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DEGRADATION OF METHYLENE BLUE DYE BY PHOTOCATALYTIC ACTIVITY OF G-C_3N_4 SYNTHESIZED BY POLYCONDENSATION PROCESS

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ABSTARCT

Wastewater contamination is greatly impacted by the textile industry. The most prevalent contaminants are taken into account by conventional wastewater treatment techniques, although they are highly costly and frequently result in hazardous by-products. Advanced oxidation processes seem to be the most attractive to scientists, and heterogeneous photocatalysis is taken into consideration for the destruction of different harmful compounds in most published work. In this study, melamine was used as a precursor to synthesize metal-free graphitic carbon nitride (g- C_3N_4) by polycondensation process. Syntheized catalyst was used with Methylene blue, a model pollutant, for degrading using the photocatalytic qualities of immobilized g-C_3N_4 under simulated solar light irradiation. FTIR, XRD and UV spectroscopy analyses were used to characterize the photocatalyst. It was discovered that the photocatalytic breakdown of MB in an aqueous solution increased with longer irradiation times.

Keywords: Photocatalysis, Graphitic Carbon Nitride (g-C_3N_4), Dye Degradation, methylene blue

1. INTRODUCTION

Water remains one of the major components of life. Out of the total, water present on Earth, only 2.5% of water is available for drinking purposes, while the remaining 97.5 % is saline water which remains primarily in oceans **[1]**. Further, because of advancements in technology, industrialization, and urbanization have adversely affected the quality of water. Heavy metals, dyes, and persistent organic pollutants are some of the prominents for polluting water. Heavy metal ions in the food chain carriers from soil/water to the human body disrupting the human system. Increased concentration of these components, can severely affect human health.

Water contamination brought on by textile businesses is currently one of the largest problems faced by the entire planet. Additionally, the inability to appropriately discard their wastewater adds to the issue. The textile business has a big impact on both the global economy and environmental damage including in China. Due to the textile industry's extensive production of wastewater that is brightly colored and contains a variety of dyes, it is a significant source of persistent pollutants that impair not just the environment but also human health. An estimated 10,000 people are employed by the textile business each year, and 7×10^7 tons of artificial coloring are made **[2]**. The entire chemical industry comprises only a small percentage of the dye manufacturing sector. Nearly there are 8 lakh tons of dyes manufactured worldwide each year. During various steps of the textile business, about 10 to 15 percent of synthetic dyes are lost. Nearly, 70% of the more than 10 thousand color azo dyes are utilized when producing textiles, which have complicated structures and are synthetic in origin **[3]**. Dyes poses a danger towards the health of the environment even when they are present in minute concentrations in this wastewater. Some dyes are extremely poisonous, and carcinogenic, slow down plant photosynthesis in water by obstructing light transmission through the water, and raise biological oxygen requirements **[4]**.

Dye is a substance that gives a material color, generally permanently. Dye molecules have chromophores and auxochrome. Chromophore is responsible for producing color while auxochrome is responsible for enhancing the intensity of color. Dyes can be produced chemically or from natural resources like plants, animals, and minerals. They are commonly employed to give items the colors they want in industries including textiles, cosmetics, and food. Since antiquity, dyes have been employed for a variety of purposes, with early civilizations like the Egyptians and Chinese among them **[5], [6]**.

Inhalation of dye particle risks leading to respiratory disease, which is the most common concern linked with reactive dyes. Sneezing, runny eyes, itching, asthma symptoms, breathing, and cough are some symptoms related to respiratory sensitivity. The main factor contributing to health problems associated with dyeing and finishing operations may be exposure to unpleasant chemicals. These may cause eye pain, nose itching or congestion, sneezing, or skin irritation. It has been found that these azo dyes are complicated in nature and display reductive cleavage tumorigenicity. These colours have the power to alter the physical and chemical composition of dirt, damage water resources, and influence the ecosystem's flora and fauna **[7]**. Textile colors make up the majority of the organic pollutants in untreated effluents produced by the textile industry. The majority (more than 60%) of the primary groups of textile dyes are azo dyes, which are the greatest prevalent dyes used in the textile sector. Azo dyes have more than one azo group in their structural makeup **[8]**. Azo dyes have a range of structural characteristics, but their most important structural trait is the existence of an azo linkage or N=N. Due to the possibility of multiple occurrences of this connection, mono azo dyes only a single azo connection, compared to correspondingly, two in diazo and three in tri azo. They are azo groupings linked to aromatics like the benzene and naphthalene moieties on both sides. In some cases, azo groups are used to join aromatic heterocyclic units. These aromatic side groups are what cause different shades of the same dye to have different color intensities. Azo groups form a complicated structure when they combine with aromatic substituents or enolizable groups, which results in a wide expression of color diversity in dyes **[9]**. Inefficient textile dyeing methods result in the release of 15–50% of azo dyes into wastewater that is not bound to fibres and fabrics. Others release wastewater from industry straight into water physiques, creating significant eco-toxicological dangers and toxic effects on living things, while certain textile manufacturers purify the free azo dyes discharged into the environment to be broken down by their effluent. When farmers in developing countries irrigated their agricultural holdings with wastewater—especially untreated industrial effluents—the quality of the soil and crop germination rates declined.

For the removal of these contaminants, different wastewater treatment techniques such as primary, secondary, and tertiary treatment are employed. Primary treatment mainly focuses on the removal of material that floats and can easily settle under the action of gravity. This process mainly includes screening, comminution, grit removal, and sedimentation. The secondary treatment process mainly aims at the removal of biodegradable & suspended solids. For the same, the processes involved are filtration, aeration, and activated sludge. Secondary treatment uses biological processes like trickling filters, activated sludge tanks, and anaerobic digesters to break down organic matter. Secondary treatment revolves around treatment and the removal of biodegradable organic matter

(BOD) and Total suspended solids (TSS). Secondary processes mainly involve processes like aeration and filtration. Secondary treatment involves treating water which has been previously treated by primary treatment and has BOD of 25 mg/L or less and a TSS of 30 mg/L or less. Tertiary treatment is a method of wastewater treatment that consists of eliminating non-biodegradable pollutants. It follows primary and secondary treatment. This technique allows the removal of phosphorus and nitrogen contained in the water to refine it. Tertiary treatment involves treating of such water which has stubborn contaminants which remains unaffected from primary and secondary treatment. However, although these processes are efficient, they produce secondary pollution from each step, and again issue of disposal and treatment of this waste becomes a concern **[2], [10], [11]**.

To overcome, the drawbacks of primary, secondary, and tertiary water treatment, AOP are have been employed. AOP has become more well-known due to its ability to detoxify resistant chemicals from wastewater. As an outcome of the hemolytic dissociation of water molecules, produces hydroxyl radicals (HO•), which oxidize the organic harmful substances. AOP includes techniques like, ozonation, ozonation with H_2O_2, UV radiation, the Fenton process, Photocatalytic process, sonolysis, and electrochemical oxidation is few of such processes which included in AOP. Photocatalysis is one of the most efficient subcategories of AOP for the degradation of toxic substances out of all the AOP techniques now available. Future energy generation, human-caused environmental damage, and security are a few of the major issues facing advanced nations. AOP reduces the number of risky and harmful components in wastewater to the proper stage, permitting reservoir discharge. Sunlight is a clean source that is freely available and can be employed to deal with these issues. The emphasis has changed to semiconductor photocatalysts to make use of these sources. However, the catalyst's efficiency in utilizing the visible light that reaches the earth's surface is still quite low. Three types of solar radiation, mainly UV (5%), visible (45%), and infrared (50%) pass through to Earth. As another advantage, AOP works in mild conditions & may decrease pollutants to levels of less toxic **[3], [5], [12]**.

Photocatalysis is a process in which materials, mostly they are semi-conductors have conduction band and valence band. In the Valence band, some electrons get excited upon illumination. Therefore, the hole is created in the valence band (h^+), and at conduction we have electrons (e^-). These electrons and holes are responsible for carrying out reactions where they oxidize the organic pollutants and convert it to some reasonably less harmful components **[13]**.

Again, it’s not as simple as it seems. Additionally, the gap/distance between the valence band and the conduction band is called a bandgap. There are chances where electrons might not be able to reach the conduction band, and again get adsorbed in the valence band. This phenomenon is called recombination. The recombination of electrons is one of the drawbacks for the photocatalysis process. To avoid the phenomenon of recombination, enough energy must be supplied through illumination. Therefore, the selection of photocatalysts becomes very important for performance. In addition to the desired bandgap other properties like high surface area, availability, and correct shape all impact the photocatalyst of choice.

Carbon nitride's chemical inertness causes a solubility issue in basic, acidic, and neutral solutions. As a result, until recently, the material's structure was not fully understood. Graphitic carbon nitride (g-C_3N_4), an allotrope of carbon nitride that is the most stable in the ambient atmosphere due to the presence of surface sites. g-C_3N_4 has attracted the research attention because of its special surface feature likes high and active surface area. g-C_3N_4 has found wide application in field of catalysis. g-C_3N_4 is synthesized by polycondensation process from nitrogen rich precursors like melamine, urea. Structure of is shown in **Figure 2**. The hydrogen is present on the terminal edges as primary and/or secondary amine groups. Hydrogen at terminal edgues of primary and secondary amines signifies that, g-C3N4 is not fully condensed and has defects which helps for electron relocalization on the surface and induce Lewis-base character toward metal-free coordination chemistry and catalysis. These defects can be helpful in catalysis. The efficacy of graphitic carbon nitride as a photocatalyst for the activation of visible light for photochemical processes has been demonstrated by numerous studies. As discussed, upon illumination, electrons get excited and jump to the conduction band from the valence band. During this time, the hole is created in the valence band and the electron remains in excess in the conduction band which helps facilitate water-splitting reactions. However, g- C_3N_4 has poor visible light use efficiency and a rapid rate of photoelectric carrier recombination, which leads to poor production to the surface's active regions caused during the photocatalytic process, and redox reaction process. This is despite the material's good electron and optical properties. It provides fewer reactive sites, has a small specific surface area, and has a lower light-harvesting capacity. Additionally, being a relatively small bandgap (2.7 eV), g-C_3N_4's limited usage implies that an important part of the visible-light spectrum is unexplored **[3], [14]–[16]**,

In this work, we synthesized g-C_3N_4 from melamine by polycondensation process and the synthesized sample was characterized. Further, g-C_3N_4 was used for the degradation of simulated dye wastewater of methylene blue. Samples were further, analyzed in UV visible Spectrophotometer for absorbance and thereupon concentration.

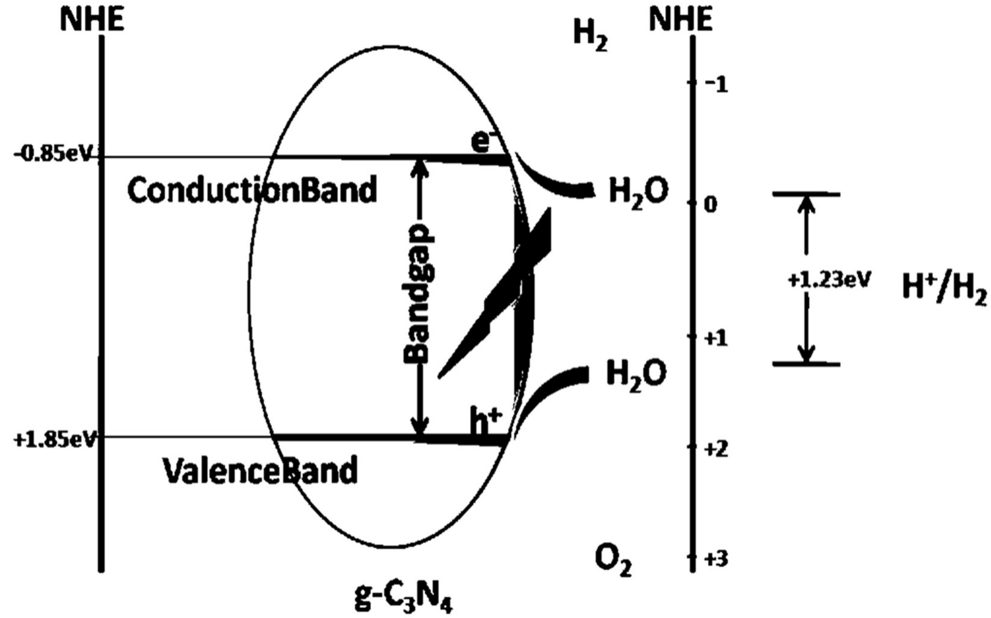

Figure 1: Photocatalytic Mechanism

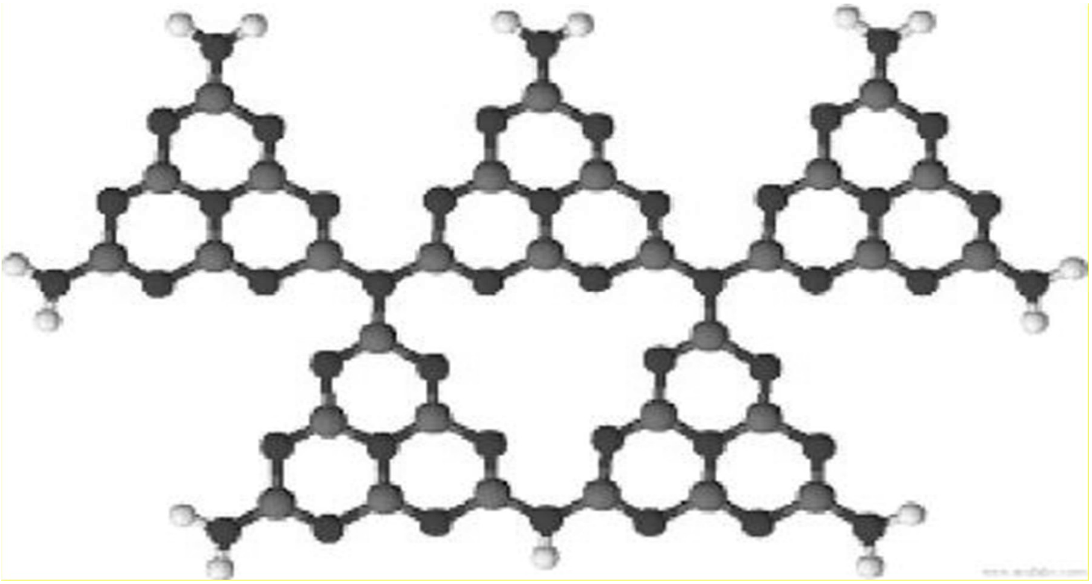

Figure 2: Structure of g-C_3N_4

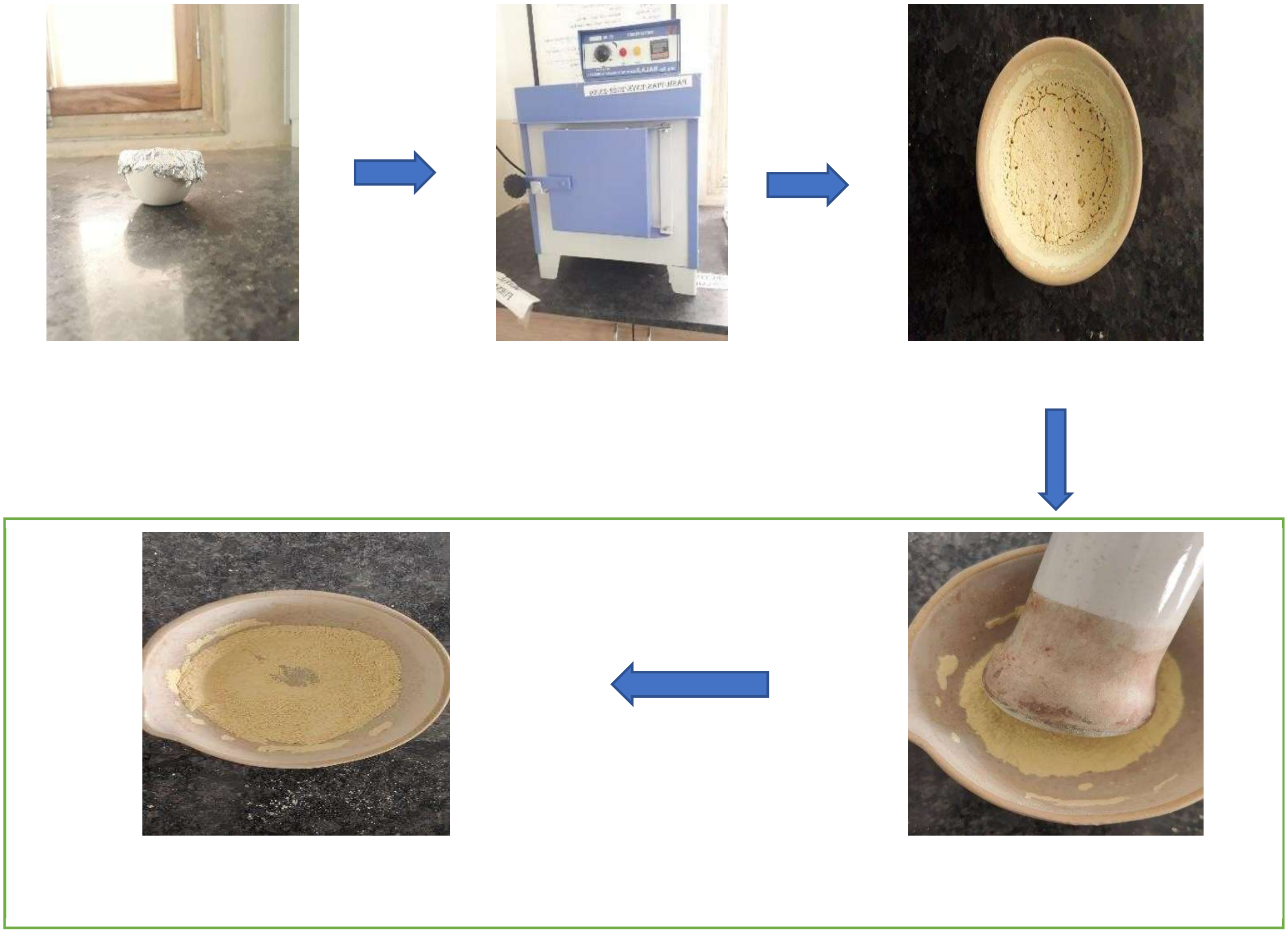

Figure 3: Synthesis of g-C_3N_4

2. MATERIAL & METHODS

2.1 Material

Melamine($C_3H_6N_6$) with a purity of 99.8% was received from the Suvidhinath laboratory Gotri, Vadodara, and Methylene Blue Trihydrate (Himedia) were collected from the laboratory with a purity of 98%.

2.2 Methods

The precursor for the manufacture of the g-C3N$_4$ photo catalyst, melamine was heated at 520°C in a muffle furnace at a rate of 5°C per minute in a covered crucible for around 2h. The resulting light yellowish solid cake was crushed to fine powder, once it was cooled naturally. The process for the same is shown in **Figure 4** below.

2.3 Dye Degradation Process

For the treatment of simulated methylene blue dye-contaminated waste water, synthesized g-C_3N_4 was used as a photocatalyst in the process of photocatalysis. For the experiment, 250 mL of 50 ppm solution of methylene blue dye was prepared to which 0.0075 gm of g-C_3N_4 was added. Before, illuminating the solution to UV light, it was stirred in the dark in the absence of light for 25 minutes to obtain adsorption-desorption equilibrium. Later, the UV-A source was ignited in the photocatalytic reactor as shown in **Figure 4** and dye samples were taken at regular intervals of 2 min, 5 min, 10 min, 15 min, 20 min & 25 min. These samples were analyzed in a UV-Visible spectrophotometer for the value of absorbance, followed by concentration.

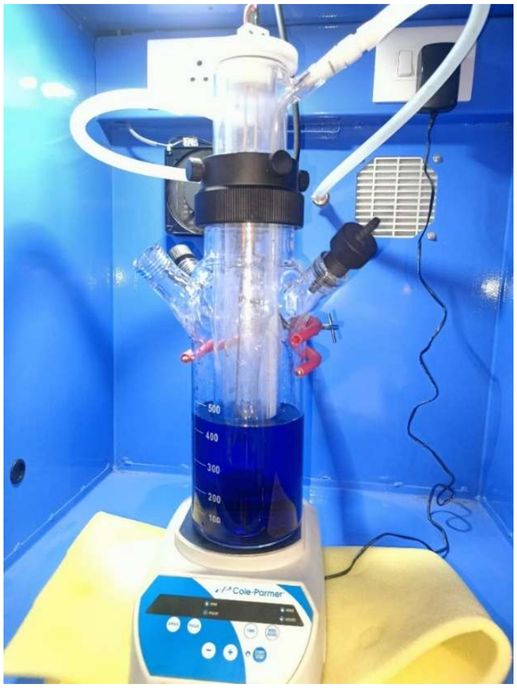

Figure 4: Photocatalytic reaction setup

3. RESULT AND DISCUSSION

3.1 Fourier Transformed infrared spectroscopy

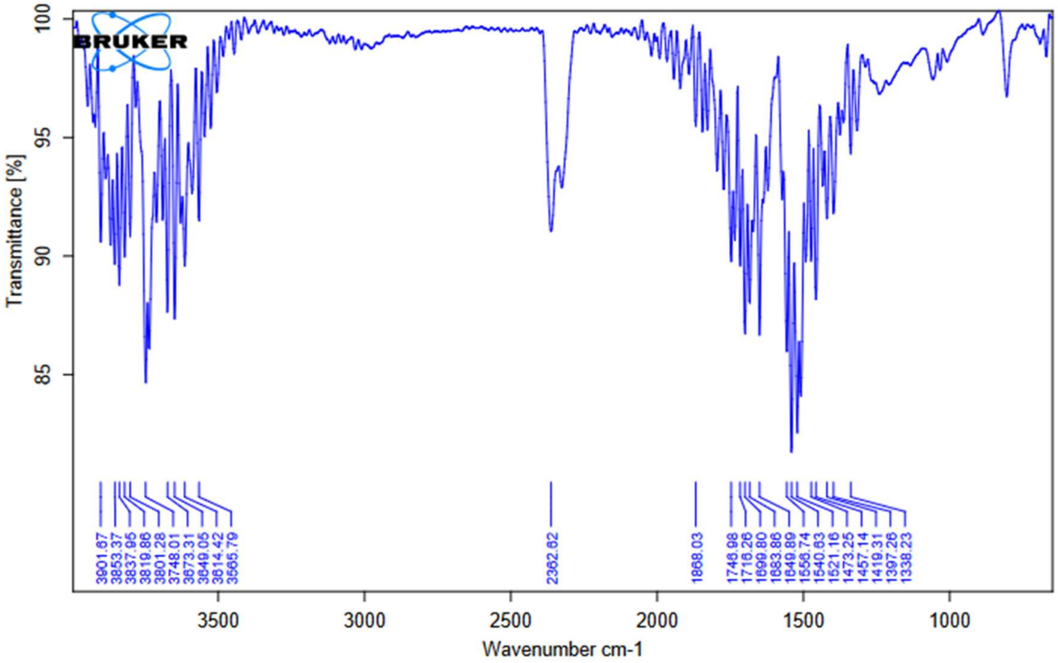

Figure 5: FTIR spectra of g-C_3N_4

FTIR stands for Fourier transform infrared spectroscopy. The FTIR method measures the amount of light absorbed by the bonds in vibrating molecules. FTIR is utilized to determine which functional group is present in an unknown sample. The g-C_3N_4 sample was analyzed in the range of 3500 cm^{-1} and 800 cm^{-1}. FTIR spectra show two broad peaks which can be attributed as, peaks in the range of 3500-3000 cm^{-1} resembling for N-H stretching of the amine group while peaks in the range of 1700-900 cm^{-1} show breathing of tri-azine ring which can also be attributed as CN heterocycles of g-C_3N_4 (Balu *et al*. 2019). Peak in range of 1200-1400 cm^{-1} for C-N of vibration. These two are characteristic peaks for g-C_3N_4 **[14], [17], [18]**.

3.2 X-ray diffraction analysis of g-C_3N_4

It can be observed that at the value of 2θ =27.5° there is an intense peak which is due to the stacking of graphite-like conjugated triazine aromatic sheets. Another peak at 2θ =13.5° corresponds to the in-plane structural packing. Sharp peaks in the pattern indicate that obtained powders are crystalline and have no impurities **[19]**.

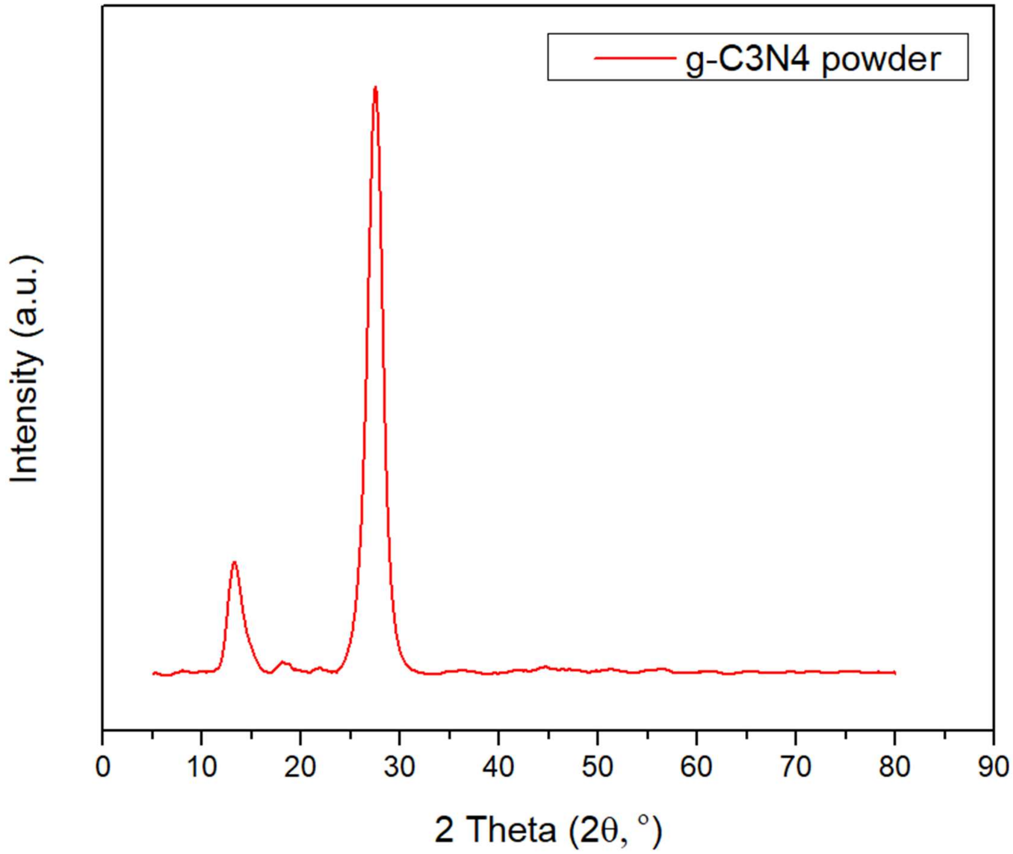

Figure 6

3.4 UV visible analysis of a sample

The fundamental principle of UV-Vis spectroscopy is that light in the UV and visible regions of the electromagnetic field is absorbed by molecules and atoms as electrons transition from lower to higher energy levels. Light absorption is associated with electron excitation. It has long been known from absorption spectroscopy that the band gap expands with decreasing particle size. To the best of our knowledge, bulk g-C_3N_4 absorbs at 665 nm. The dye deteriorates by the time UV-A light is provided, evidenced by UV-visible spectroscopy. **Figure 7** shows a kinetics plot of change in concentration of dye concerning time. This graph signifies that with time, the concentration of dye decreases. This graph is derived from the absorbance value of the sample taken with the help of the calibration curve plotted for certain known concentrations **[6]**.

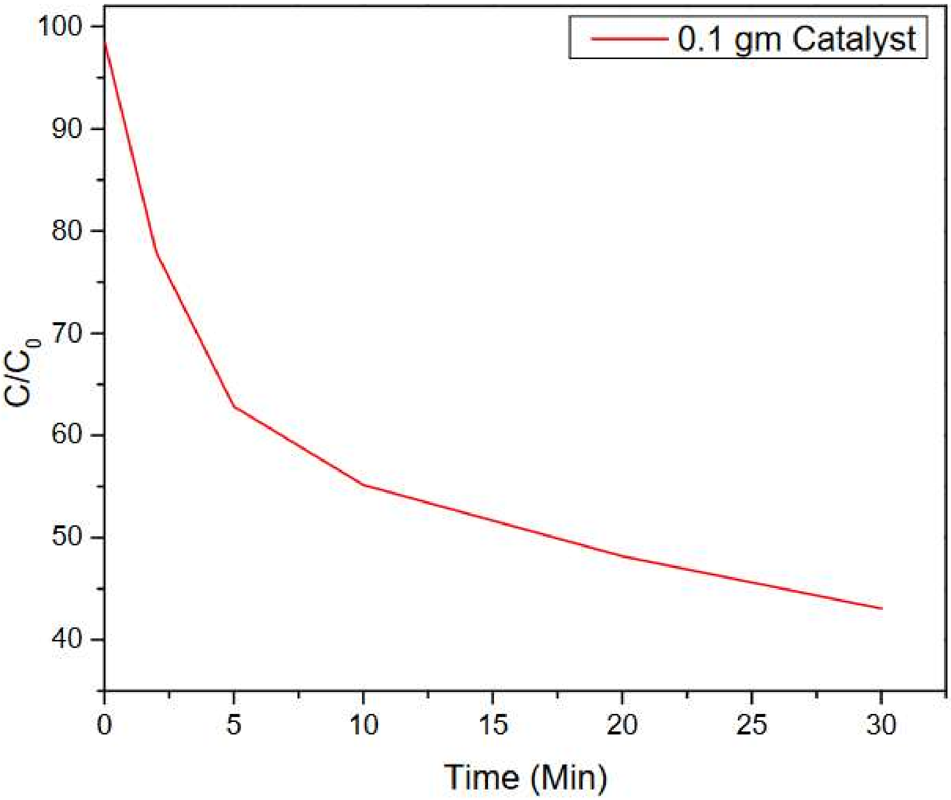

Figure 7: Dye-degradation kinetics plot for g-C_3N_4

To understand the effect of pH on the degradation of methylene blue, dye solution was made in different pH solutions with the help of 0.01 N HCl and 0.01 N NaOH. Three different pH studies were done to better understand the effect of the environment on the degradation dye. Three pH values were 5pH, 6pH, and 7pH. During the practical study of dye degradation, the same procedure was followed keeping the concentration of dye and weight of catalyst constant. 50 ppm solution at different values of pH was stirred for in the dark initially to obtain adsorption equilibrium. Later, samples were taken at 0 min, 2 min, 5 min, 10 min, 15 min, 20 min, 25 min and analyzed in a UV-Visible Spectrophotometer and based on which graph was plotted.

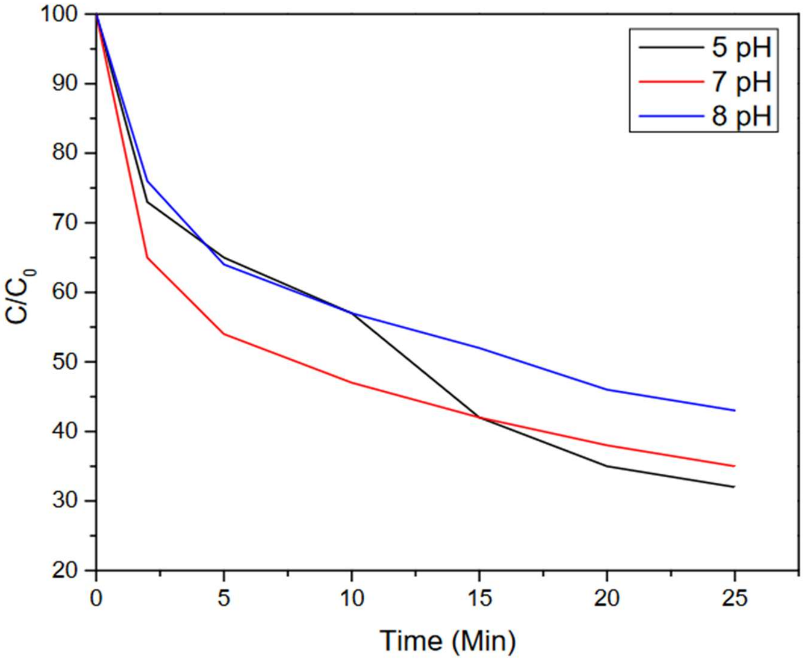

Figure 8: Effect of pH on degradation Methylene blue dye w.r.t. time

Figure 8 shows how pH affects the degradation of dyes. The pH ranged from 5 to 8. The indicates that the short pH range is preferable to the high pH side. It is expected that the dye's absorption and degradation over the catalyst will be more significant in the acidic pH range as methylene blue dye is a cationic dye in nature **[20-22]**.

4. CONCLUSION

In this work, g-C_3N_4 was used as a photocatalyst for the degradation of methylene blue. Photocatalyst was synthesized from melamine at a temperature around 500°C. later samples were characterized using FTIR and XRD which shows that g-C3N4 was successfully synthesized. Since g-C3N4 has a lower band gap it showed significant, g-C3N4 showed significant change in the concentration of simulated wastewater contaminated with methylene blue dye. Resulted showed a significantly lowered concentration of methylene blue dye over time whereas to understand the effect of pH, the dye solution was made in three different pH solutions i.e., 5,6,7. The result showed that being cationic in nature, methylene blue showed higher efficiency under acidic conditions.

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