being an abundantly available lignocellulosic biomass can be considered as a promising source of lignin [29]. Lignin can be extracted from lignocellulosic biomass via kraft process, organosolvents extraction, and alkaline process [30-32]. Oxidation of recalcitrant lignin substrates such as kraft lignin, lignosulfonates etc. has been extensively studied over the past. (Lignin oxidation is mostly performed in alkaline reaction media with oxygen as oxidant).Kansal et al.[33] utilized TiO_2 and ZnO catalysts to study the effects of photocatalytic degradation of kraft lignin. The study revealed that the rate of lignin degradation was enhanced at pH 11and oxidant (sodium hypochlorite) concentration of 12.2×10^{-6} M. Another work pertaining to degradation of lignosulfonates was investigated byMachado et al. [35]. The result showed that the addition of H_2O_2 oxidant could increase the degradation efficiency by 173.5 % in presence of TiO_2 (Degussa, P-25).Moreover, it is worthwhile to note that although few works have been reported on photocatalytic degradation of lignin in visible range, however no scientific works using glass fiber supported TiO_2-CuO as visible range photocatalyst has been reported [36].

In addition to its abundant availability and minimization of waste, the lignocellulosic biomass is promising feedstock for production of valuable chemicals mainly because of its low environmental impacts. Aligned with the global endeavour to mitigate climate changes, research and development in many countries are now trying to identify alternative energy sources to minimize greenhouse gas emissions.

Johnson et al. [37] states that amongst the lignocellulosic biomass, grain crops tends to have the highest overall residue ratio (lignin), amounting to as much as double the crop weight and due to this, utilization of straw from grains should have a greater priority in lignocellulosic biomass utilization. Among the grain crop residues, rice straw is one of the most plentiful crop residues in the world and is annually produced at the rate of approximately 731 million tons with Asia as the largest producer that contributes about 667.6 million tons.

Lignin, constituting to about 10–25% of rice straw, is the second most abundant natural polymer [38]. However, the exact composition of lignin in rice straw varies from species to species. The areas in which lignin is applicable include emulsifiers, dyes, synthetic floorings, sequestering,binding, thermosets, dispersal agents, paints, and fuels for treatments of roadways [39-41].Therefore, rice straw has the potential to serve as a relatively inexpensive feedstock for production of biofuel and bio based products because of its abundance and low value for other application [41].Since the composition of lignin in rice straw is quite high compared to other biomasses and also because of its abundant supply, rice straw has been chosen as the feedstock for production of vanillin.

[1.7] Methods of extraction of lignin from lignocellulosic biomasses

In recent times, extraction of lignin from rice straw has been investigated by a number of researchers, incorporating various methodologies. These effective pre-treatments of rice straw are necessary to convert them into highly valued chemicals viz. vanillin, syringaldehyde etc. However,Chemical pretreatment has become one of the most promising methods used to degrade lignin in biomass, Acid solution; alkaline solution and ammonia are solution examples in chemical pretreatment. Alkaline pretreatment is the most effective methods compare with acid and ammonia pretreatment. In alkaline pretreatment, different types of alkaline solution can be chosen to degrade lignin such as NaOH, KOH, $CaCO_3$ and other [42-43].Pretreatment using NaOH is one of the effective pre-treatments, and could digest the hardwood from 14% to 55% by reducing the lignin composition from 55% to 20%

thus proving that NaOH pretreatment is the most effective method to break down the lignin [43].It also states that the parameters that could affect the effectiveness of NaOH pretreatment are the NaOH concentration, ratio of biomass to NaOH solution loading, reaction temperature and residence time[44].

In short, WPCB being an abundant source of metals like copper has been utilized to effectively dope TiO_2so as to enhance its working range to the visible spectrum**.** In addition,WPCB also is an abundant source of glass fiber primarily consisting of silica. Also, electromagnetic irradiation is used in the preparation of this photocatalyst to reduce the uncertainties associated with using sunlight as natural source[45]. Hence this glass fiber is used as a fruitful support for the production of cost-effective TiO_2 doped copper supported glass fiber photocatalyst. The performance of this prepared photocatalyst is then investigated in the eventual production of vanillin, which is a highly valuable chemical, from rice straw, which is abundantly available in Asia.

This work primarily focuses on effective separation of glass fiber and Cu from WPCB using mild organic acid (acetic acid) along with an oxidizing agent (H_2O_2) and application of extracted glass fiber and Cu to produce a cost-effective nano TiO_2-CuO doped glass fiber photocatalyst. In addition, application of near-infrared radiation (NIRR) was also investigated in preparation of nano TiO_2-CuO doped glass fiber catalyst. The efficacy of our prepared novel photocatalyst has been investigatedin rice straw derived kraft lignin (recalcitrant) oxidation process using tungsten-halogen lamp (NIRR).Furthermore, the photo oxidation process was also optimized using Taguchi orthogonal design (TOD) to maximize the vanillin yield (aromatic monomer).

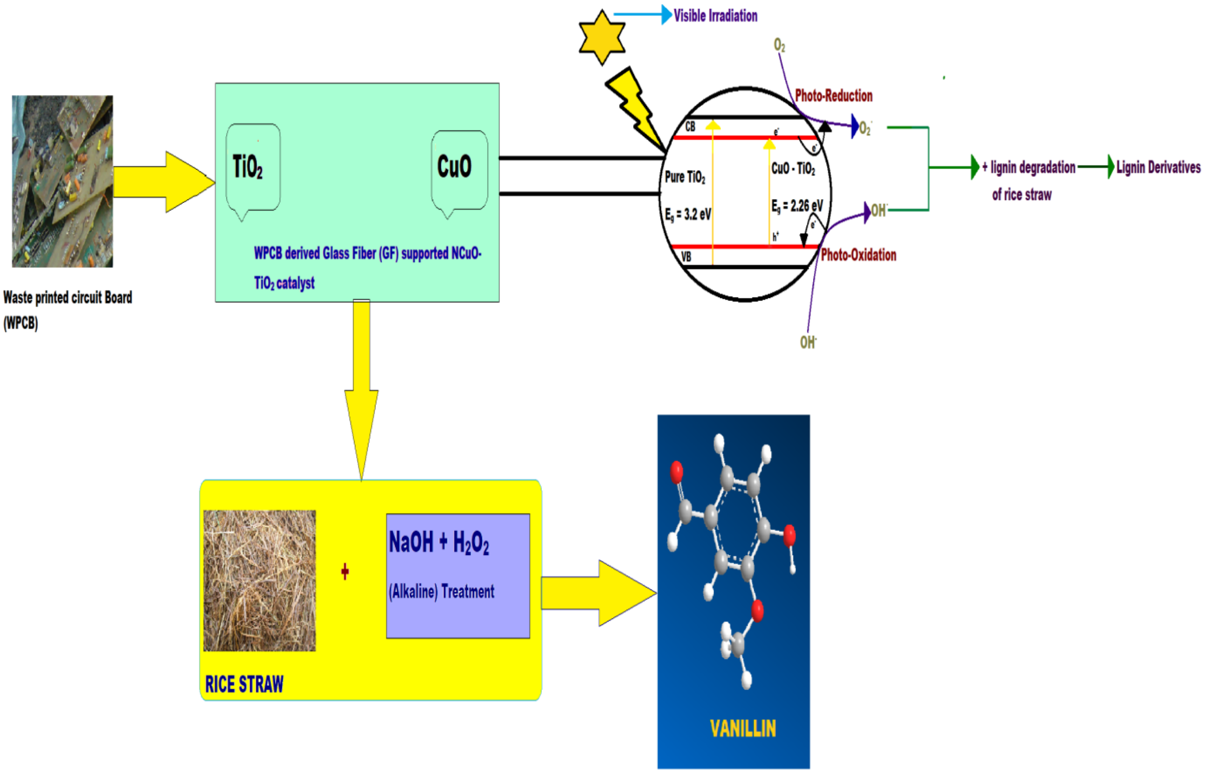

Figure 1: A schematic diagram of the entire experimental study

LITERATURE REVIEW

[2] LITERATURE REVIEW

As already discussed in the previous chapter,WPCBs consists of several metallic as well as non-metallic ingredients. Extraction of these valuable metallic and non-metallic ingredients from WPCBs is a rather challenging as well as error-prone task, primarily because of the complexities associated with extracting the valuable components from WPCBs and discarding the toxic components. In this chapter, relevant methodologies pertaining to extraction of valuable components will be highlighted and discussed in detail. Afterwards, several relevant works related to preparation of cost-effective photocatalysts will also be presented with primary focus on various technologies and processes involved in preparation of photocatalysts from e-wastes. Subsequently, several relevant works associated with the application of these photocatalysts in extracting and isolating the kraft lignin derived from several lignocellulosic biomasses especially rice straw and converting them into various valuable products viz. vanillin, syringaldehyde etc. [31-32].

Extraction of valuable ingredients from WPCBs can be accomplished in several ways. The most predominant and effective methods include thermal degradation methods, hydrometallurgical separation for extraction of metals, mechanical treatment andchemical treatment methodologies using organosolvents [33]. If we delve further into literature, it would become clear that chemical pretreatment methods prove to be the most viable and promising technique primarily due to the less consumption of energy, and lesser green-house gas emissions. All these important methodologies of extraction are discussed in detail in this chapter.

[2.1] Different methods of extraction from e-waste resources

Thermal degradation method constitutes mainly of pyrolysis and gasification.

[2.1.1] PYROLYSIS

Over recent times, researchers have demonstrated pyrolysis as a promising thermal technique for conversion of e-wastes into valuable products. Before pyrolysis, the WPCBs comprising of large and vain components like capacitors, solder joints, insulators, resistors etc. are generally separated through a pre-treatment procedure; wherein, separation of the dispensable components can be accomplished via manually disassembling or treating these components at higher temperatures. The resultant WPCBs obtained after pre-treatment, or directly collected and classified in its nascent stage are then pyrolysed at higher temperatures. The reaction temperatures of pyrolysis can usually range from 200 °C to several thousand degrees. However, the optimal temperature conditions at which pyrolysis occur generally range from approximately 500-700 °C [36]. Through pyrolysis technique, several non-metallic fractions of PCBs are pyrolysed to obtain various valuable compounds like Pyro-oils viz. phenol, furans and pyro-gases like CO_2, H_2O etc., and solid residues viz. char, tar etc. from which various materials can be retrieved. In addition, most PCBs contain valuable amount of glass fibers and other solid products which can be separated and recycled for re-use. As can be observed from Table 1, Jie et al. [37] pyrolysed waste derived PCBs in a non-catalytic quartz tubular reactor with nitrogen as carrier gas at pyrolysis temperatures ranging from 300 to 700 °C. It was reported that a temperature of at least 500 °C was required to ensure complete pyrolysis of PCB resulting in 78% yield of carbonaceous solid residue, 9 % liquid oilsand 13% gaseous products. The gases mainly comprised of C_1-C_4 hydrocarbons, CO and CO_2. Conversely, Quan et al. [38] obtained a significantly high yield (solid-76.8, liquid-17.8 and gas-5.4), specifically higher amount of pyro-oils with a requirement of lower temperature and time, signifying low energy requirement and operating cost due to the presence of Ammonium Hydroxide as catalyst for synthesis of phenol-formaldehyde resin from pyrolysis oil, which evidently highlights the advantages of catalytic pyrolysis over conventional/non-catalytic pyrolysis. Besides, this process also generated lower amount of toxic compounds.

Comparatively, Vasile et al. [39] obtained various products from pyrolysis of PCBs in a catalytic semi-batch operation at an optimum temperature of 540 °C. They reportedly obtained a significantly high liquid yield of 23%, the liquid obtained comprises of approximately 5 wt% of aqueous fraction, in addition to pyrolysis oil. Moreover, due to the presence of DHC-8 and metal loaded activated carbon as catalyst, the rate of catalytic hydrogenation of pyrolysis-oils vehemently increased as compared to conventional pyrolysis.

[2.1.2] Gasification Route:

Recently, production of valuable products through steam and atmospheric gasification of waste PCB is an emerging technology nowadays and can be used as an effective replacement of pyrolysis methodology. Although retrieval of metals and production of valuable solid, liquid and gaseous products from waste PCB through pyrolysis route is routinely common nowadays, however it has been significantly reported by several researchers that Pyro-oils derived from pyrolysis of waste PCB produces several toxic compounds comprising of benzofuran, cresol, thymol etc. which can have severe harmful impacts on the environment. Hence certain supplementary stages are required in addition to pyrolysis to further separate or discard these toxic compounds from Pyro-oils. A 2 stage decay step of waste PCB comprising of pyrolysis and catalytic treatment was therefore reported by several researchers. This proves to be an effective and precious methodology for separation of toxic compounds from resultant pyro-oils obtained by pyrolysis [39].

As evident from table 2, it can be observed that Salbidegoitia et al. [42] investigated catalytic steam gasification of Waste Derived Phenolic Boards (WPB) in presence of eutectic ternary carbonates which was processed at temperatures of 823-948 K for efficient hydrogen production using a TG analyser. It was reported that unsupported nickel metal powder or small nickel pieces in molten carbonate could be used as an effective catalyst for hydrogen production from steam gasification of WPB. Moreover, it was also observed that a significant decrease in char (from nearly 49% to 23%) formation in the presence of unsupported nickel as catalyst and a subsequent increase in the carbon yield of gases. On the other hand, yamawaki et al. [43] reported significant decrease in the production of toxic compounds like brominated dioxins from atmospheric gasification of Waste electrical and electronic equipments under proper operating conditions. In addition, it could also be reported that the gasification process was done at significantly higher temperatures of over 1200 °C, followed by shock cooling of the gases at temperatures fewer than 200 °C. Although this process significantly reduced the production of toxic compounds, but higher reaction temperature resulted in significant energy consumption. Moreover, Zhang et al. [44], investigated steam gasification of epoxy board samples (EBS) in the presence of eutectic carbonate products having activation energy of 122 KJ/mol. It was reported that subsequent higher yields (60.8 %) of gaseous products consisting mainly of H_2 and CO_2 could be obtained. A 2 step degradation processes was reportedly followed for gasification of EBS comprising of an initial fast pyrolysis followed by steam gasification of resultant char obtained from pyrolysis for better H_2 production. Although extraction of valuable ingredients from WPCBs by thermal degradation methods is actually feasible, however, these ingredients extracted cannot be recycled further when compared to chemical recycling methods in addition to being cost-effective.

[2.1.3]Mechanical Route for WPCB Valorisation:

Mechanical treatment for WPCBValorisation indicates the recycling techniques for valorisation and recovery of non-metallic ingredients without bringing any changing its physical state. In this process, the WPCB are finely grinded and are subsequently passed through several physical separation systems. In recent times, physical processes involving magnetic separation, corona electrostatic separation, eddy current separation, floatation etc. have been significantly reported by a number of researchers [48-49]. These recycled Non-Metallic Fractions (NMF) obtained from mechanical treatment of WPCB are either added to new materials or are converted to several new valuable materials for their effective and efficient commercial usage. Rajagopal et al. [50] reported that theNMF (char) derived from WPCB can be effectively convertedto activated carbons which can be subsequently used for fabrication of supercapacitors, specifically because of its developed surface area properties and high capacitance values.

Although, mechanical treatment significantly reduces generation of solid wastes, significant changes or improvements are necessary here. This is because the non-metallic fractions of WPCB contain several toxic compounds which are not really discarded by means of physical treatment. In addition, the presence of various components in these non-metallic fractions may drastically reduce the efficiency of physical treatment which is generally not observed in newer and trending technologies like thermal, chemical (using organic solvents) etc.

[2.1.4] Chemical Route for WPCB Valorisation:

This review article would mainly focus on extracting and recycling the non-metallic fractions of waste printed circuit boards using non-aqueous solvents. Nowadays, various cost-effective non-aqueous solvents have been used for treatment of the non-metallic ingredients comprising mainly of epoxy resins and therefore valorize WPCB at temperatures above Glass Transition Temperature (Tg). Zhu et al. [45] investigated usage of a solvent 1-ethyl-3-

methylimizadolium tetrafluoroborate for effective treatment of brominated epoxy resins (BER) at optimum temperatures of 260 °C and maintaining a reaction time of 20 minutes respectively. However, it is to be noted that the regeneration of the aforementioned solvent was done at 300 °C which is quite high. As a result, this drawback made the procedure highly energy-consuming which subsequently resulted in higher production costs. Moreover, complete and effective separation of products was also not accomplished.

These drawbacks led the aforementioned researcher to shift towards utilization of cheaper solvents which could be seen from their next work Zhu et al. [46] in which a polar solvent Dimethyl Sulfoxide (DMSO) was reportedly utilized. This resulted in complete separation of the NMI at an optimum temperature of 170 °C. This process also resulted in lower yields of toxic conditions because a lower temperature (below 300 °C) doesn't promote the degradation of epoxy resins present in WPCB. In addition, several researchers have also reported the use of N, N- Dimethyl Formamide (DMF) to degrade the brominated epoxy resins [24]. Verma et al. [48] reported significant advantages of using DMF because of its low specific heat, low hygroscopicity, and low viscosity as compared to other solvents. In addition, utilization of an ionic liquid such as $[EMIM^+][BF^-_4]$ have also been significantly utilized by a number of researchers [26]. Several reports have cited that ionic liquids results in higher degradation of epoxy resins with subsequent increase in temperature. Hence, from these literature reviews, we can conclude that utilization of non-aqueous solvents is highly effective in WPCB valorisation and hence this field is required to be explored for development of cheaper, less toxic non-aqueous solvents [45].

[2.2] Development of energy-intensive and environment friendly metal extraction methods from WPCB

Various metallic fractions present in WPCBs are covered by a chemical coating. This makes metal recovery a highly challenging and complicated task because of this chemical coating that inhibits the contact between a lixiviant and the metal. Therefore, the primary task is to remove this chemical coating to the best extent possible. In recent times, several literatureshave suggested that a mechanical–physical method can be widely employed to treat waste PCBs and separate the metallicingredients [19-20]. One importantliability of physical separation processes is a significant loss of valuable metals. The reasons for theselosses include the insufficient liberation of metals due to their intimate association with plastics, the generationof fines during size reduction and the inefficiency of separation processes for metal recovery fromfine fractions [20]. Therefore, it is necessary to find an alternative process for discarding the chemical coatingsfrom PCBs without any loss of metals. Adhapure *et al.*[23] used sodium hydroxide to remove the chemicalcoating from WPCB. A similar process have been used in the present study to remove the chemical coating because of the complete ability of NaOH to remove completely remove the chemical coating apart from being cost-effective. In addition, this alkaline treatment also helps in removing metals like aluminium and tin to a considerable extent since the main objective in this study is to extract the copper from WPCB to prepare the TiO_2 copper doped glass fiber supported photocatalyst.

There has been several works reported on hydrometallurgical recovery for extraction of copper from WPCBs.The factors that affect the selection of an appropriate methodare the leaching reagent system (e.g., Cl−, SO42−), concentration of metal(s), impurities, and economy ofthe process. However, a very limited number of articles is available on the purification and recovery ofindividual metals from PCB leach liquor [24]. It is interesting to note here that hydrometallurgical treatmentprovides more flexibility during the upscaling and control processes [47-48]. Previous literature reveals thatHNO_3, HCl, and H_2SO_4 solutions along with acids having mild acidic strength viz. acetic acid ($C_2H_4O_2$), citric acid ($C_6H_8O_7$) are often used as leaching agents in hydrometallurgical treatments. However, several studies related to hydrometallurgical treatments for extraction of metals from WPCBs reveals that although use of strong acids like HNO_3, HCl etc. greatly leaches and removes the metals present in WPCBs, these acids are highly corrosive and hence can dissuade the main objective of extracting metals from WPCBs as reported by the works of jadhav et al. [21] and jadhav et al. [22]. In addition, H_2SO_4although being an attractive leaching agent due to its low cost, it has poor metal leaching capacity and it forms a water insoluble species when it reacts with Pb present in WPCB. Again, use of HNO_3 in metal leaching from WPCBs is also feasible. However, evolution of nitrous oxides makes the process hazardous. Inaddition, after leaching, the HNO3 must be completely removed from the solution prior to metal separation,which makes the process complex and increases the cost [26].Moreover, both nitrate and sulfate ions have different chemical characteristics, acting withlower strength, thereby lowering the metal dissolution rate. Thus we can conclude citing previous literatures that HCl, $C_2H_4O_2$,$C_6H_8O_7$ proves to be the most suitable reagents for extraction of metals. However, as already mentioned previously that HCl is highly corrosive and therefore use of corrosion resistant equipment is necessary which greatly increases the production cost. Hence acetic acid ($C_2H_4O_2$) and($C_6H_8O_7$) proves to be the highly effective reagents for metal leaching specifically due to their mild acidic strength and less corrosive nature. In fact, their use is environmentally benign because the leaching is carried out at moderately acidic conditions, and they are biodegradable also [49].

To discuss further, use of an oxidizing agent like H_2O_2 along with an organic acid having mild acidic strength would greatly enhance the rate of hydrometallurgical separation or leaching of metals from WPCBs as reported from the work of jadhav et al. [21].Li et al. [25]

usedH_2O_2 alongwith citricacid for leaching of metals from waste lithium cobalt batteries.It is worthwhile to mention here that acetic acid along with H_2O_2as oxidizing agent has been used in this study for preparation of the aforementioned highly effective photocatalyst.

[2.3] Synthesis of effective and cost-intensive doped solid photocatalysts

On having delved into several extraction methodologies, important literatures pertaining to viable preparation of supported photocatalysts along with the use of effective doping agents will be discussed. TiO_2 by itself acts as a good photocatalyst because of its excellent resistive property to chemical and photochemical corrosion in aggressiveaqueous environments anddue to its activity towards both lightand water. It is also less expensive than many other photo-sensitivematerials [50].However, pure TiO_2 is not photosensitive under illumination by visible light (wavelength from 400 to 800 nm).

Interestingly, young et al. [52] mentioned that TiO_2 photocatalyst (undoped)can only absorb near-UV range of approximately 388 nm or less.The band gap for the anatase form is E_g= 3.2 eV, and this why it isexcitable only in the UV range. This part of the spectrum accountsfor only 3–4% of solar radiation [53] and use of UV radiation alone forphotocatalytic splitting of water to hydrogen is not an economicallyfeasible option. Therefore, in order for TiO_2 to harvest the energyfrom the visible region of sunlight, the absorption edge of TiO_2must be shifted to this region. It is well known that when a semiconductorphotocatalyst such as TiO_2 is exposed to radiant energyof suitable wavelength, an electron in the valence band jumps tothe conduction band leaving a ‘hole’ behind. However, once in the excited state, the conduction band (CB) electron and the valenceband (VB) hole can recombine very quickly releasing energy in theform of unproductive heat or photons without undergoing anyphotoreaction. This phenomenon explains the slow hydrogenproduction by photocatalytic water splitting using TiO_2 alone [54].In order to overcome this problem, numerous studies have beenconducted to enhance the photocatalytic activity of TiO_2 by incorporatingan adequate amount of a transition metal oxide such asthat of Fe, Zn, Cu, Ni and V [53-54]. Doping of these metalsessentially lessens the band gap of TiO_2 for the photo-excitationand simultaneously reduces the recombination rate of photogeneratedelectron–hole pairs.

[2.4] Development of cost-effective photocatalysts from waste resources

Production of highly valuable and cost-effective photocatalysts from waste resources is one of the emerging and challenging area in the field of chemical engineering that are being immensely investigated by significant number of researchers. Recently,chakraborty et al. [55] used hydroxyapatite (hap) support derived from waste button for preparation of an effective hap supported TiO_2photocatalyst. The efficacy of the photocatalyst was investigated in its ability to adsorb methylene blue. It was reported that the degradation efficiency of the photocatalyst was 92.9 % after 2 cycles of reuse. It came to 84.5 % even after 10 cycles of reuse which showed the high stability of the photocatalyst due to immobilization of TiO_2nanoparticles. Pradhan et al. [56] utilized highly cost-effective bio-hydroxyapatite supported mesoporous Cr heterogeneous catalyst derived from ram bone. The efficacy of the catalyst was studied in production of bio-diesel from used frying mustard oil. A significantly high FAME yield (96.85 %) of biodiesel was observed by use of the waste-derived catalyst in presence of infrared radiation as compared to FAME yield (40.22 %) obtained from conductive heating system. In addition, the energy consumption was reported to be 25 % lower compared to conventional heating system. The utilization of ram-bone amongst several waste resources has opened up new challenging for preparation of highly cost-effective and energy intensive catalysts. Furthermore, chakraborty et al. [57] employed a novel and cost-effective Ni−Ca−hydroxyapatite heterogeneous solid acid catalyst with pretreated waste fish scale (PWFS) as an effective support for sustainable production of biodiesel having fame yield of 59.90 %. It was also reported that on further transesterification of the unreacted triglycerides present in the product stream resulted in 98.40 % of biodiesel. Moreover, Xiu et al. [58] utilized copper extracted from waste printed circuit boards for development of Cu_2O/TiO_2nanocomposites by electrokinetic process. The performance of the nanocomposites was investigated in photocatalytic degradation of methylene blue. The results indicated that the presence of Cu_2O/TiO_2nanocomposites with copper loading of 4.53 wt. % significantly enhanced the photocatalytic degradation of methylene blue as compared to commercial P25. In addition, presence of copper oxide on TiO_2surface increased the rate of absorption of oxygen in the presence of light thus reducing the probability of electron-hole recombination thus enhancing the effect of its photoactivity. However, optimal presence of CuO on TiO2 surface is necessary which could otherwise screen the photocatalyst from its irradiation source if present in excessive amount.

Thus, a careful glance on these few mentioned literatures significantly highlights the role of waste resources in its use as highly effective support for preparation of cost-effective and energy intensive heterogeneous solid catalysts. All these previous works reported that the utilization of waste resources as supports for production of catalysts could significantly enhance the production of valuable chemicals and fuels from waste raw materials. In addition, they are highly effective in enhancing the kinetics of various chemical reactions reported, which in turn increases the performance of various reactions viz. photocatalytic., chemical etc. Thus it can be easily concluded that use of waste resources especially e-wastes for development of catalysts effectively prevents them from being incinerated or land-filled which in turn leads to production of a greener environment and also increases the socio-economic conditions of a country. Furthermore, waste resources contain several harmful ingredients which can be removed if utilized properly. As already mentioned previously, e-wastes especially waste printed circuit boards contains several toxic materials like brominated retardants and other bromine containing compounds which can be easily discarded if these waste resources are used in preparation of catalysts and other fields. It could also reduce the emission of greenhouse gases and produce a sustainable environment.

[2.5] Utilization of glass fiber as effective support for production of cost-effective catalysts

Several literatures have suggested the use of glass fiber as an effective support for preparation of cost-effective photocatalysts. Ao et al. [59] developed glass fiber supported TiO_2photocatalyst for effective purification of indoor air. It was reported that the aforementioned photocatalyst showed higher levels of photodegradation of NO and BTEX at typical indoor ppb levels as compared to P25. Yang et al. [60] utilized a new type of glass fiber-supported Pt complex catalyst for hydrosilylation of styrene and triethylsilane. The results showed the high selective reactivity of the complex catalyst to the hydrosilylation reaction between styrene and triethylsilane. Thus we can safely conclude from previous literatures that glass fiber can be used as an effective support for development of highly performance-effective photocatalysts. Moreover, glassfiber (GF) can be selected as a support, considering there areamounts of hydroxyls on its surface, and that’s why it hasbeen more widely used in polymer composites than theSiO_2. In addition, glass fiber mainly comprises of silica particles having very high surface area which can further enhance the photocatalytic efficiency of a reaction. Thus use of glass fiber as an effective support could bring formidable results and open up new gears in the field of catalysis.

[2.6] Effects of electromagnetic radiations on development of solid photocatalysts

Also, it is absolutely necessary to mention here that use of electromagnetic radiations especially infrared radiations in the preparation of doped photocatalysts has been widely investigated several researchers particularly because it has the ability to significantly reduce the processing time compared to conventional hydrothermal treatment. In addition, it serves as an efficient cleaner energy source to enhance the performances of several reactions and also in extraction of several value-added chemicals. Escobedo et al. [53] reported near infrared radiations are more efficient than middle and far infrared irradiations, being easily controllable and with the quality of having a fast responding heat source. So, to be precise, near infrared radiations provides a rather greener technique for efficient heating of materials as per requirement, along with overcoming all the disadvantages associated with using conventional heating techniques. Several previous literatures have cited the use of infrared radiations especially NIRR in wide varieties of applications, primarily in the preparation of photocatalysts.More recently, barman et al. [47] reportedly developed a highly effective glass fiber epoxy resin supported copper doped Molybdenumcatalyst under NIRR radiation and its performance was reportedly assessed in the effective production of glucose and other products from pretreated jute fiber. Approximately 75.84 % of glucose was produced by employing NIRR treatment compared to using conventional hydrothermal treatment in which only 63.16 % of glucose was produced. Yoong et al. [52] reported usage of near infrared radiation for preparation of an effective cooper doped TiO_2 catalyst and its performance was studied in its ability to produce hydrogen under visible light. It was reported that the Cu-Tio2 catalysts prepared by wet impregnation method and complex precipation method with a copper loading of 10 % produced hydrogen amounting to 8.5 mL h^{-1} and 4.0 mL h^{-1} at calcination temperatures of 300 ℃respectively. Hence, in this study, based on the previous observations,NIRR was employed for effective preparation of a photocatalyst.

Copper doping has been less investigated compared to other transitionmetals mentioned above. Also it appears from the limitedliterature reports available on copper doping that the doped catalystshave been tested only in the UV or near-UV range of radiation[55]. Thus, the principal objective of thework is to develop Cu/TiO_2 photocatalysts for production of valuable materials from rice strawfrom water under irradiation with visible light. Since it was intendedto shift the absorption edge of TiO_2 to the visible region, thephotoreaction was conducted using a 500-W tungsten halogen lamp tosimulate visible light.

[2.7] Production of valuable chemicals from lignocellulosic biomasses

Nowadays, production of valuable chemicals from lignocellulosic biomass like rice straw has been a matter of interest amongst several researchers. Several researches have sought to improve the nutritivevalue and pulp quality by chemical, physical, andenzymatic treatments to remove lignin and decreasecellulose crystallinity. Moreover, processessuch as auto-hydrolysis, alkaline cooking, andsteamexplosion require substantial energy inputin the formof heat and tend to generate toxic sideproducts. Another drawback typical of conventionaltreatments includes loss of the hemicelluloseswith the oxidized products such as aliphaticcarboxylic acids. Among the chemical treatments,oxidative treatments are directed to principallyaffect the degradation of lignin, whereas lytic agents are expected to cleave the lignin–carbohydrate linkages. Previous literatures have shown that coupling of the hydrolysisand the oxidative treatment proved to achievebetter delignification efficiency. [56]

[2.8] Different pathways for extraction of lignin from lignocellulosic biomasses

Since this major work is based on the extraction and simultaneous isolation of lignin into several value-added chemicals, a lot depends on the source and species from which lignin is derived. However, Lu et al. [64] reported that the major primary ingredients in lignin consists of G (guaicyl), S (syringyl), H (p-hydroxyphenyl) units, commonly called G/S/H ratios as detected by H-NMR analyzer. These primary constituents are incorporated into lignin from three lignols namely p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [61]. Tarabanko et al. [62] reported that softwood lignin possesses simple composition consists primarily ofguaiacylpropane structural units. However, hardwood lignin consists, in addition of syringylpropane units in addition to those already mentioned. In addition, rice straw, a primary ingredient in production of value added chemicals, is the major, constituent of lignin amongst lignocellulosic biomasses as reported from the findings of sun et al [66]. Hence, rice straw has been used in this study primarily because of the huge fractions of lignin it possesses.

[2.9] Thermal oxidation of lignocellulosic biomasses using waste resources

Lignocellulosic biomasses can be oxidized using a homogeneous orheterogeneous catalyst to obtain vaue-added chemicals which can be further treated to generate biofuel andvalue-added chemicals [66]. However, in recent years, heterogeneousacid catalysts have been observed to be advantageousover homogeneous catalysts owing to convenience of productseparation, less corrosiveness, and minimal waste stream generation [67]. Takagaki et al. [68] investigated usage of a water-tolerantHNbMoO6 catalyst for the production of glucose fromsaccharides. A study revealed that approximately 0.35 g of the aforementioned catalyst can produce about 24.1 mmol g−1 glucose from sucrose in 1 h and 373 K, whereas 6.6 mmol g−1 glucose was produced using thecommercial Amberlyst-15 catalyst. Another work reported byHegner et al.26 revealed that $FeCl_3$ supported onamorphous silica could effectively generate glucose with a maximum yieldof 9% from cellulose at 463 K in 24 h. Thus, it can be wellperceived that although supported metal oxide acid catalystsare efficient, nevertheless, hydrolysis of biomasses requires severereaction conditions. Hence, usage of supports would provide the catalysts to work better under drastic conditions along with making itself resistant to photo-corrosion and chemical sintering as reported by several studies. Accordingly, several researchers investigatedthe application of electromagnetic radiations (350 W)[65] along withultrasonication (750 W) [58] to augment the chemical reaction;still these require high energy input, which in turn makes theoverall process economically less favored.

Figure 2: A general image of a rice straw collected from local paddy fields in India

[2.10] Alkaline peroxide treatment in lignin oxidation

Alkaline peroxide treatment is the most followed pathway for simultaneous extraction and isolation of lignin from rice straw primarily may be because of its environmental friendly approach and less corrosive a=when compared to using acidic treatment. Several literatures have cited the use of an alkaline peroxide pathway for lignin extraction not only from rice straw but also from other lignocellulosic biomasses. Alkaline peroxide treatmentmay offer a more practical and environmentallybenign approach toward the improvement ofthese shortages incurred by selective delignification. Hydrogen peroxide has beenunderstood to react with ligninunder specific conditions and has been widelyused for many years to bleach high-lignin woodpulps [69]. More recently, some European mills haveinitiated the commercial productionof bleached kraft pulps in which at least one sequence consists of extensive peroxide delignificationstage[71]. Lachenal et al.[73]reported that within temperatures of80–120°C under the aid ofalkaline conditions, hydrogenperoxide will delignify kraft pulps along with partialdegradation of the cellulose. However, the increasing demand for high energy and reagent inputs diminishesthe appeal of applying this process to agriculturalresidues. Gould et al. [75] reported that approximatelyone-half of the lignin and most of the hemicellulosespresent in agricultural residues such aswheat straw and corn stover are instead solubilized whenthe residue is treated at 25°C in an alkaline solutionof hydrogen peroxide. The delignificationreaction is most productive when the ratio of hydrogenperoxide to substrate is at least 0.25 (w/w)and the pH is maintained at 11.5 as observed from the findings of li et al [77]. Furthermore,several literatures have reportedthat the hydroperoxide anion (HOO^{-}), formed in the alkalinemedia, are the principal active species in hydrogenperoxide bleaching processes. It was also reported that the major characteristic of this anionis that it is a strong nucleophile that, preferentially attacks ethylenic and carbonylgroups present in lignin, when bleaching is initiated and continued. As a consequence, suchchromophores as quinones, cinnamaldehyde, andring-conjugated ketones are rapidly converted to nonchromophoricspecies under the alkaline pretreatment conditions.On the other hand, hydrogen peroxide is absolutelyunstable in alkaline conditions and readily decomposesto more intensive and active radicals such as hydroxyland superoxide anion radicals (HO$^{\bullet}$, O2$^{-\bullet}$),which greatly involves itself in the delignifying mechanism[78].

The advantages of delignification with hydrogenperoxide as the oxidizing agentinclude low investment cost and theaccompanying strong bleaching effect. In addition,the degraded or solubilized lignins obtained duringthe alkaline peroxide treatment under mild conditionsare both theoretically interesting for ligninstructural studies and also studies related to lignin degradation products as well as commercially interestingfor the cosmetics, adhesions, and pharmaceuticalindustries. In other words, delignificationusing alkaline peroxide cangreatly envisage the utilizationof by-products and therefore a more completeuse of the raw material.

AIMS AND OBJECTIVES

[3] AIMS AND OBJECTIVES:

The aims and objectives of this project are highlighted below:

[1] Preparation of supported metal photocatalysts derived from natural resources.

[2] Characterization of the waste derived supported photocatalysts.

[3] Performance analysis of this developed photocatalyst in lignin degradation from rice straw.

[4] Comparative analysis of the effects of electromagnetic radiation and conventional hydrothermal treatment on the developed photocatalysts.

[5] Optimization of the reaction using Taguchi Orthogonal Design.

[6] Characterization of the products procured from lignin degradation of rice straw.

MATERIALS AND METHODS

[4] MATERIALS AND METHODS:

[4.1] Materials: For this study, WPCBs were procured from a local scrap market in kolkata, India. Hydrogen peroxide, vanillin, acetic acid, titanium isopropoxide, N-N dimethyl fluoride purchased from Merck were of analytical grade. The rice straw was collected from a local paddy field.

[4.2] Preparation of Glass Fiber (GF) support: All the unnecessary parts viz. conductive tracks, RAM etc. was dismantled and removed manually from the WPCB. After that, the WPCBs were grinded in an ultrafine grinder viz. drum sander through a200 mesh screen. After that, the ferrous materials present in WPCB were removed by using a wet magnetic stirrer. Heavy particles consisting of tin, aluminium, zinc, lead etc. were partially removed from glass fiber by sedimentation. Further, concentrated alkaline treatment (with 100 ml of 10 M NaOH solution at 80 °C for a time period of 3 hrs) was conducted for the resultant solution toremove remaining materials like tin, zinc, aluminium etc. through dissolution. Following this, the resultant mixture consisting of glass fiber, epoxy resin, copper etc. were washed and oven-dried at a temperature of 60 °C. After that, DMF (Di-Methyl Formamide) was added to the resultant dried powder to remove epoxy resin from it. Subsequently, copper was completely extracted by treating the sample with 1M acetic acid and10 ml of H_2O_2 (30 %w/w in H_2O) solution over2 h. Finally, the resultant solution consisting of glass fiber was collected. The extracted glass fiber was further treated with ultrasonicator for size reduction, which was then hot air oven dried (60 °C) and used as a support for catalyst preparation.

[4.3] GF-NCuO-TiO_2catalyst preparation: Different copper-titanium nano-gel was prepared by varying the titanium precursor (Titanium Isopropoxide [Ti (OCH $(CH_3)_2)_4$]) loading (5, 7.5, 10 wt. % per g of GF) with fixed amount of Cu precursor (Copper acetate [$Cu(CH_3COO)_2$]; derived from WPCB) loading (2 wt.%). This was achieved by stirring the

Ti (OCH $(CH_3)_2)_4$with ethanol and $Cu(CH_3COO)_2$ at a temperature of 70 °C using tungsten halogen radiator (150 W; 0.36–2 µm) for a time period of 5 h.After that, a measured amount of GF (as support) was mixed with the nano gel and stirred for 2h. The mixture was left to age for 24 h and then dried in a hot-air oven. Eventually, the oven-dried powder was calcined at a temperature of 500 °C for 4 h. The prepared thermally activatedcatalysts was termed as GF-NCuO-TiO_2^5 (TiO_2 loading 5 Wt. %), GF-NCuO-$TiO_2^{7.5}$ (TiO_2loading 7.5 Wt. %), GF-NCuO-TiO_2^{10} (TiO_2 loading 10 Wt. %). In order to study the effect of tungsten halogen radiation system on the prepared catalyst, the optimum GF supported catalyst (CGF-NCuO-$TiO_2^{7.5}$)was also prepared by means of conventional hydrothermal method using a heating mantle (500 W) at optimal TiO_2 loading (7.5wt.%).

[4.4] Lignin Extraction from Rice Straw: The procured rice straw was thoroughly washed with hot water and was grinded to uniform fine particles (mesh 200). Afterwards, lignin was extracted and purified from rice straw by following the works of Watkinset al., 2015 [35]. Finally the extracted organosolv lignin was further washed with distilled water and dried over P_2O_5.

[4.5] Reactor configuration and simultaneous extraction and oxidation of lignin: Photocatalytic degradation of organosolv lignin extracted from rice straw was performed in a closed tungsten–halogen radiator (150 W; 0.36–2 µm) assisted batch reactor (THRBR) system. The photocatalytic reaction was carried out in a one necked flask (250 ml) by stirring (400 rpm) a 50 ml solution of extracted lignin in a mixture of H_2O_2 and water (1% w/w in H_2O) at a concentration of 0.30 mg ml^{-1}.Thereafter temperature was maintained by a PID temperature controller and the photocatalytic reaction was monitored by varying four independent process parameters i.e. reaction temperature (γ_T), time (γ_t), catalyst concentration (γ_C) and titanium precursor loading (γ_{Ti}) (Table 1).

The effect of four process factors on lignin degradation process were assessed andoptimized through nineexperimental runs derived from L9 TOD (Minitab Inc. USA for Windows 7)(Table 2).The optimal processfactors corresponding to maximum lignin degradation (L_{THRBR}) were determinedthrough evaluation of signal-to-noise (S/N) ratios (employingthe "larger is better" criterion) (Equation 1) and analysis of variance(ANOVA).

$$\frac{S}{N} = -10\log(\frac{1}{n}\sum_{m=1}^{n} 1/L_{THRBR,m}{}^{2}) \qquad (1)$$

Where, n is the number of experimental runs performed at aparticular set condition (Table 2), m is the number of replications, and $L_{THRBR,m}$ is L_{THRBR} corresponding to run n.

In order to assess the efficacy of GF-NCuO-TiO$_2$ catalysts, photocatalytic lignin degradation process was also conducted using conventionally prepared CGF-NCuO-TiO$_2^{7.5}$ catalyst at other TOD derived optimized condition. The photocatalytic lignin degradation percentage was evaluated using UV-Vis Spectroscopy (PerkinElmer, Lamda-365) by comparing thedifference of absorbance at 205 nm of lignin solution before and after reaction.

Factors	Units	L_{-1} Level	L_0 Level	L_1 Level
Temperature	°C	50	60	70
Precursor Loading	Wt. %	5.0	7.5	10
Catalyst Concentration	Wt. %	2.5	5.0	7.5
Time	min	30	50	70

Table 1: Self-governing process parameters for oxidation of extracted lignin

Trial no	**γ_T(°C)**	**γ_{Ti} (wt. %)**	**γ_C(wt.%)**	**γ_t (min)**	**$L_{THRBR}(\%)$**	**Std.**	**SN ratio**
1	50	5.0	2.5	30	40.12	± 0.02	32.0672
2	50	7.5	5.0	50	58.16	± 0.14	34.5117
3	50	10	7.5	70	66.93	± 0.11	39.0617
4	60	5.0	5.0	70	71.24	± 0.16	37.0545
5	60	7.5	7.5	30	78.39	± 0.21	35.7733
6	60	10	2.5	50	68.91	± 0.28	37.8028
7	70	5.0	10	50	89.76	± 0.15	36.0541
8	70	7.5	2.5	70	75.31	± 0.08	37.3163
9	70	10	5.0	30	69.43	± 0.14	36.8309

Table 2:TOD Layout for extracted lignin degradation process using GF-NCuO−TiO_2Catalysts

[4.6] Characterization of the Prepared Catalyst: XRD analysis of the calcined GF support and the prepared catalysts were performed using a Cu Kαsource coupled with an Inel CPS 120 hemispherical detector and the infrared spectra of the corresponding samples were performed using FTIR-SHIMADZU (Alpha) ranging from 400 to 4000 cm^{-1} at 2θ ranging from 10° to 90° at a scanning speed of 1° min^{-1}. The specific surface area, pore size and pore volume were quantified by BET and BJH methods using Quantachrome Instruments, Nova 4000e. For BET analysis, the samples were initially pre-treated and degassed (temperature

150 °C) for removal of moisture from the surface. In addition, TGA analyses of calcined GF support and the prepared catalysts were conducted in a Perkin-Elmer TGA analyser (Pyris Diamond TG/DTA) comprising of nitrogen atmosphere (20 mL/min) in which temperature was increased from 30 to 900 °C at the rate of 15.0 °C/min. The acidity of the samples was measured through NH_3-TPD analysis (Quantachrome Instruments), TPR win v2. Furthermore, high resolution transmission electron microscopy (HR-TEM) analysis of the requisite samples were performed in a JEOL 3010 instrument with a UHR pole piece at an accelerating voltage of 300 kV. Thelattice spacing of the crystallites was determined with the help of a "GATAN digital micrograph" through processing the micrographs. XPS analysis of the optimal catalyst was conducted to determine the binding energy of Ti 3d and Cu 2p of the optimal catalyst. Photocatalytic properties of the CGF-NCuO-$TiO_2^{7.5}$and the optimal GF-NCuO-$TiO_2^{7.5}$ catalyst were analysed by using Perkin Elmer LAMBDA 950 UV-VIS-NIR Spectrophotometer in the range of 200-900 nm having tungsten halogen lamp as light source. Moreover, efficacy of the tungsten halogen radiation system over conventional thermal system in preparation of titanium-copper nano gel (at optimum loading, 7.5 wt. %) was also analysed in UV-vis spectrophotometer (Perkin Elmer LAMBDA 950).

The photocatalytic lignin degradation percentage was evaluated using UV-Vis Spectrophotometer (PerkinElmer, Lamda-365) at 280 nm wavelength. The products obtained from oxidative treatment of extracted lignin form rice straw were detected and eventually quantified using high-performance liquid chromatography with a UV detector (Perkin Elmer200 Series) along with a C-18, 9 μm column. A water and acetonitrile mixture (2:5) was used as a mobile phase having a flowrate of 0.8 ml min^{-1} and the products were quantified at a detection wavelength of 280 nm with a column temperature of 30°C.

[4.7] Characterization of Rice Straw and lignin oxidation products: After simultaneous extraction and oxidation, vanillin concentrations were measured by HPLC analysis.The oxidated product compositions obtained from lignin were analysed by HPLC with UV detector (Perkin Elmer 200 Series) along with 300×7.8 mm Bio-Rad HPXP, 9 μm column at a flow rate of 0.6 ml min^{-1} of 0.005 M of sulfuric acid (mobile phase). The constituent's concentrations in oxidized lignin sample were quantified from the calibration plots of respective standard constituents. Compositional analysis of the rice straw was done according to the NREL LAP method.

RESULTS AND DISCUSSION

[5] RESULTS AND DISCUSSION:

[5.1] Optimal Process Conditions of extracted lignin degradation process: Individual ranks ofprocess parameters based on their effects on the response variable (L_{THRBR}) have been presented in Table 4. The process parameter corresponding to the maximum Δ-value has higher effect on L_{THRBR} whereas higher S/N ratio represents the optimum level for that process factor. Thus, from Table 4, it may be concluded that L_1 of γ_T(70°C), L_0 of $\gamma_{\boldsymbol{Ti}}$ (7.5 wt. %), L_1 of $\gamma_{\boldsymbol{C}}$ (7.5 wt. %), and L_0 of $\gamma_{\boldsymbol{t}}$(50 min) were the optimum process values rendering maximum lignin degradation. Moreover, ANOVA analysis (Table 3) for photo-catalytic lignin degradation process revealed that the degradation temperature ($\gamma_{\boldsymbol{T}}$) and catalyst concentration ($\gamma_{\boldsymbol{C}}$) were statistically significant process parameters at 95% confidence level (p-value < 0.05).

Table 4represents ranks of the process parameters based on relative significance (Temperature> catalyst concentration>time>precursor loading) on the response variable (ω_V) using ‘higher the better’ criterion for S/N ratios. Notably, the process parameters corresponding to larger Δ-value exhibited (Table 4) superior effect on the response variable (ω_V) compared to other parameters. Hence the process parameter having Δ corresponding to its maximum value has been ranked as 1.

Additionally, the maximum S/N ratio values corresponding to a particular level of the process parameters (Table 2) which are represented by the asterisk marks, implied that maximum ω_V (89.76mole %) could be attained at 70°C (temperature), 7.5 (catalyst concentration), 50 min (time) and 7.5 (precursor loading)for US-NIRR.

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Regression	4	1340.86	335.215	7.52	0.038
Temperature (γ_T) (°C)	1	800.18	800.184	17.95	0.013
Titanium precursor Loading (γ_{Ti}) (wt. %)	1	2.87	2.870	0.06	0.812
Catalyst Concentration (γ_C) (wt. %)	1	429.09	429.091	9.63	0.036
Time (γ_t) (min)	1	108.72	108.715	2.44	0.193
Error	4	178.32	44.580		
Total	8	1519.18			

Table 3: Analysis of variance (ANOVA) of process factors affecting lignin degradation process

Level	**γ_T(°C)**	**γ_{Ti} (wt. %)**	**γ_C(wt.%)**	**γ_t (min)**
L_{-1}	34.62	36.06	35.46	35.59
L_0	37.24	36.90*	36.39	37.04*
L_1	37.81*	36.70	37.82*	37.03
Delta	3.19	0.84	2.36	1.45
Rank	1	4	2	3

Table 4: Δ value and S/N Ratio of Process Parameters for lignin degradation process

[5.2] Individual and Interactive Effects of Process Parameters on lignin degradation: Figure 4demonstrates the individual parametric effects onL_{THRBR} (based on S/N ratio), keeping other factors at theiroptimum levels. It could be observed that the degradation of lignin is enhanced by increasing theγ_T as higher temperature facilitates the generation and transportation of charge carriers between TiO_2-CuO surface and reaction medium which eventually accelerates the production of hydroxyl radicals [36]. Furthermore, the degradation process was also performed up to 90 °C, to understand the influence of temperature on L_{THRBR}. However, upon additional increase in temperature, the degradation rate started to decrease which might be due to accelerated thermally-assisted decomposition of H_2O_2. Figure 4 also demonstrates an enhanced L_{THRBR}at higher $\gamma_C$due to greater availability of catalyst's active sites. On the other hand, Figure 4 also reveals that lignin degradation rate could be augmented through increasing γ_{Ti}up to 7.5 wt. %; whereas, above 7.5 wt. %, a negative impact onL_{THRBR} was observed.Above 7.5 wt. % ofγ_{Ti}, the increased nanoparticle size resulted in blocking of the GF support's pore and drastically reduced the overall surface area of the catalyst (BET analysis and XRD). Moreover, the increased particle size has also reduced the lignin adsorption rate [37] on catalyst surface which clearly corroborated well with lignin degradation results. Notably, it is observed that on increasingγ_t up to 50 min degradation of lignin increases considerably. However, further increment of γ_t had little effect onL_{THRBR}.

Parametric interaction for the photocatalytic lignin degradation process has been depicted in Figure 3. Interaction between catalyst concentration and temperature (maintaining two other parametersat the optimum level) revealed that an increment in catalyst concentration resulted in higher lignin degradation (L_{THRBR}) [Figure 3b] at all levels of temperature, which clearlysuggested that the prepared GF-NCuO-TiO_2catalyst immensely facilitated the lignin degradation process. A similar trendwas observed for all values of reaction time. On the other hand, Interaction between catalyst concentration and titanium precursor loading has an antagonistic effect on L_{THRBR} because of the formation of larger nanoparticles at higher precursor loading during catalyst preparation Figure 3d.

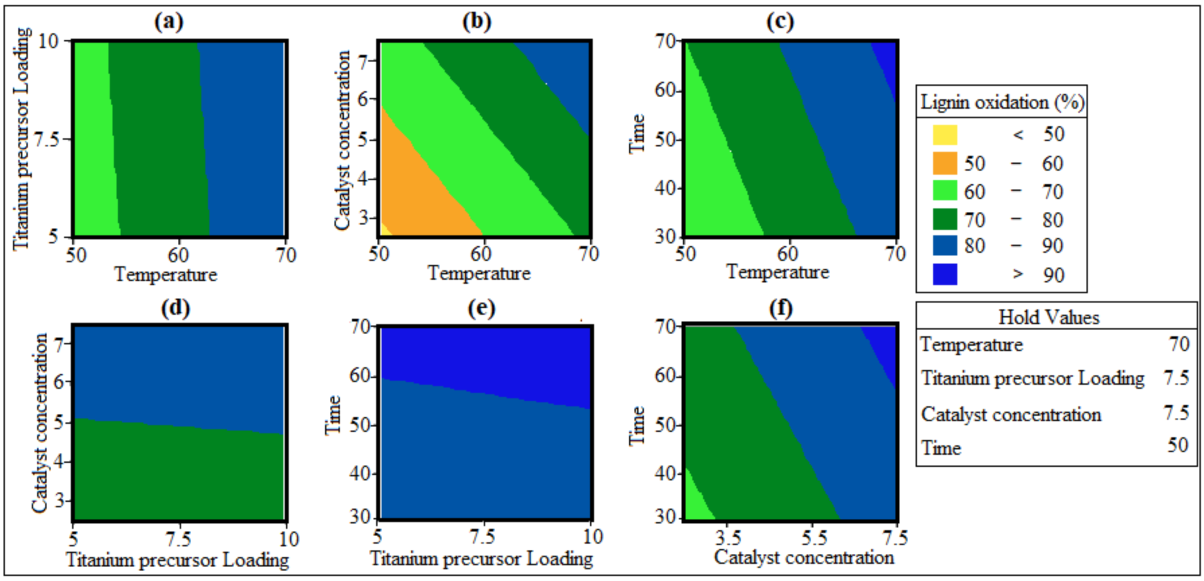

Figure 3: Interaction plots for the lignin oxidation process parameters

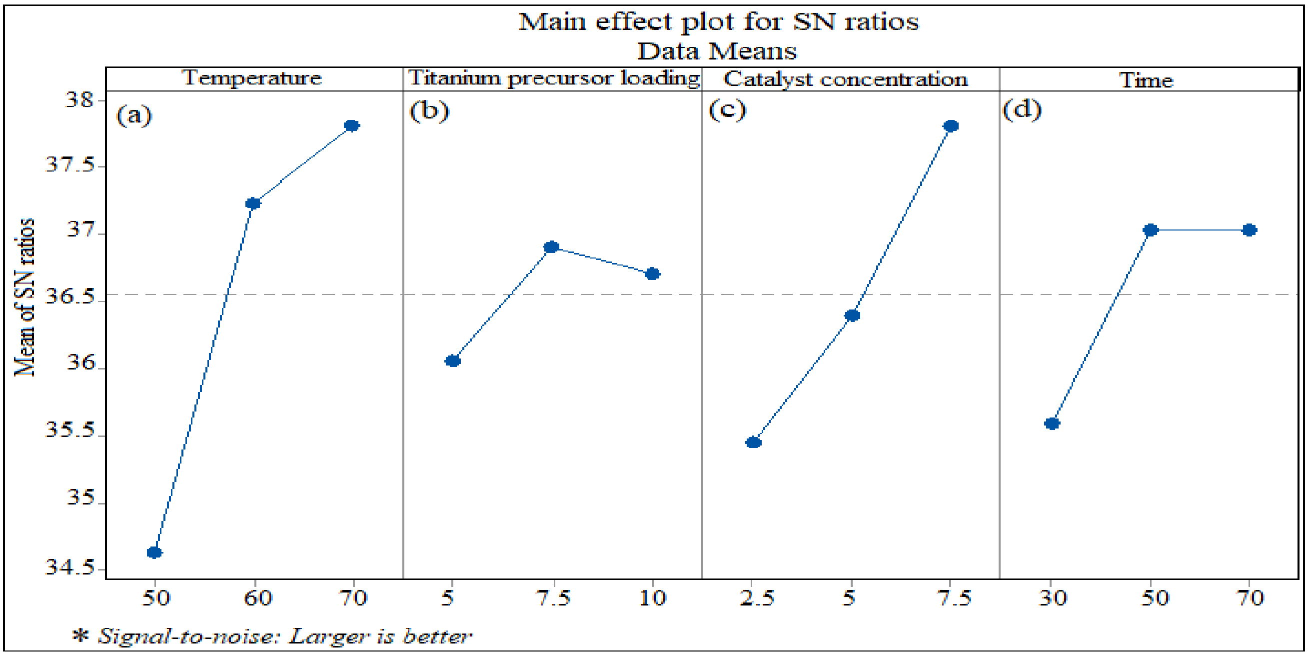

Figure 4: Main Effect plot for S/N ratio for lignin degradation process

[5.3] Catalyst Characterization:

[5.3.1] FTIR Spectrum: Figure 5 depicts the Fourier Transform Infrared (FTIR)spectrum of GF support and catalysts (GF-NCuO-TiO_2^{5}, GF-NCuO-$TiO_2^{7.5}$, GF-NCuO-$TiO_2^{10}$and CGF-NCuO-$TiO_2^{7.5}$). FTIR analyses of the catalysts and support showed a broad peak at 3447.62 cm^{-1} due to the presence of strong OH stretching mode of absorbed water [38]. Peaks corresponding to wavenumbers of 1401.83 $cm^{-1}$and 463.09 cm^{-1}showed the presence of Ti-O-Ti stretching modes in the prepared catalysts [39]. Furthermore, spectra of all catalysts also exhibited peaks at 957.55 cm^{-1}which corresponds to vibration of Ti-O-Si. It could also be perceived that the peak intensity increases gradually with increasing loading of TiO_2 precursor [40]. In addition to this, vibrational modes at667.99 cm^{-1}could be assigned to the Cu-O stretching in Cu-O-Si bonds in the prepared catalyst [41].

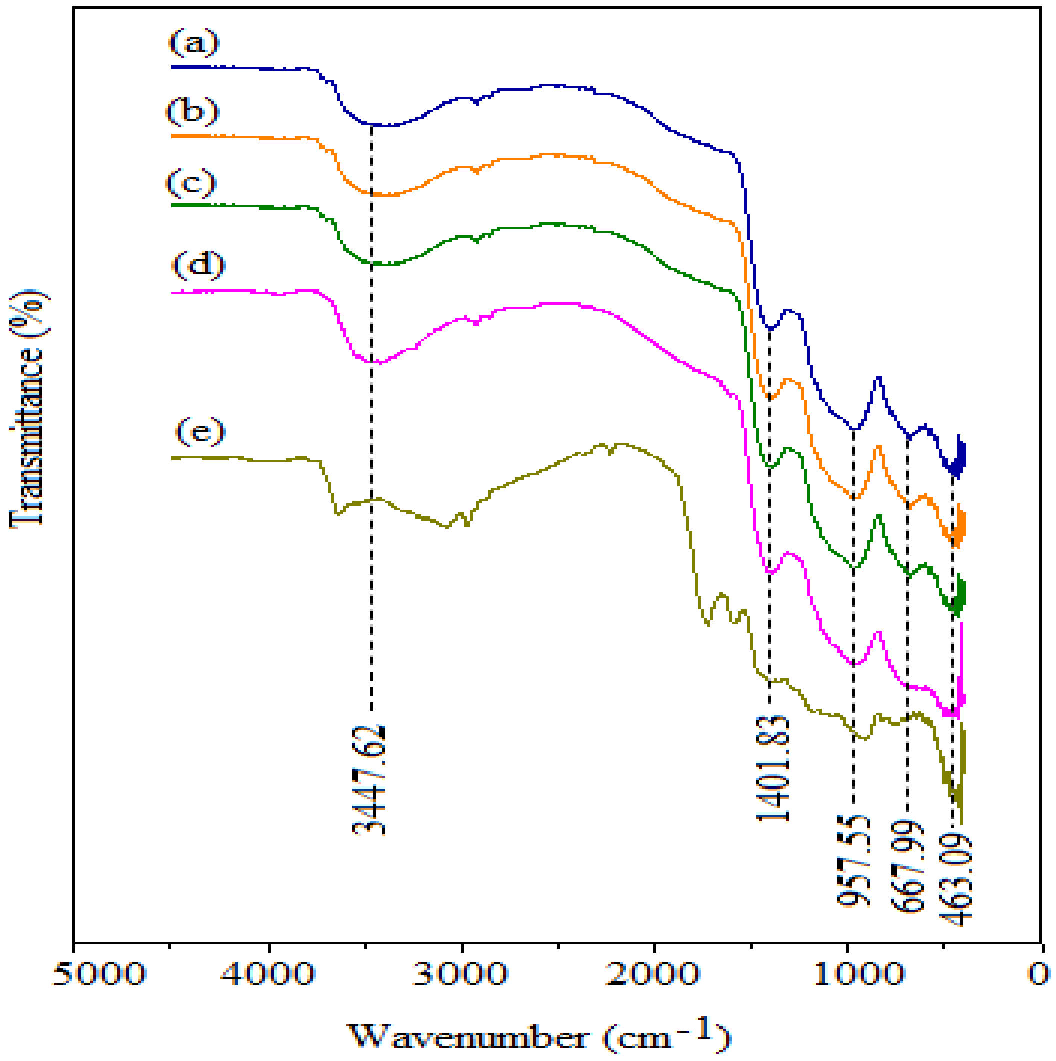

Figure 5:FTIR analysis of (a) GF-NCuO-TiO_2^{10}, (b) GF-NCuO-$TiO_2^{7.5}$, (c) GF-NCuO-$TiO_2^{5.0}$, (d) CGF-NCuO-$TiO_2^{7.5}$ and (e) GF

[5.3.2] X-Ray Diffraction: Figure 6 depicts the X-Ray diffraction pattern of the prepared support as well asthe prepared catalysts i.e. GF support, NCuO-TiO_2^{5}, GF-NCuO-$TiO_2^{7.5}$, GF-NCuO-TiO_2^{10} and CGF-NCuO-$TiO_2^{7.5}$(Table 5). The XRD diffractogram of all the catalysts showed peaks at 32.442°, 35.550°, 38.694°, 58.160°, 74.972°(JCPDS card no.45-0937) corresponding to crystalline phase of copper oxide and peaks at 25.260°, 37.790°, 48.10°, 62.135°, 70.305°(JCPDS card no. 21-1272; JCPDS card no. 21-1276) representing the crystalline phase of titanium dioxide. Furthermore, peaks representing the SiO_2crystal (26.602°, 50.069°, 54.838°and 65.621°) (JCPDS card no. 39-1425) were also found in all the catalysts ascribing the presence of GF. It is worthwhile to mention here that with increasing concentrations of Titanium Isopropoxide precursor, the peaks corresponding to TiO_2strongly increased in the GF-NCuO-TiO_2 catalyst. The diffraction pattern of GF support depicts the presence of Na_2O-Al_2O_3-SiO_2 (21.092°) (JCPDS Card no. 48-0038) and MgO (42.949°) (JCPDS Card no. 89-7746) revealing the constituent phases of the GF support.

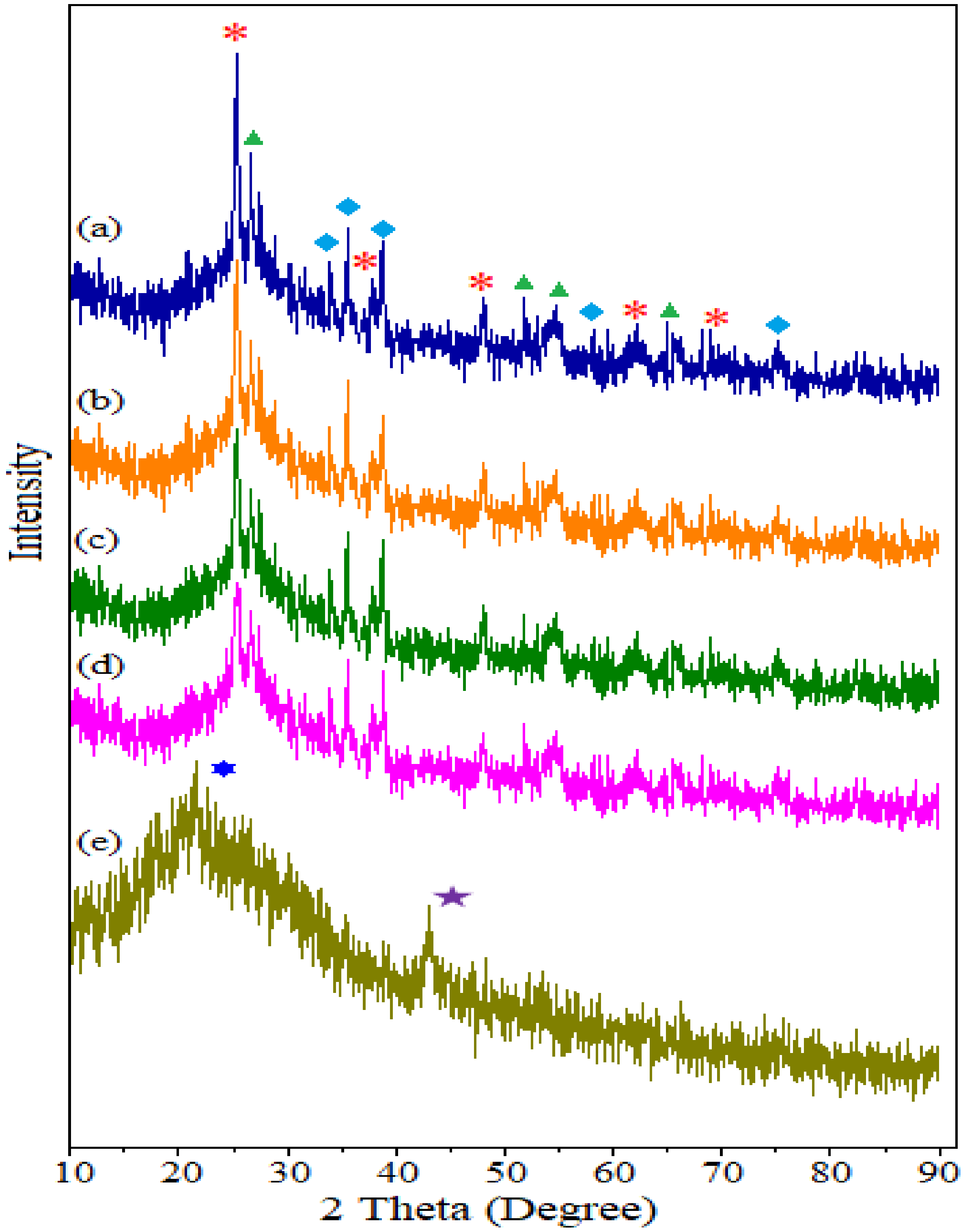

Figure 6:XRD pattern of (a) GF-NCuO-TiO_2^{10}, (b) GF-NCuO-$TiO_2^{7.5}$, (c) GF-NCuO-$TiO_2^{5.0}$, (d) CGF-NCuO-$TiO_2^{7.5}$ and (e) calcined GF powder

[5.3.3] NH_3-TPD: NH_3-TPDanalyses of calcined GF support and prepared catalyst (Figure 7) indicated that within the temperature range of 100-900° several weak (signal maxima at 180-200°C), medium (signal maxima at 350-390°C) and strong (signal maxima at 730-780°C) acidic sites were distributed for all the prepared catalysts, whereas only strong acidic site (signal maxima at 590°C) was observed for calcined GF support. Moreover, with increase in titanium precursor loading, it could be observed that NH_3 desorption peak increased in lower temperature zone while depicting lower peaks in higher temperature zone, which clearly indicated that the concentration of weak acidic sites increases with increment in titanium precursor loading [45]. Notably, weak acidic sites could be beneficial for lignin depolymerisation as strong acidic sites could promote the re-polymerisation of degraded lignin [46].

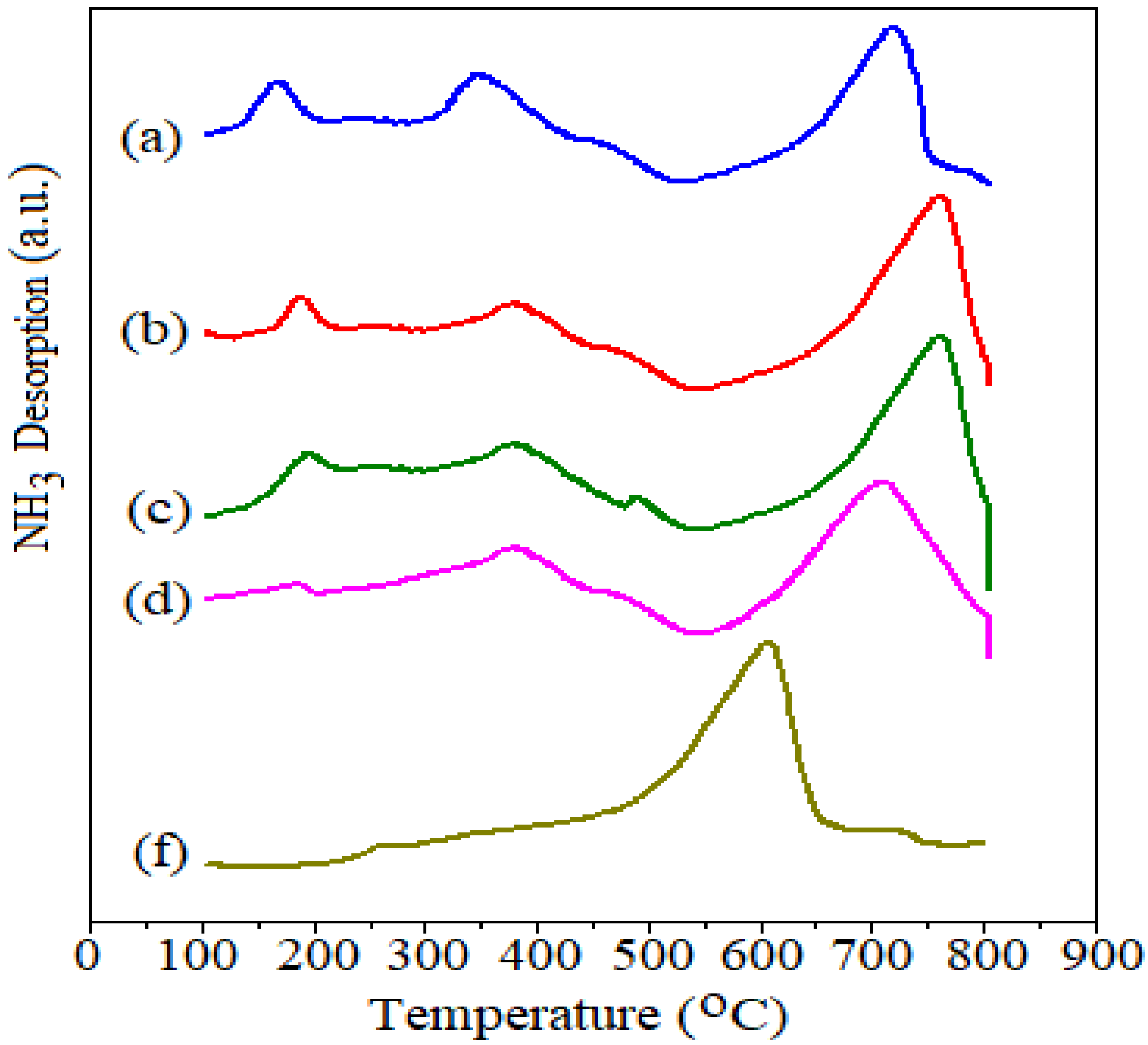

Figure 7:NH3-TPD analysis of**(a)**GF-NCuO-TiO_2^{10} (b)GF-NCuO-$TiO_2^{7.5}$ (c)GF-NCuO-$TiO_2^{5.0}$ (d) CGF-NCuO-$TiO_2^{7.5}$ (e) GF

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[5.3.4] BET: The specific surface area of the prepared catalysts and the support was assessed through BET (Brunauer-Emmett-Teller) analysis. From Table 5, it could be observed that thespecific surface area of the prepared catalyst were a little lower in cases of both GF-NCuO−$TiO_2^{5.0}$(62.682 m^2/g) and GF-NCuO−$TiO_2^{7.5}$ (62.107 m^2/g)catalysts compared to the GF support (67.318 m^2/g) whereas for GF-NCuO−TiO_2^{10} (49.622 m^2/g), a substantial decrease in specific surface area was observed. Evidently, at a higher precursor loading, the size of the nanoparticles increased (Table 5) which partially blocked the GF support's pore and rendered lower overall surface area of the GF-NCuO−TiO_2^{10} catalyst. Theadsorption isotherm of the optimal catalyst GF-NCuO−$TiO_2^{7.5}$ corroborated with type II isotherm (IUPAC) (Figure 8)implying unrestricted multilayer adsorption. BJH method was employed to calculate the GF-NCuO−$TiO_2^{7.5}$ catalyst pore volume (0.132, 0.141 cc/g for GF) andmodal pore diameter (5.47, 5.76 nm for GF) (inset of Figure 8) representing mesoporous catalyst. Furthermore, Figure 9 revealed that 15.61 % micropores and 84.39% mesopores were present in the optimum GF-NCuO−$TiO_2^{7.5}$ catalyst. Reasonably the mesoporous structure of GF-NCuO−$TiO_2^{7.5}$ favoured diffusion of larger lignin molecules [3.5 nm] [50] inside the pore structurewhichaugmented the lignin degradation reaction.

Catalyst	**BET analysis**			**NH3-TPD (mmol NH_3/g catalyst)**	**XRD**
	Surface area (m^2/g)	Total pore volume (cc/g)	Pore diameter (nm)		Average particle size (nm)
GF-NCuO−$TiO_2^{5.0}$	62.682	0.134	5.53	1.724	5.42±0.02
GF-NCuO−$TiO_2^{7.5}$	62.107	0.132	5.47	1.872	6.31±0.01
GF-NCuO−TiO_2^{10}	49.622	0.122	4.91	1.890	10.29±0.01
CGF-NCuO−TiO_2^{10}	42.170	0.113	4.68	1.532	20.38±0.02

Table 5: Effects of Ti Precursor Loading on specific surface area on the Prepared Catalyst

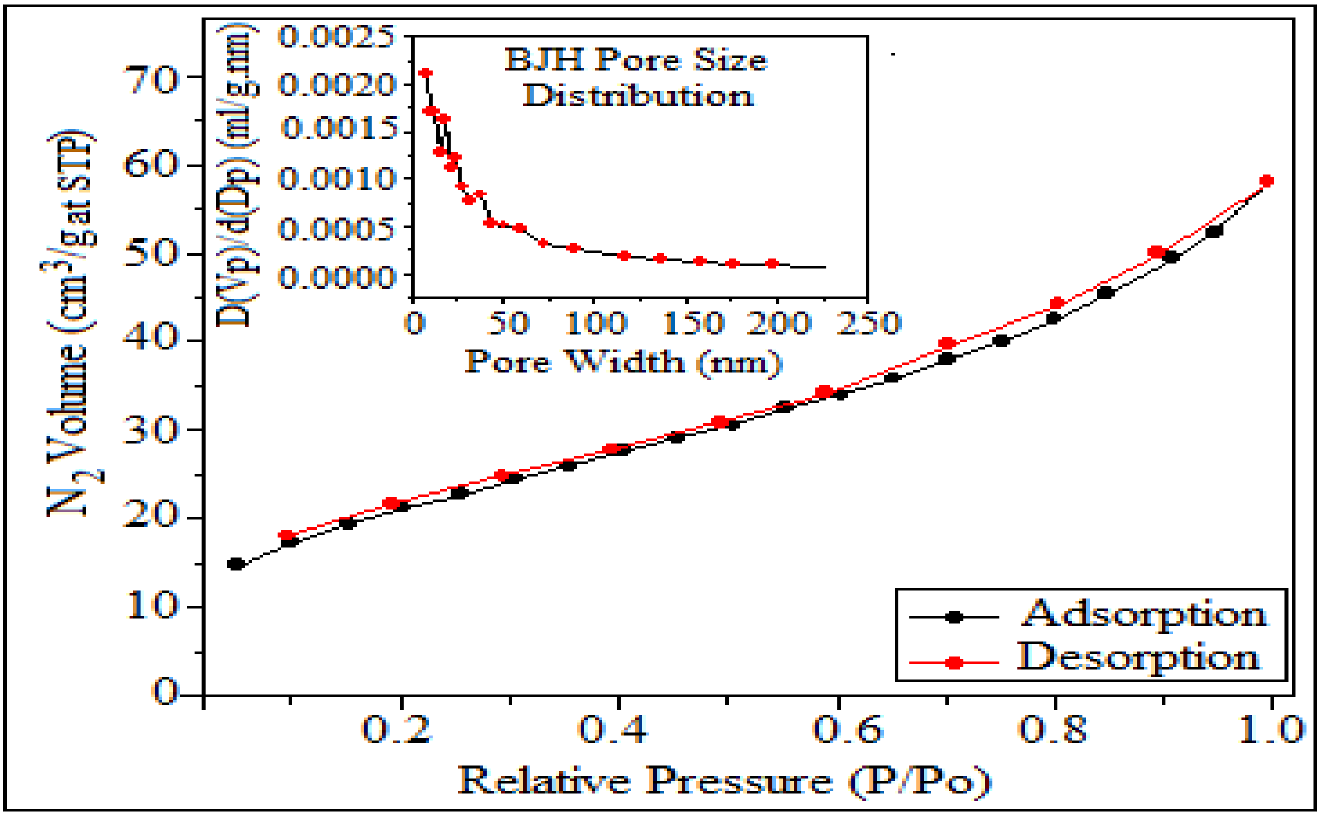


Figure 8: Pore volume vs relative pressure (P/P0) of the optimum catalyst NCu−$TiO_2^{7.5}$ [inset: DFT pore size distribution for the determination of modal pore diameter].

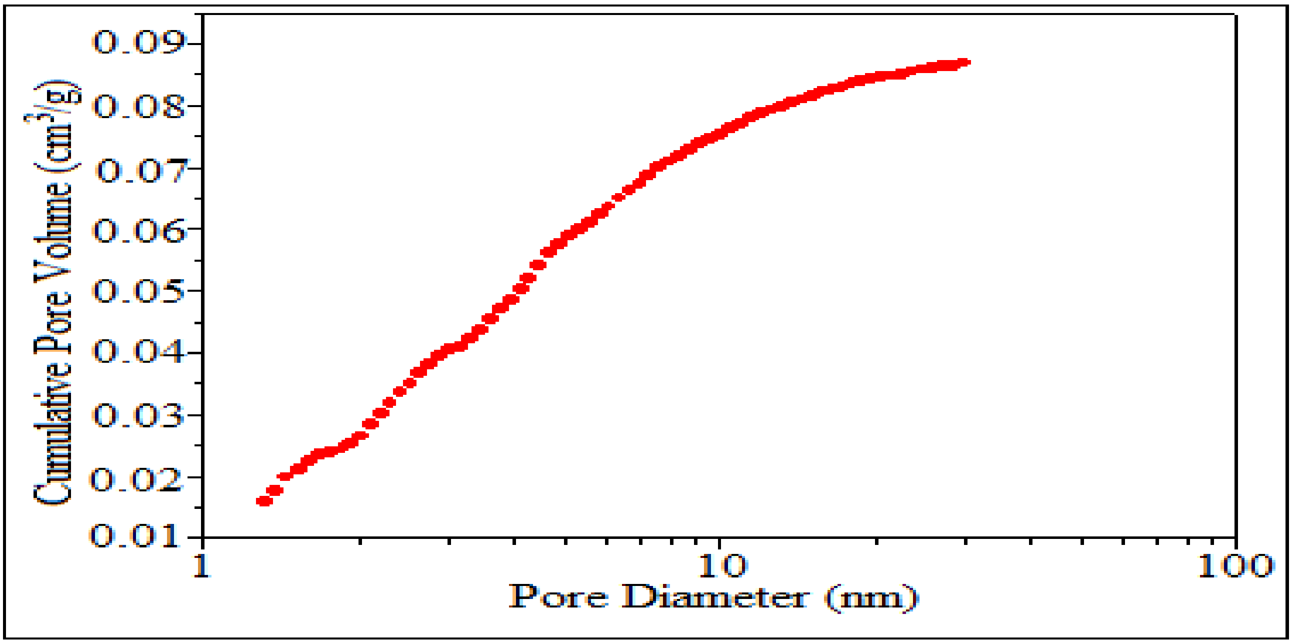


Figure 9: Cumulative pore volume vs pore diameter for the GF-NCuO-$TiO_2^{7.5}$ catalyst

[5.3.5] CHNS Analysis: The percentages of carbon, hydrogen, nitrogen and sulphur in rice straw were determined using a CHNS analyser. The results depicted the percentages of carbon and hydrogen was 44.35 and 42.38 % respectively. The percentages of nitrogen and sulphur content on the contrary were found to be negligible.

[5.13.6] UV-VIS (Diffuse) Spectroscopy: The UV-VIS-NIR spectrophotometric analysis of optimal GF-NCuO-$TiO_2^{7.5}$ catalyst showed a large absorbance peak at a wavelength of 239.40 nm indicating the presence of TiO_2 in the prepared photo-catalyst. In addition, Figure 10a also exhibits a long absorbance hump in the visible range as well as near infrared range (up to the wavelength of 860.52 nm). Notably, the absorption band in the range of 600-800 nm indicated the presence of CuO in crystalline phase [42]. The band gap energy (Eg=2.26 eV) of GF-NCuO-$TiO_2^{7.5}$was computed from reflectance spectra utilizing Kubelka–Munkequation and Tauc plot (Figure 10b). It could be inferred that the presence of copper ions considerably shifted a major part of the absorbance spectrum towards the visible and near infrared range leading to enhancement of the photocatalytic activity of the catalyst. Furthermore, with reference to the Figure 4b, the diffuse reflectance spectra of CGF-NCuO-$TiO_2^{7.5}$ and GF-NCuO-$TiO_2^{7.5}$clearly indicated the higher absorption ability of the latter one, which in turn advocates that the THRBR rendered better hydrothermal activation during sol-gel process compared to conventional protocol.

The UV-VIS-NIR spectrophotometric analysis of optimal GF-Cu-$TiO_2^{7.5}$catalystshowed a large absorbance peak at a wavelength of 237.40 nm indicating the presence of TiO_2 in the prepared photocatalyst. In addition, the figure also exhibits a long absorbance hump in the visible rangeas well as near infrared range (up to the wavelength of 860.52 nm) which indicates the presence of Cu^{1+} as well as Cu^{2+} ions[55]. To add further, the absorption band in the range of 600-800 nm indicated the presence of CuO in crystalline phase. The band gap energies of GF-Cu-$TiO_2^{7.5}$was calculated from reflectance spectra utilizing Kubelka–Munk equation and Tauc plot [56]. Furthermore, with reference to the said figure, the absorption band in the wavelength range of 290-310 nm indicates the presence of silica nanoparticles in GF support [56-57]. As a result, we can infer that the presence of copper ions considerably shifted a major part of the absorbance spectrum in the visible and near infrared range and thus enhanced the photocatalytic activity of the catalyst.

From previous literatures, for a semiconductor material, a plot of $[F(R).h\nu]$ against $h\nu$ show s a linear region just above the optical absorption tip forn=½if the band gap is a direct transition, or for n = 2 if it is indirect[57-58]. Over the linear region of the plots, the relationship can be

described as

$[F(R).h\nu] = k [h\nu - E_g]$ …………………………(1)

where $h\nu$=photon energy, E_g =the band gap energy, and K = aconstant characteristic of the semiconductor material.

Also, it is interesting to note here that the band gap energy of the optimal $NCu\text{-}TiO_2^{7.5}$ catalyst was determined to be 2.26 eV, calculated from Tauc plot, significantly lower than the otherwise large band gap (3.2 eV) of TiO_2, determined from extrapolation of the tauc plot, thus greatly signifying the purpose of doping copper in the original TiO_2 photocatalyst of the optimal $NCu\text{-}TiO_2^{7.5}$ catalyst. This analysis concludes that the prepared $NCu\text{-}TiO_2^{7.5}$ catalyst had the ability to absorb wavelengths of light in the visible spectrum range. As a result, this greatly enhances the performance of the prepared photocatalyst in the lignin degradation process. This phenomenon also increases the ability of the prepared photocatalyst to act in the broad electromagnetic spectrum range of light ranging from UV to visible spectra.

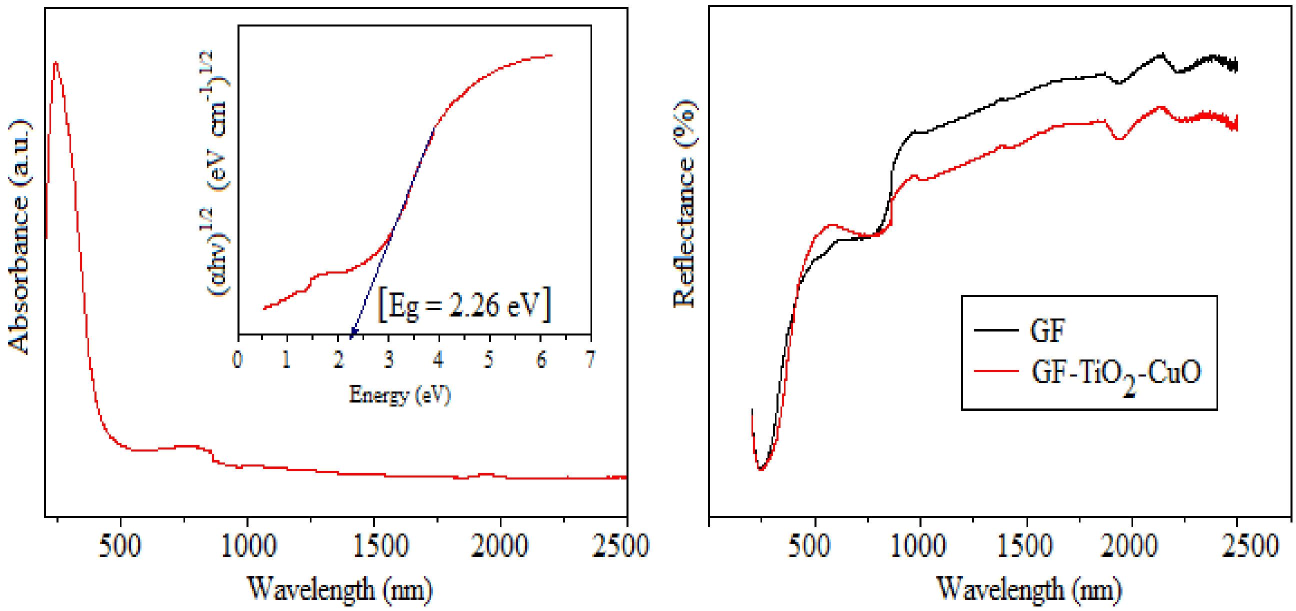
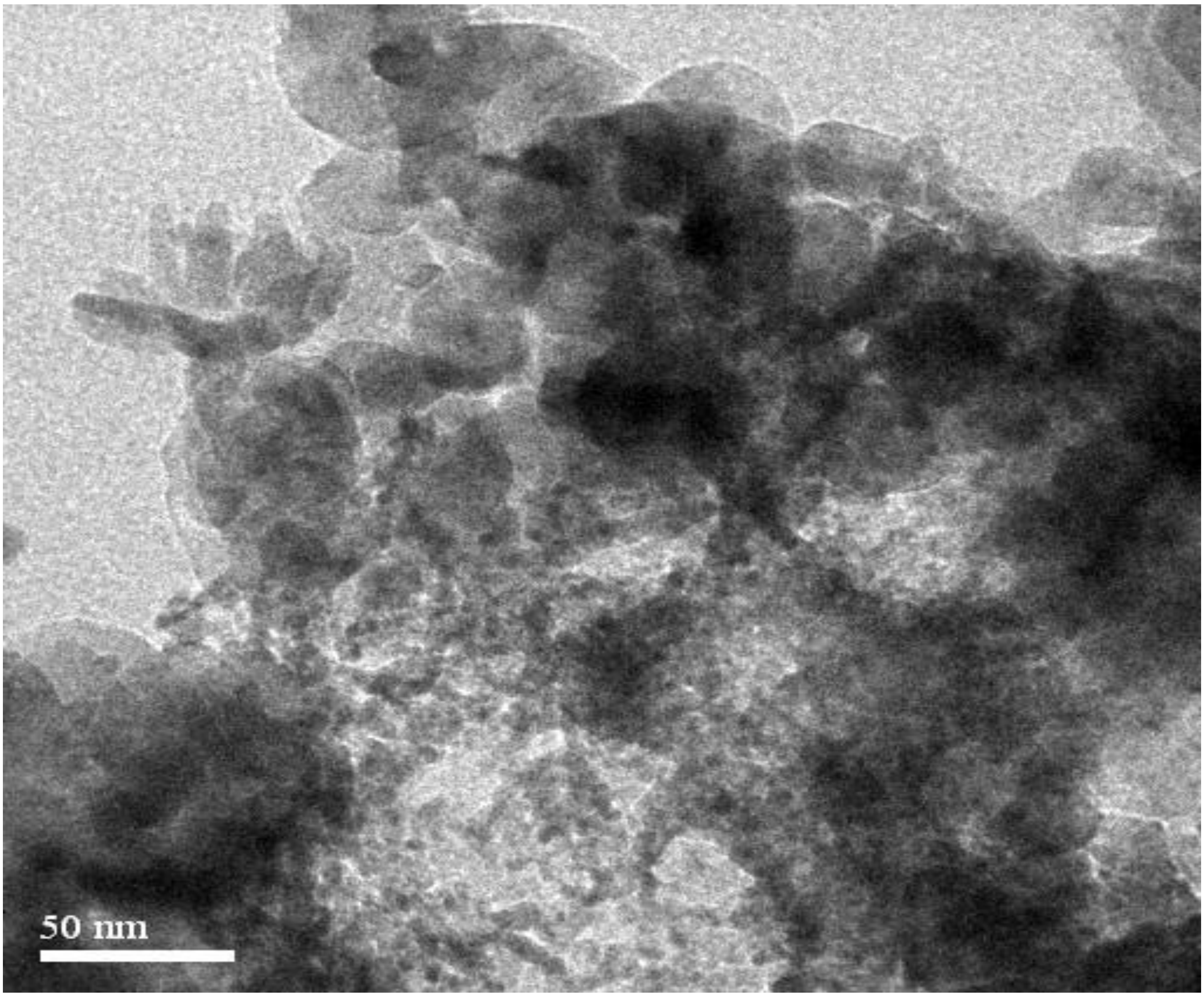


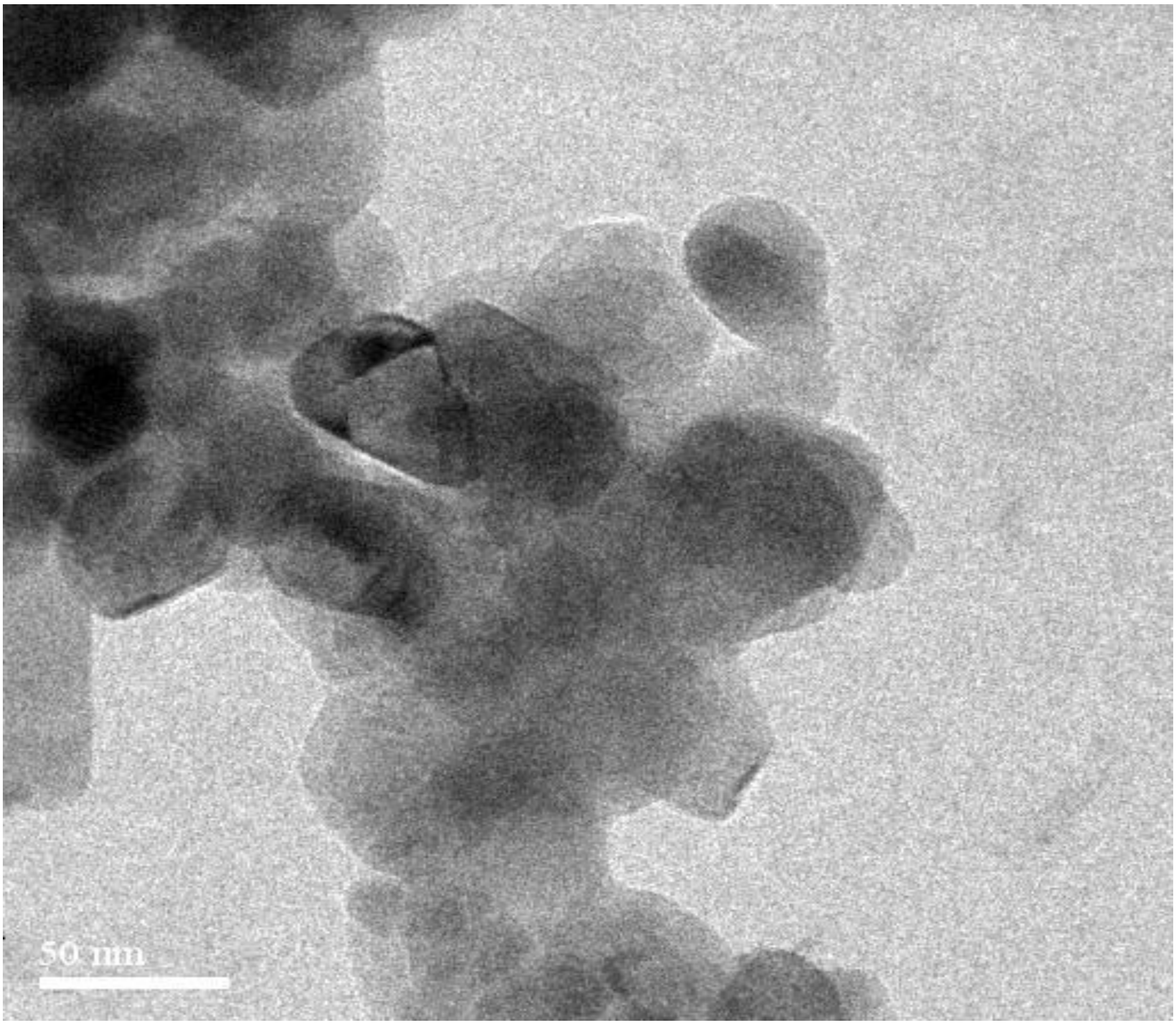
Figure 10:UV-VIS diffuse spectroscopy of GF-NCuO-TiO$_2$$^{7.5}$

[5.3.7] HR-TEM: Transmission electron microscopic analyses of GF, GF-NCuO-$TiO_2^{7.5}$, CGF-NCuO-$TiO_2^{7.5}$ were performed to interpret their structural pattern as shown in Figure 11. It could be clearly observed from Figure 11 that there was a clear and distinct visual enhancement after titanium and copper precursors were doped onto GF. Furthermore, a meticulous assessment of the figures [9a, 9b, 9c] evidently revealed the presence of more porous sites in GF-NCuO-$TiO_2^{7.5}$ as compared to CGF-NCuO-$TiO_2^{7.5}$. The lattice spacing of 0.127 nm revealed the presence of 004 plane (JCPDS card no. 45-0937) of CuO crystallites; whereas the lattice spacing of 0.166 nm was due to the presence of 211 plane (JCPDS card no. 21-1272; JCPDS card no. 21-1276) of TiO_2 crystallites respectively [Figure 12].

A)



B)



C)

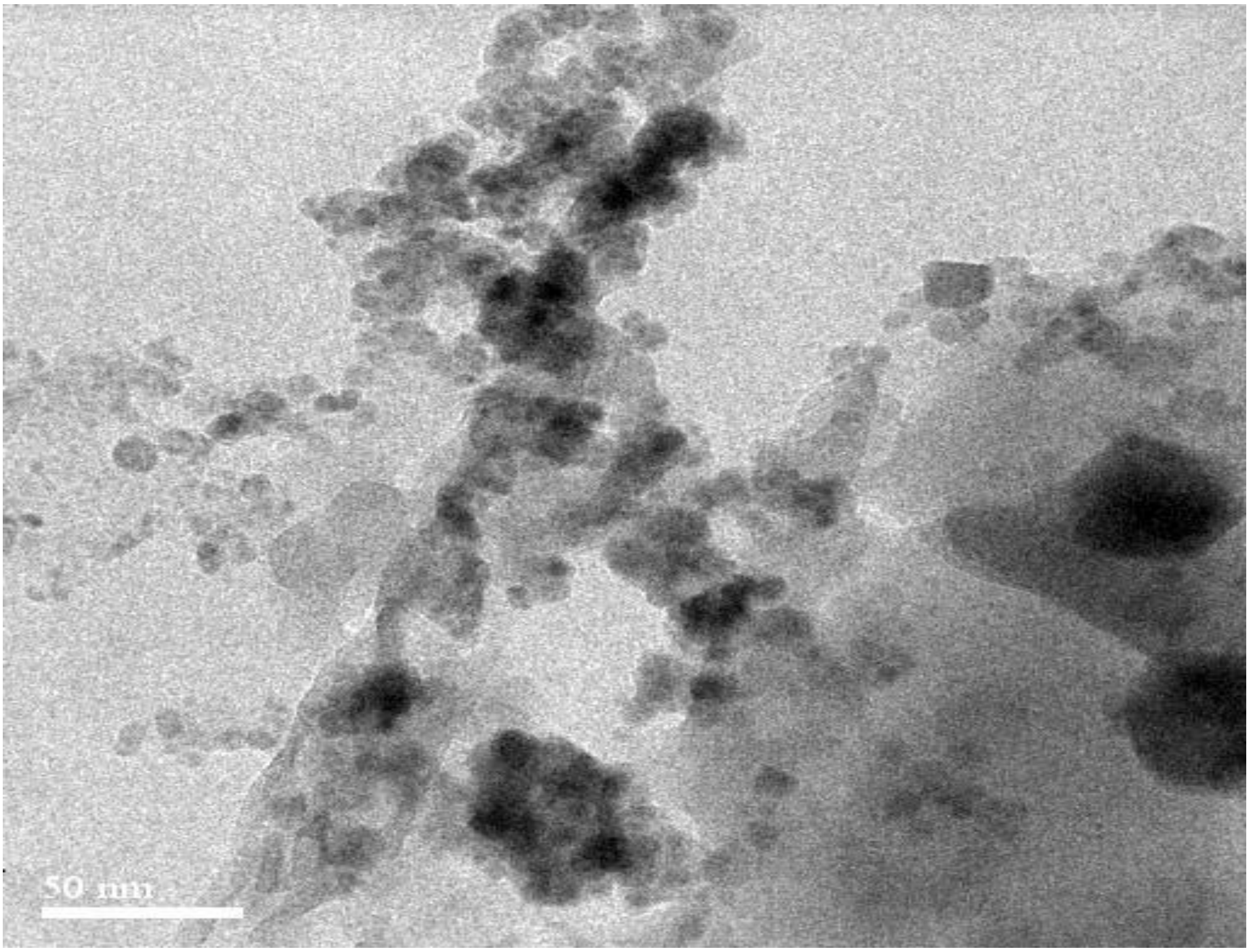


Figure 11:(Starting from top) TEM images of (A) NCu-TiO$_2^{7.5}$; (B) NCu-TiO$_2^{7.5}$; and (C) calcined GF powder.

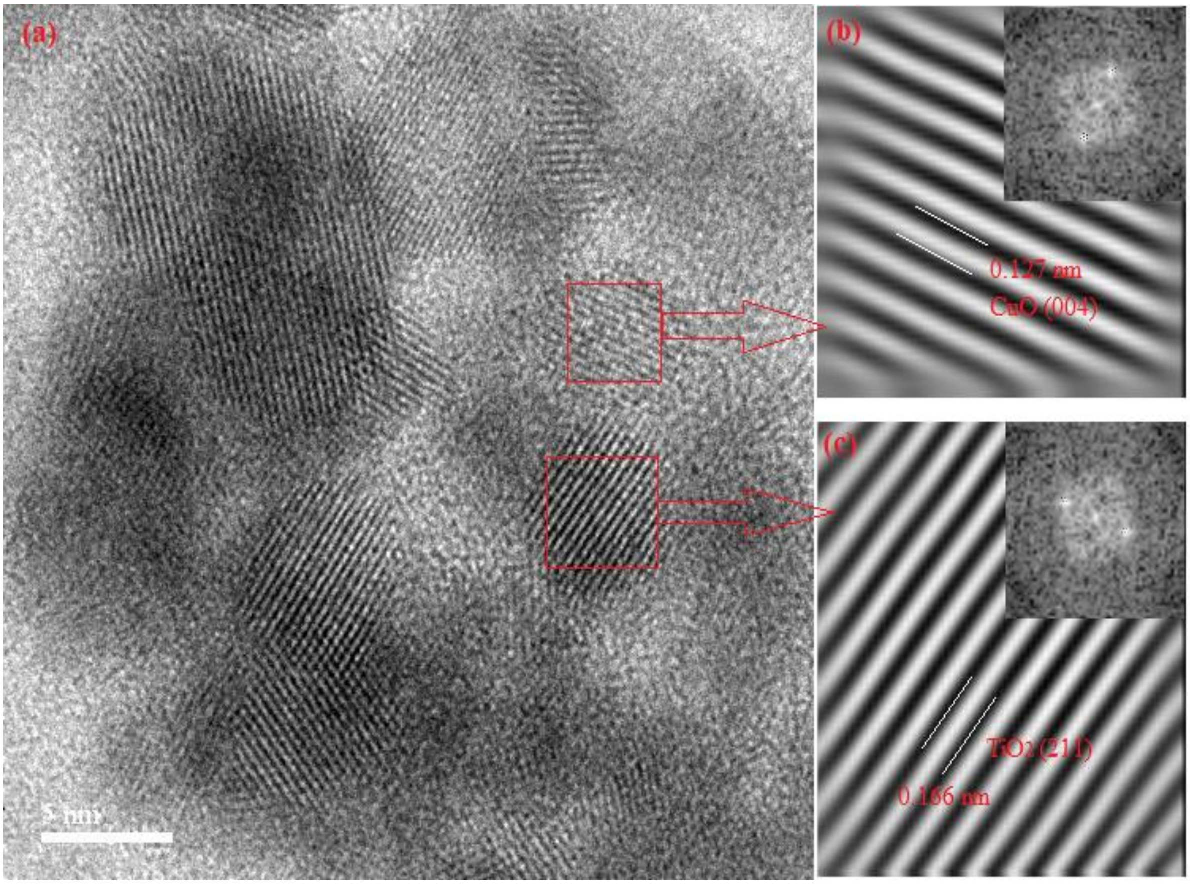


Figure 12: HRTEM image of (A) GF-NCuO−TiO^2; (B) magnified view of the red rectangle section for CuO [inset shows the fast Fourier transform (FFT) of the enclosed region]; and (C) magnified view of the red rectangle section for TiO$_2$ [inset shows the FFT of the enclosed region].

[5.3.8] XPS: The XPS diagram of the optimal GF-NCu-TiO_2 catalyst (Figure 13) depicted the XPS spectra of catalyst support's constituents (Si 2p, C 1s, Al 2s, Ca 2p and O 1s) and Ti 2p and Cu 2p. The binding energies located at 463.33 and 457.45 eV evidenced the presence of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ spin-orbital splitting photoelectrons which could be ascribed to Ti^{4+}in a tetragonal structure [43].To discuss further, it is interesting to note that the binding energy at 932.65 eV and 952.56 eV depicted the presence of Cu $2p_{3/2}$orbital and Cu $2p_{3/2}$orbital respectively, whereas one satellite peak lies at 941.63 eV, which revealed that only CuO phase was present in the catalyst framework [44].

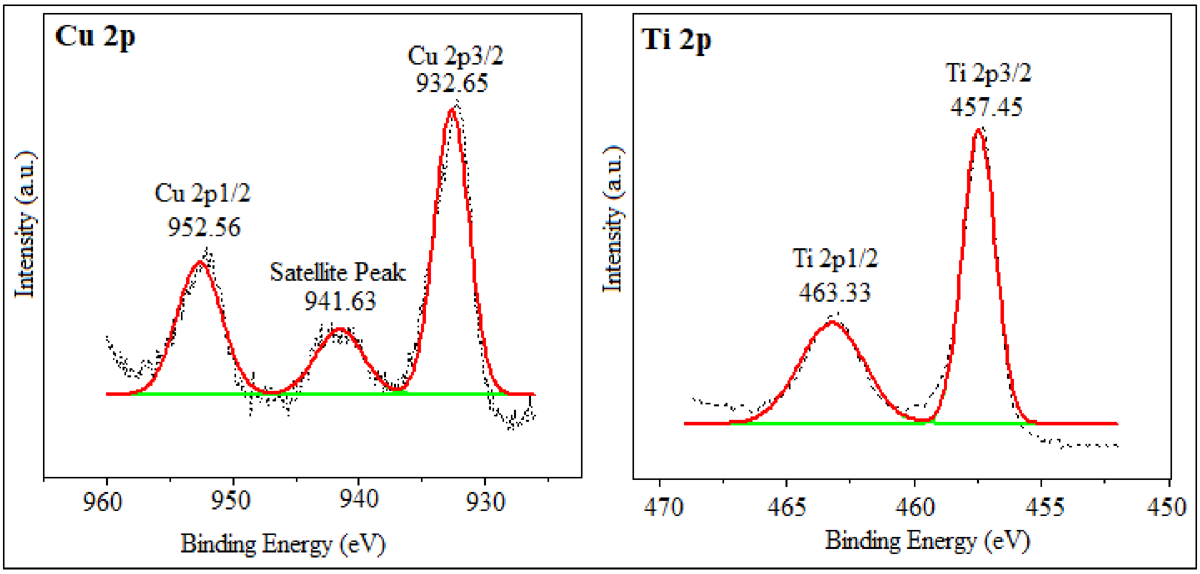
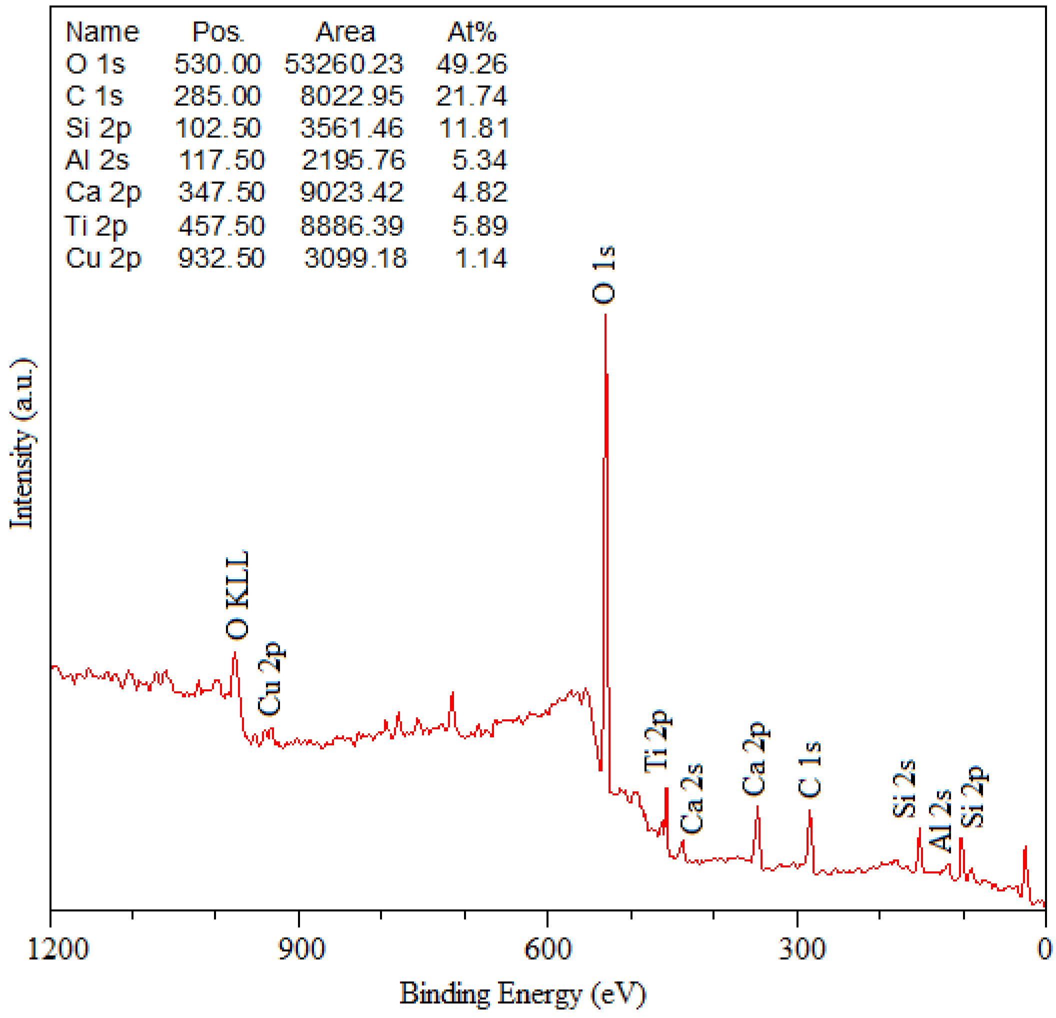


Figure 13:XPS spectra of the (A) Cu 2p and (B) Ti 2p of the NCu−$TiO_2^{7.5}$ catalyst.



Name	Pos.	Area	At%
O 1s	530.00	53260.23	49.26
C 1s	285.00	8022.95	21.74
Si 2p	102.50	3561.46	11.81
Al 2s	117.50	2195.76	5.34
Ca 2p	347.50	9023.42	4.82
Ti 2p	457.50	8886.39	5.89
Cu 2p	932.50	3099.18	1.14

Figure 14: XPS Survey spectrum of GF-NCuO−$TiO_2^{7.5}$

[5.3.9] TGA: Thermogravimetric analysis of thepretreated glass fiber powder, N-Cu-$TiO_2^{7.5}$ was carried out to determine the thermal stability and its disintegration when heated over a wide cumulative range prevalent from 30 to 900 °C. In addition,thermal decomposition of glass fiber was observed to be lessquick as compared to MWPCB powder on account of chemical treatment of MWPCB powder to produce glass fiber.

Thermo-gravimetric analyses of the GF, GF-NCuO-$TiO_2^{7.5}$and CGF-NCuO-$TiO_2^{7.5}$(Figure 15) were carried out to determine the thermal stability when heated over a wide range prevalent from 30 to 900 °C. The sample weight % vs. temperature plot showed a major weight loss of 16 % in the temperature range of 30-450 °C observed in case of CGF-NCuO-$TiO_2^{7.5}$. A weight loss of 9 % was observed in the case of NGF-NCuO-$TiO_2^{7.5}$over the temperature range of 30-450 °C. The occurrence of this phenomenon could be best ascribed due to the evaporation of adsorbed water and thermal decomposition of copper and titanium precursors. Furthermore, the TGA plot of NGF-NCuO-$TiO_2^{7.5}$ rendered 3 % weight loss within the temperature range of 400-450 °C owing to the decomposition of the titanium precursor (Titanium Isopropoxide [$Ti\ (OCH\ (CH_3)_2)_4$]) (decomposition temperature 400 °C) [48]. In addition, a small % weight loss over 180-290 °C inNGF-NCuO-$TiO_2^{7.5}$occurs due to the decomposition of copper acetate [49].On the other hand, GF showed 10 % lower weight loss over the same temperature range of 30-450 °C. Notably the TGA plot of CGF-NCuO-$TiO_2^{7.5}$showed better thermal stability overCGF-NCuO-$TiO_2^{7.5}$ which in turn substantiated the better thermal superiority of NIRR over conventional hydrothermal treatment. Furthermore, as the lignin oxidation temperature (70 °C) was much lower than the calcination temperature (500 °C), thermal decomposition of catalysts was unlikely to occur during lignin oxidation.

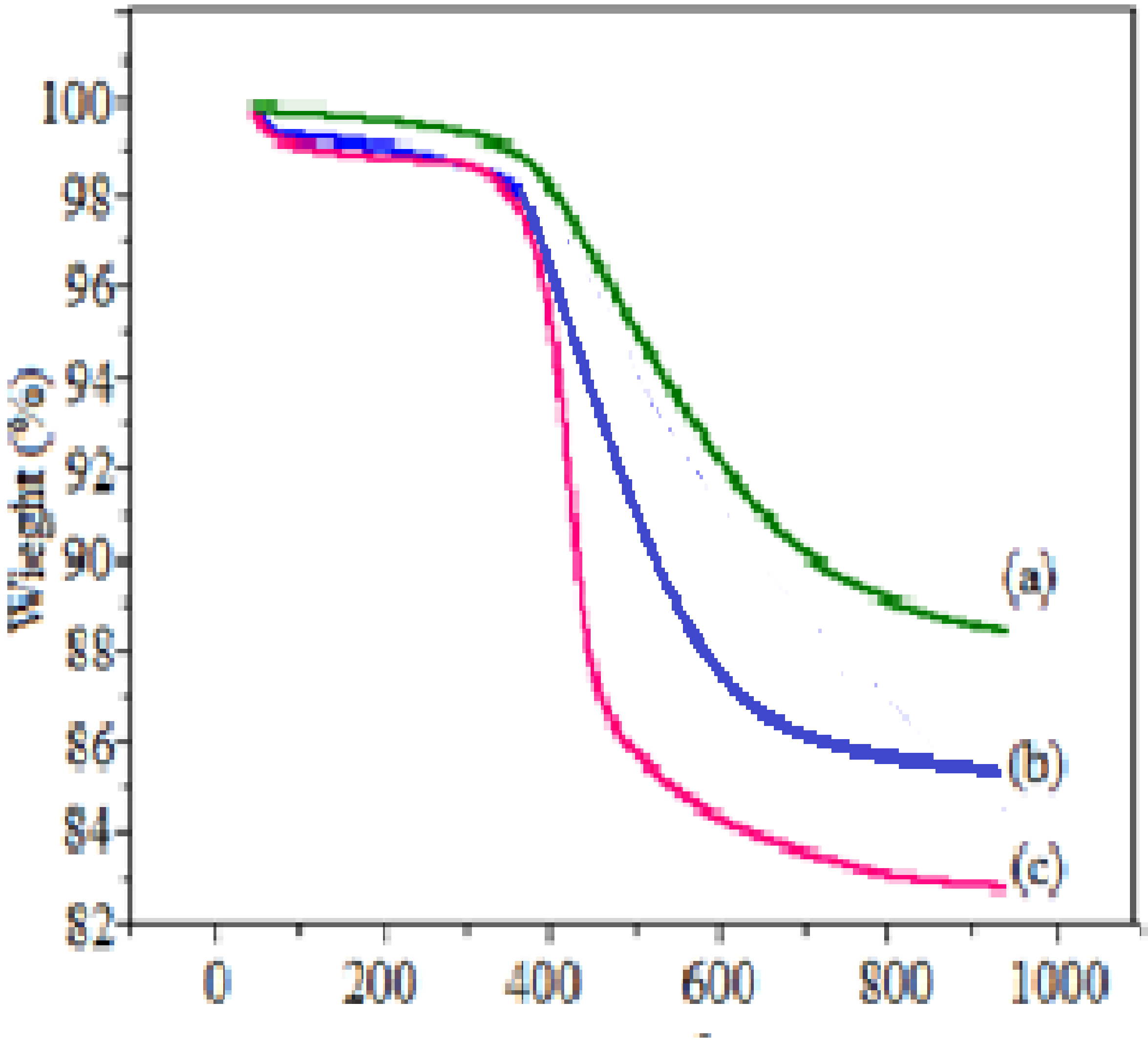


Figure 15: TGA analysis of (a) calcined GF powder (b) GF-NCuO−$TiO_2^{7.5}$ (c) CGF-NCuO−$TiO_2^{7.5}$

[5.3.10] Product characterization:

The lignin degradation using prepared photo-catalyst has been monitored by UV-VIS spectroscopy. The photocatalytic lignin degradation percentage was evaluated at 280 nm wavelength (Figure 16). Furthermore, compositional of the degradation product obtained at optimal condition, were also quantified using HPLC in which vanillin, syringaldehyde, vanillic acid were retained at 4.630 min, 5.32 min, 3.62 min respectively (Figure 17). The phenolic compounds concentration were remarkably higher (vanillin: 11.5 Wt. %; syringaldehyde: 0.63 wt. %; vanillic acid: 1.23 wt. %) in case of lignin degradation using GF-$NCuO-TiO_2^{7.5}$ compared to CGF-$NCuO-TiO_2^{7.5}$ (vanillin: 7.9 wt. %; syringaldehyde: 0.84 wt. %; vanillic acid: 0.73 wt. %) which confirmed the superiority of GF-$NCuO-TiO_2^{7.5}$ for selective degradation of lignin.

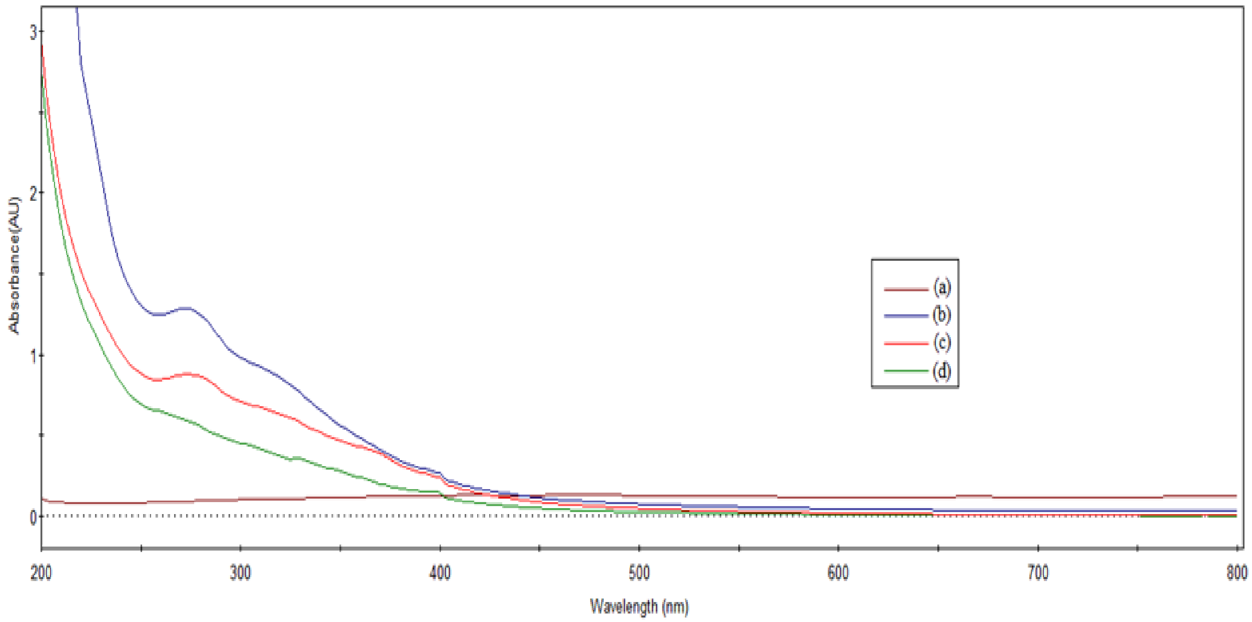


Figure 16: UV-Vis spectroscopy analysis of (a) baseline (water) (b) initial lignin solution and degrdation products at optimal condition using (c) CGF-NCuO−$TiO_2^{7.5}$; (d) GF-NCuO−$TiO_2^{7.5}$

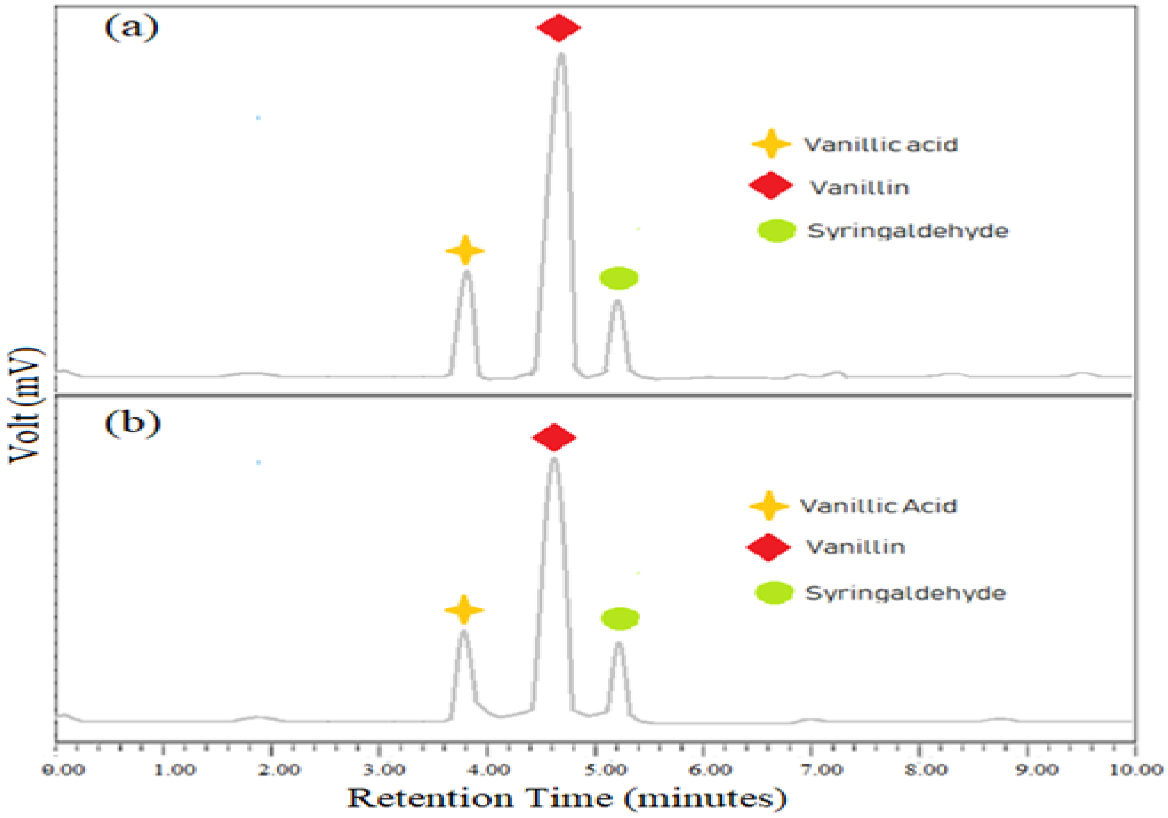


Figure 17:HPLC of products derived from lignin degradation using (a) GF-NCuO−$TiO_2^{7.5}$ and (b) CGF-NCuO−$TiO_2^{7.5}$

[5.3.11] Catalytic Performance of the optimal N-Cu-$TiO_2^{7.5}$on the rice straw (lignin)oxidation process: Photo-catalyticefficiencies of the optimum GF-NCuO-$TiO_2^{7.5}$, CGF-NCuO-$TiO_2^{7.5}$, and commercial TiO_2in rice straw derived lignin degradation process were investigated at the TODderived optimal condition. GF-NCuO-$TiO_2^{7.5}$shows better photo-catalytic activity interms of lignin degradation (89.76 %) over CGF-NCuO-$TiO_2^{7.5}$(L_{THRBR}: 54.53 %); TiO_2 (L_{THRBR}: 23.46 %). The superior catalytic activityof GF-NCuO-$TiO_2^{7.5}$over TiO_2 could be attributed to the better light-absorbing ability of the prepared catalyst due to thepresence of CuO (UV spectra).Furthermore, to better understand the effect of THRBR over conventional heating on catalyst preparation, the prepared titanium-copper nano gel was also analysed in UV-vis spectrophotometer, which revealed that higher concentration of titanium-copper nano gel (which increases the acidic sites in the prepared catalyst) was rendered by THRBR (figure 18). On the other hand, lower particle size of the THR activated GF-NCuO-$TiO_2^{7.5}$ also enhanced the adsorption efficiency of the lignin particles on catalyst surface. Thus, high acidic sites as well as lower particle size of the THR activated GF-NCuO-$TiO_2^{7.5}$made it a superior catalyst compared to CGF-NCuO-$TiO_2^{7.5}$. Notably, the GF-NCuO-$TiO_2^{7.5}$catalyst facilitated almost same L_{THRBR}(89.76 %; degradation time: 50 min)compared to the L_{THRBR}reported in the previous work by Rangel et al., 2015 (92.46 %; degradation time: 120 min)[47] within a much shorter time.

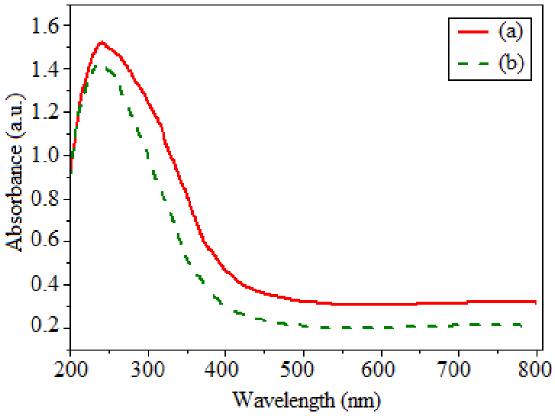


Figure 18: UV-Vis Spectroscopy of (a) Titanium-copper nano gel produced under THR (b) Titanium-copper nano gel produced under conventional heating

[5.3.12] ^{1}H-NMR analysis: The products obtained from lignin degradation using GF-NCuO−$TiO_2^{7.5}$wasexamined by ^{1}H-NMR analysis as shown in Figure 19. Table 2S shows the different proton chemical shifts and the assignments of these signals to different compounds [51-54]. The sharp peak having chemical shift of 9.642 ppm belongs to the region of aldehyde-protonic groups, with the major compounds presumed to be benzaldehyde type units obtained from light-intensified degradation of lignin [55].Vanillin, vanillic acid and syringaldehyde were identified to be the predominant low-molecular degradation products in the alkaline oxidation of lignin [55]. The NMR spectra were detected using a BrukerAVANCE 500 MHz spectrometer at 290 K using CD_3Cl as thesolvent. Chemical signals were referenced to TMS (0.0 ppm) [56].The HMQCanalysis was performed with ca. 5% solution of lignin using a 90°pulse width, a 0.12 s acquisition time, a 1.0 s pulse delay, and 1JC-H of 148 Hz. Detailed information about different chemical shifts and product assignments can be found in different publications already cited.

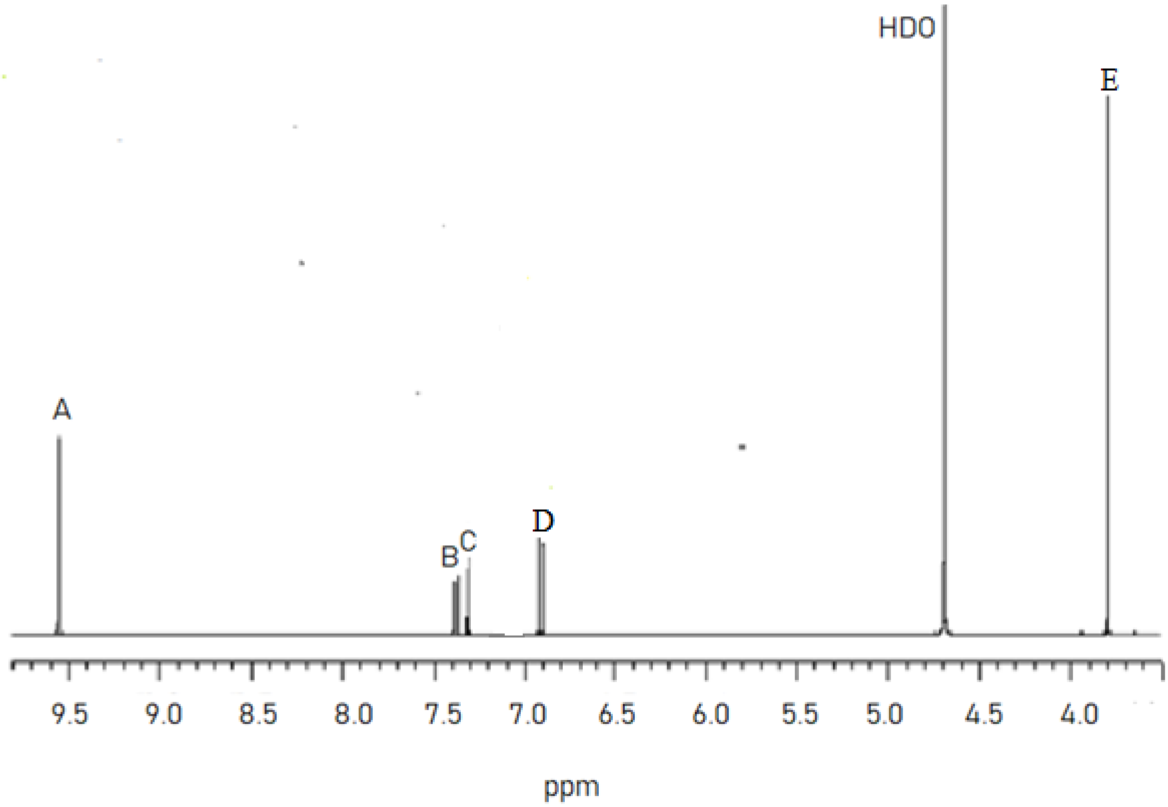


Figure 19: ^{1}H-NMR spectrum of products derived from lignin degradation using GF-NCuO−TiO$_2^{7.5}$ catalyst

Proton	Chemical shift/ppm	Assignments
H-A	9.642	Benzaldehydes and cinnamaldehydes
H-B	7.474	vanillin
H-C	7.462	Vanillic acid
H-D	7.148	syringaldehyde

H-E	6.923	syringaldehyde
$–CH_3$	3.872	Methoxyl group

Table 6:H-NMR chemical shift valuesof lignin degradation products usingGF-NCuO−$TiO_2^{7.5}$ (in CD_3Cl) [51-54]

[5.3.13] Catalyst Reusability: The catalyst reusabilitywas investigated by taking 10thconsecutive experimental runs at the TOD derived optimal condition using the optimal catalyst GF-NCuO-$TiO_2^{7.5}$. After each batch lignin oxidation, the catalyst could be easilyrecovered by membrane filtration and subsequently oven-dried at 105 °C for 1.5 h. The L_{THRBR}decreased from 89.76 to 87.53 % after 7th recycle while no further decrease in $L_{THRBR}$was observedin subsequent three more reaction cycles. Inductively coupledplasma (ICP)-optical emission spectroscopy of the reusedcatalyst revealed that an insignificant amount of active sites(0.14 ppm of Ti) was leached from GF-NCuO-$TiO_2^{7.5}$, while CGF-NCuO-$TiO_2^{7.5}$suffered leaching up to 2.36 ppm of Ti, which further reinforces thesuperiority of THRBR over Conventional heating system. Thus the optimalGF-NCuO-$TiO_2^{7.5}$catalyst demonstrated appreciable reusability attributes.

CONCLUSION

[6] CONCLUSION

Overall through this work, it can be concluded that waste PCB derived supported glass fiber Cu-TiO_2 catalysts can be prepared by employing both conventional treatment and NIRR electromagnetic radiation. Effects of the four process factors on vanillin yield have been studied usinganalysis of variance (ANOVA) and optimized through TOD. Furthermore, the waste PCB-derived GF could be used as a catalyst support to produce a cost-effective Cu-TiO_2 catalyst. Thus, in other words, we can easily conclude that WPCBs can be used to produce effective, environmentally benign and cost-effective noble acid catalysts. In fact, due to its environmental friendly procedure for preparation of these noble catalysts, it can be easily used by several industries and scaled, thereby opening up new gears in the subject of catalysis. Moreover, usage of NIRR proved to be far more effective in efficient production of vanillin from lignin derived from rice straw. It was also observed that employment of NIRR proved to be a rather greener and environmental friendly pathway for efficient production of photocatalysts compared to conventional hydrothermal treatment. In addition, significant reduction in processing time was observed in case of NIRR. Lastly, significant reduction in band gap (2.26 eV) was observed when copper was doped with TiO_2 thereby enhancing the photocatalytic performance of the catalyst in the visible spectrum compared to pure TiO_2 having a band gap of 3.2 eV which restricts its ability to work in the visible spectrum.

WPCB derived GF can be effectively used as a promising inexpensive support for production of GF-NCuO-TiO_2 as well as CGF-NCuO-TiO_2 photo-catalysts by utilizing THR and conventional hydrothermal treatment respectively. The experimental results clearly indicated that the THR activated GF-NCuO-TiO_2catalyst was more efficient in terms of lignin degradation as compared to conventionally activated catalyst. Furthermore, XRD analysis confirmed the presence of much smaller nanoparticles in GF-NCuO-TiO_2 compared to CGF-NCuO-TiO_2 authenticated the efficacy of using THR. The effects of different process parameters have been investigated by using analysis of variance (ANOVA) and the optimal process conditions have been evaluated by using TOD. Thus utilization of WPCB for production of effective, recyclable photo-catalyst with enhanced performance has opened up new gears and foundations in the green and cost-effective synthesis of highly efficient photocatalysts.

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Future Scope of Work

[7] Future Scope of Work

On having developed an environmentally benign waste PCB derived catalyst in this study, there is a lot that remains to be effectively studied in terms of the procedures involved in preparation of these catalysts. Also, since the entire field of e-waste is vast and varied, effective supports derived from these e-wastes can be prepared and its performance can be studied in its ability to enhance the production of-value added chemicals. In addition, since the effect of doping transition metals on metals effective only in a small spectrum hasn’t been investigated much, a lot needs to be done to study the effects of doping of these transition metals, with its absorption ability predicted using sunlight as natural source.

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