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ENHANCED PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE: SYNTHESIS AND CHARACTERIZATION OF METAL-DOPED GRAPHITIC CARBON NITRIDE

1. Vijay Kumar, Assistant Professor, Department of Chemical Engineering, SCRIET, CCSU Campus, Meerut, Mail ID: vijaychaudhary91@gmail.com.
2. Aman Kumar, Assistant Professor, Department of Chemical Engineering, SCRIET, CCSU Campus, Meerut, Mail ID:aman.jaiswal43@gmail.com.
3. Pratyush Upadhyay, Assistant Professor, Department of Chemical Engineering, SCRIET, CCSU Campus, Meerut, Mail ID:pratyush023@gmail.com.
4. Vikas Mishra, Assistant Professor, Department of Chemical Engineering, SCRIET, CCSU Campus, Meerut, Mail ID:vikasknmiet123@gmail.com.

ABSTRACT

This research looks at how graphitic carbon nitride (g-C3N4) is affected by metal doping and how its band-gap is tuned to improve dye degradation when exposed to visible light. To enhance its photocatalytic performance and optimize its electronic structure, g-C3N4, a potential photocatalyst, is changed by adding different metal ions. Energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), ultraviolet visible spectroscopy (UVVIS), and X-ray diffraction (XRD) were the methods used to characterize the pure and doped g-C3N4. The impact of metal doping on band-gap tuning, visible light absorption, and photocatalytic activity is studied. Under visible light, the modified g-C3N4 samples are evaluated for their capacity to break down common organic dyes in water-based solutions. The results show that g-C3N4 with certain metal dopants has far better photocatalytic performance than g-C3N4 without dopants, which results in faster dye degradation rates. The study delves into the mechanics of enhanced photocatalytic activity, covering topics like broader light absorption and better charge separation efficiency. This study demonstrates that g-C3N4 doped with metals could be a long-term solution for environmental cleanup.

Keywords: Dye Degradation, Photocatalysis, Environmental Remediation, Charge Separation.

1.1 INTRODUCTION

It is crucial to find sustainable and efficient ways to purify water since organic pollutants, including dyes, are becoming more common in bodies of water. The persistent and poisonous synthetic dye methyl orange is widely employed in the textile industry but also presents serious health and environmental dangers. Using photocatalysts, which can convert light energy into chemical reactions, photocatalytic degradation has recently arisen as a potential solution to this problem. Graphitic carbon nitride (g-C_3N_4), one of many photocatalytic materials, has attracted a lot of interest because of its unusual electrical characteristics, chemical stability, and transparency to visible light. Nevertheless, g-C_3N_4's photocatalytic efficacy is sometimes hindered by its inherent limitations, such as its quick charge recombination and restricted light absorption.

Extensive research into the synthesis and characterisation of metal-doped g-C_3N_4 has been conducted in an effort to address these obstacles. Doping with metals alters the electronic structure of g-C_tN_4 and improves its photocatalytic efficacy. This extensive research examines the production of metal-doped g-C_3N_4 and its usage in improving the photocatalytic breakdown of methyl orange. Incorporating transition

metals such as Fe, Co, and Ni into the g-C₃N₄ structure enhances charge separation, extends the light absorption spectrum, and creates active sites for the degrading reaction.

Thermal polymerization of melamine, dicyandiamide, or urea is a common step in the synthesis of metal-doped g-C₃N₄, and the metal dopants are added either directly during polymerization or as a post-synthesis modification. The optical, structural, and morphological features of the produced materials are examined using characterization techniques as UV-vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Success in incorporating metal dopants, alterations to surface morphology and crystal structure, and enhancements to light absorption capabilities are all illuminated by these characterizations.

Through the measurement of the degradation rate of methyl orange under visible light irradiation, the study assesses the photocatalytic performance of the metal-doped g-C₃N₄. To get the best photocatalytic activity, various parameters are methodically adjusted, including the kind and amount of metal dopants, the intensity of the light, and the reaction conditions. The results show that metal doping significantly improves degradation efficiency, which is due to greater surface area, better charge separation, and a wider range of light that can be absorbed.

Not only does this study add to our knowledge of metal-doped g-C₃N₄ as an effective photocatalyst, but it also helps find workable ways to clean wastewater. Cleaner water resources and a healthier environment can be achieved through the optimization of synthesis and application of these materials in this study, which aims to provide more efficient, cost-effective, and environmentally friendly techniques for degrading organic contaminants.

1.2 REVIEW OF LITERATURE

Motamedisade, Anahita et al., (2024). Merging Au 9 nanoclusters (Au 9 NCs) with N functionalized mesoporous TiO 2 (NMTiO 2) creates a new catalyst for dye degradation. A process called chitosan-assisted soft templating is used to make NMTiO 2. This process creates an N-terminated surface that enhances the loading with Au 9 and prevents the agglomeration of the Au 9 NCs adsorbed surface. The surface characteristics and adsorption capacity of the NMTiO 2 for the Au 9 NCs were affected by the calcination environment. We tested these materials' photocatalytic capabilities by degrading methyl orange (MO) dye. Because of its substantial reaction constant (0.176 min^{-1}), the black-colored Au 9 /NMTiO 2 catalyst is able to totally breakdown MO dyes in about 20 minutes. Statistical analysis and three-dimensional plots were used to assess the dependence of MO degradation on the influencing parameters, and response surface methodology (RSM) was used to investigate parameter interactions for the dye degradation process.

Paul Chowdhury, Arpita et al., (2023). There has been persistent environmental contamination in the last several decades due in large part to the textile sector. Examples of synthetic colors typically discovered in wastewater include phthalocyanine derivatives, indigoid, azo, sulfur, anthraquinone, and triphenylmethyl. Aquatic life is negatively impacted by these contaminants because they obstruct the passage of light into water bodies, which in turn hinders photosynthesis. Several technologies have been investigated as potential solutions to the pollution challenge. When compared to other methods, photocatalysis stands out for being environmentally friendly, easy to implement, and cost-effective. Numerous photocatalysts, including heterostructured nanocomposites, metal ferrites, and metal oxides, have been studied by researchers across the globe in an effort to enhance the photocatalytic activity. This review paper primarily aims to suggest a hybrid photocatalyst that is both cost-efficient and highly effective for the potential remediation of azo dye pollutants. The difficulties and unknowns of photocatalytic dye degradation were also intended to be brought to light in this review study.

Sathishkumar, K. et al., (2022). AT stands for Ag-doped TiO2 and AT/CSAC for Ag-doped TiO2 loaded cassava stem activated carbon, both of which were previously synthesized using the sol-gel process. By adding silver doping and cassava stem activated carbon loading, the XRD findings showed that the anatase-TiO2 and crystalline size were reduced by 12.37 nm. The AT/CSAC exhibits a red shift from the absorption edge in comparison to pure and AT samples, as revealed by UV-Vis. Subsequently, the band gap is decreased to 2.81 eV. The AT/CSAC sample's surface area increased by 238.51 m^2/g due to the Ag and CSAC, respectively. Results show that samples of TiO2 following silver doping and cassava stem activated carbon loading had the maximum photodegradation efficiency (98.08%) when exposed to sunshine. These samples also exhibited brilliant green (BG) coloration.

Pang, Yean et al., (2021). The photocatalytic activity was determined to be the highest by g-C3N4/biochar composite when compared to other biochar composites. Response surface methodology (RSM) was used to study the photocatalytic degradation of methyl orange and the interactive effects of parameters such catalyst dosage, peroxymonosulfate (PMS) oxidant dosage, and solution pH. After 30 minutes, the optimal conditions for photocatalytic degradation were a catalyst dosage of 0.75 g/L, an oxidant dosage of 0.6 mM, and a solution pH of 3. The maximum efficiency reached was 96.63%.

Tsuji, Masaharu et al., (2018). Photocatalysts made of TiO2 and Au/TiO2 were tested for their ability to degrade methyl orange (MO) in both acidic and neutral conditions. The presence of P25 TiO2 during the microwave-polyol technique allowed for the synthesis of Au/TiO2 photocatalysts with an atomic ratio of 1.5±0.1% Au: 98.5±0.1% Ti. At pH 7, TiO2 degraded MO at a rate of 0.13 min-1, but at pH 2, the rates climbed to 0.96 min-1 and 3.06 min-1, respectively. This rise was due to changes in pH. These findings show that in neutral solutions, putting Au nanoparticles on TiO2 speeds up MO degradation by 1.7 times, whereas in acidic conditions, it speeds up degradation by 3.2 times. According to our mass spectroscopic studies, the main reaction products are formed in neutral solutions when the benzenoid form of MO is demethylated and added an OH group, and in acidic solutions, they are formed when the quinonoid form of MO is ring opened and carboxylated following scission of a central N-NH bond. To improve the photocatalytic activity of Au/TiO2, the authors examine the relative significance of electron trapping and surface plasmon resonance (SPR) effects of Au nanoparticles.

Luo, Jin et al., (2015). Using phosphorus doping and coupling with CeO2 species, composite photocatalysts made of CeO2/P-C3N4 were created. Scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, photoluminescence spectroscopy, UV-vis diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy were used to describe the optical characteristics and structure of the as-prepared samples. Under visible light irradiation (λ>420 nm), the photocatalytic degradation of methyl orange (MO) was used to assess the photocatalytic activity of the CeO2/P-C3N4. The results showed that at a weight level of 13.8% CeO2, the ideal photocatalytic activity of CeO2/P-C3N4 for MO degradation was 7.4 times higher than that of pure CeO2 and 4.9 times higher than that of g-C3N4, respectively. Thanks to the synergistic effect of CeO2 and P-C3N4, which was discovered to increase the efficiency of photogenerated electron-hole pair separation after doping with phosphorus and coupling with CeO2, as well as to extend the visible light absorption range, the photocatalytic activity was significantly enhanced. In addition, the experimental results suggested a potential photocatalytic mechanism over a CeO2/P-C3N4 composite photocatalyst, with superoxide radical anions (•O- 2) and holes (h+) being the principal reactive species throughout the photodegradation MO process.

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1.3 MATERIAL AND METHODS

Materials

Thermo Fisher Scientific in Mumbai supplied the MO (C14H14N3NaO3S) and SDFCL (C3H6N6) melamine, respectively. Throughout the process, distilled water was utilized. Except where noted, all procedures were carried out under room temperature.

Methods

g-C3N4 nanoparticle synthesis

The g-C3N4 nanoparticles were created by subjecting melamine to a direct heating of 600°C for 6 hours in a sealed crucible set in a muffle furnace. During the reaction, the crucible's lid was sealed to maintain the surrounding air.

Synthesis of metal-doped g-C3N4 nanoparticles

The photocatalyst of Ni, Cu, and Fe doped g-C3N4 (denoted as g-C3N4/X) was produced by combining 250 mg of metal salts with 5 mg of melamine and 5 mL of water to create a slurry.

Table1:g-C_3N_4dopedwithmetal,theirbandgapandphotocatalyticapplication

Dopingelement	Precursor	Synthesis	E_g(eV)	Application	Reference
Fe	$Fe(NO_3)_3 9H_2O$(Fe)Melamine(CN)	Thermalcondensation	2.64	RhBdegradation	21
Cu	$CuCl_2$(Cu)Melamine(CN)	Thermalcondensation	2.25	MOdegradation	22
Ce	$Ce(SO_4)_2 \cdot 4H_2O$(Ce)Melamine(CN)	Annealing	2.57	RhBdegradation	23
Co	CoPc(Co)Melamine (CN)	Thermalcondensation	2.62	H_2evolution	24

Characterization of the synthesized samples

Energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), ultraviolet visible spectroscopy (UV-VIS), and X-ray diffraction (XRD) were the techniques used to characterize the pure and doped g-C3N4. The synthesised catalyst's structure was investigated by collecting XRD data utilizing RIGAKU's equipment. In order to find the band gap, the CARY, 100 bio, UV.vis spectrophotometer was utilized in conjunction with data from UV-visible spectroscopy. The shape of the particles was determined by scanning electron microscopy (SEM) with a Quanta 450 and elemental analysis by energy dispersive X-ray spectroscopy (EDX) with an EDAX.

Photocatalytic studies on g-C3N4/X

Under visible light, a reactor containing a catalyst (5 mg) and a solution of MO dye, a potentially harmful pollutant, was used to study the photocatalytic activity. Achieving absorption-desorption equilibrium required 30 minutes of dark incubation of the dye solution prior to the experiment. To 100 mL of MO dye solution, a specified amount of prepared catalyst was added.

For the first ten minutes, the solution was maintained in the dark in order to achieve adsorption-desorption equilibrium. After that, the solution was left in the sun to undergo a photocatalytic process. The change in absorbance was recorded using a UV-visible spectrophotometer after every 10 minutes after a certain volume was taken.

1.4 EXPERIMENTAL RESULTS

The catalytic process and its formulation Melamine can be converted into g-C3N4 and doped g-C3N4 through polyaddition and polycondensation reactions carried out at a constant temperature. Melamine was first cooked to a high enough temperature to remove ammonia20.

It is also possible that the polycondensation of heptazine units19 led to the development of the g-C3N4 polymeric network at 600℃.

Characterization of g-C3N4/X

You can see the XRD patterns of both the pure and doped g-C3N4 in Figure 1. A hexagonal phase and carbon are both revealed. Significant peaks at 12.78o and 27.38o, which correspond to the (100) and (002) plane reflections, respectively, suggest the synthesis of g-C3N4, while smaller peaks demonstrate the existence of oxides and sulfates of the relevant metals.

The high crystalline nature of the catalyst is demonstrated by the excessive intensity of the peak at 27.38o compared to others. The development of copper sulfide is shown by a tiny peak at 48.88 degrees when the material is doped with copper. The presence of copper oxides (CuO and Cu2O) was confirmed by peaks at 35.62o and 38.80o, respectively. A tiny peak at 44.25 degrees was seen in nickel, indicating the existence of nickel oxide.

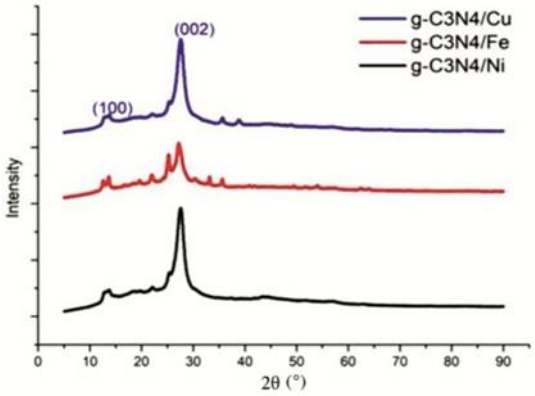

Figure 1.1: XRD plots of Ni, Fe and Cu doped g-C3N4

Figure 2a displays the synthesized catalysts in all their glory. Figure 2b displays the equivalent Tauc plots for the absorption spectra that were measured in the reflectance mode. When comparing doped and pure catalysts, a little decrease in band gap is observed in the latter. The bandgaps for g-C3N4/Cu, g-C3N4/Ni, and g-C3N4/Fe are 2.46 eV, 2.47 eV, and 2.54 eV, respectively.

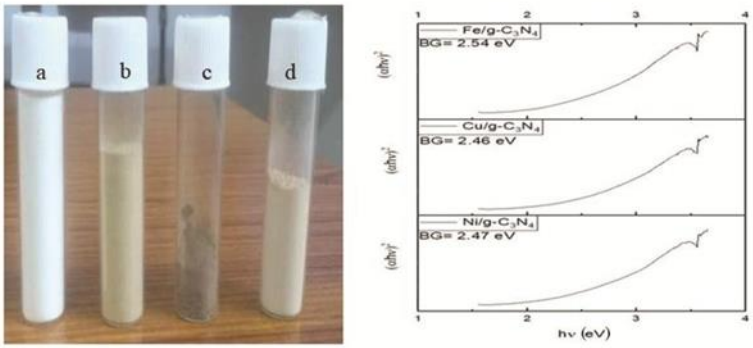

Figure 1.2: (a) Photographs of synthesized catalysts A and (b) Tauc plots

SEM analysis verified that g C3N4 contains metal. Upon doping with various metals, the shape of the g-C3N4 catalyst (Fig. 3a) changed somewhat (Fig. 3b-d). The doped samples were found to contain the corresponding metals, according to the EDX examination.

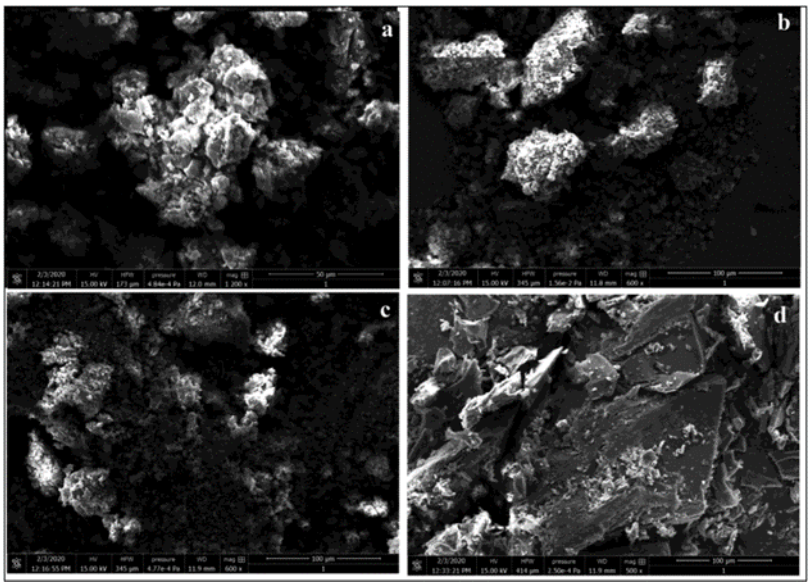

Figure 1.3: SEM images of different catalysts, g-C3N4 doped with metal a) Nickel b) Iron and c) Copper, and d) undoped g-C3N4

Photocatalytic activity of g-C3N4/X

In Figure 4, we can see the percentage changes in dye solutions that were exposed to direct sunlight at room temperature using various synthetic photocatalysts. After 70 minutes, when no changes in absorption were seen, the absorbances of the solutions were recorded. For an undoped g-C3N4 photocatalyst, the percentage of degradation in 1 hour after exposure to sunshine was around 15%; however, for g-C3N4/Fe, 54%, and g-C3N4/Cu, 62%, respectively, the value increased to 30%, 54%, and 62%. Its photocatalytic activity was mainly due to the photocatalyst's electron-hole recombination rate.

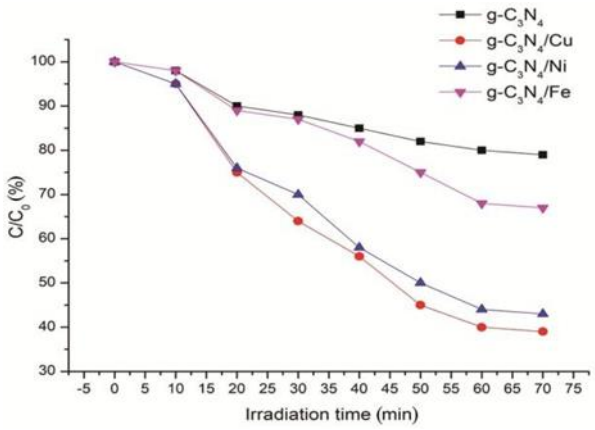

Figure 1.4: %Degradation curves for MO removal by using different catalysts

1.5 CONCLUSION

This study not only proves that metal-doped g-C_3N_4 can be a better photocatalyst, but it also shows that it may be used to clean wastewater. These materials are ideal for use in large-scale environmental restoration projects due to their improved degrading efficiency and stability. This research helps advance greener, more efficient, and less expensive methods of organic pollution removal from water by elucidating the processes underpinning the enhanced photocatalytic activity and optimizing the synthesis parameters.

In sum, this study's results will likely have far-reaching consequences for how environmentalists use photocatalytic materials in the future. Improvements in the synthesis and performance of metal-doped g-C_3N_4 not only strengthen our capacity to address water pollution, but also motivate additional studies to develop sophisticated photocatalysts for a wider variety of pollutants, leading to a cleaner and more sustainable world in the long run.

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