International Journal of Information Technology and Management
Vol. 17, Issue No. 2, August-2022, ISSN 2249-4510

DOI: https://doi.org/10.29070/aep8sb81

A study on Nanocomposite under visible light for photocatalytic degradation of organic contaminants

Sandeep Kumar Suman [1] * , Dr. Rajesh Kumar Kushwaha [2]

1. Research Scholar, Shri Krishna University, Chhatarpur, M.P., India
mrsandeepkumarsuman@gmail.com ,
2. Associate Professor, Shri Krishna University, Chhatarpur, M.P., India

Abstract: Nanocomposites have a huge amount of promise to help solve environmental problems, especially when it comes to breaking down biological pollutants with visible light. This article talks about the latest progress made in making and using hybrid materials for photocatalysis. Different kinds of nanocomposites, how they are made, and how well they break down organic toxins are all talked about. It is also looked at how important factors like shape, makeup, and surface features affect the photocatalytic activity of nanocomposites. There are also problems and opportunities for the future in the field, which emphasises how important it is to keep researching to improve nanocomposite-based photocatalytic systems for long-term environmental cleanup.

Keywords: Nanotechnology, photocatalytic degradation, organic contaminants

X

INTRODUCTION

The escalating contamination of water and air by organic pollutants poses a significant threat to environmental and human health. Most of the time, traditional ways of getting rid of pollutants are not very successful or cost-effective. In this situation, nanocomposite materials have become interesting options for breaking down organic pollutants through photocatalysis, especially when visible light is present. Nanocomposites, which combine distinct nanoscale components, offer enhanced photocatalytic activity owing to synergistic effects and tailored properties. This paper provides an overview of the current state-of-the-art in nanocomposite-based photocatalysis, encompassing various types of nanocomposites, including metal-semiconductor, semiconductor-semiconductor, and polymer-semiconductor hybrids. Additionally, the synthesis strategies employed to fabricate these nanocomposites and their implications on photocatalytic performance are discussed. Furthermore, the factors influencing the photocatalytic efficiency of nanocomposites, such as crystallinity, surface area, and charge separation, are elucidated. By elucidating the mechanisms underlying photocatalytic degradation and highlighting recent advancements, this paper aims to underscore the potential of nanocomposites as effective tools for environmental remediation.

FUNDAMENTALS OF NANOTECHNOLOGY

Nanotechnology, in its broadest sense, refers to the use of technological means for the purpose of creating and executing nanostructures and nanomaterial applications. Material dimensions (grain size, layer thickness, and materials below 100 nm) that exhibit nanostructures are largely responsible for the growing fascination with nanotechnology (Hornyak et al. 2009). Nanomaterials are unique in their peculiar characteristics due to the size of these particles. According to Chattopadhyay et al. (2009), materials that have a dimension smaller than 100 nm are considered nanomaterials. The chemical, physical, and biological domains are all rich in potential uses for nanotechnology and nanomaterials.

During the 1959 American Physical Society annual meeting, Richard Feynman delivered his now-iconic speech titled "There is a plenty of room at the bottom," marking the beginning of nanotechnology. During the previous twenty years, there have been numerous advancements in the field of nanomaterial manufacturing, including new discoveries and technologies. Innovative nanostructured materials with a broad variety of dimensions and qualities are now within reach, thanks to improved theoretical and experimental synthesis methodologies and procedures for the discovery of novel materials. This innovation paves the way for brand-new areas of study and technological development.

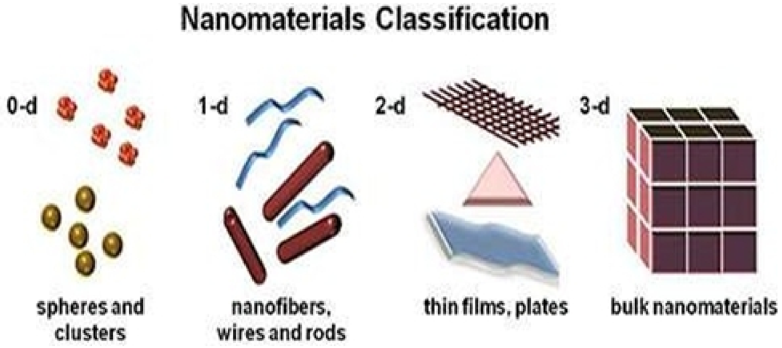


Figure 1: Classification of Nanomaterial under dimensions(Source: Bhattacharya 2014)

There are a number of ways to categorize nanomaterials, but the most common is by their size (Figure 1). Particles of zero-dimensional carbon black made up the first generation of nanomaterials. Nanowires and nanorods, which are typically one-dimensional materials, make up the second generation of nanomaterials. Thin films and coatings are examples of third-generation materials; they only have two dimensions. The fourth generation of materials, carbon nanotubes (CNTs), have three-dimensional structures.

BASIC CONCEPTS OF NANOTECHNOLOGY AND NANOMATERIAL

Catalytic Property

Metal oxide dispersions often employ templates such as zeolite, carbon, silica, and alumina as catalysts. Nanoparticle shape and dispersion over a template are notoriously difficult to keep consistent. A controlled reaction with uniform dispersion and particle size can be achieved by using silica as a template on a metal oxide coating. When it comes to SO2 adsorption, Klabunde and colleagues showed that Fe2O3@MgO and Fe2O3@CaO are more efficient than pure metal oxides, MgO, and CaO. The most important factor in these catalytic behaviors is the interaction between the catalyst's shell, core, and reactants.

Stabilization of Colloidal Nanoparticle

Surface modification of Ag, CdSe, Fe_2O_3 and Au over SiO_2 (10- 100 nm thickness) prevents coagulation even with higher concentration salt solution (e.g. 0.15 M NaCl) for a longer time period due to the fact that

SiO_2 has lower Hamaker constant than most metals.

DIVERSE APPLICATIONS OF NANOMATERIALS

The vast array of potential uses for nanotechnology has garnered a lot of interest from both the business world and the academic world in the last 10 years. The commercial sectors, including food and cosmetics, as well as the biomedical, electrical, optical, mechanical, and chemical industries, are finding new uses for nanoscale materials through nanotechnology. Many sectors of the economy are anticipating a resurgence in innovation and discovery thanks to its convergence with IT, biology, and the social sciences.

MECHANISM OF PHOTOCATALYSIS

Semiconductors don't have a continuous range of electronic states like metals do. Instead, they have a void energy area where there are no energy levels to encourage photoactivated electrons and holes to mix again. The band gap is the empty space between the top edge of the full valence band and the bottom edge of the empty conduction band. When a photon hits a semiconductor or photocatalyst, if the photon energy, hω, is equal to or greater than the band gap of the semiconductor or photocatalyst, an electron (e-) is moved from the valence band to the conduction band. At the same time, the valence band makes a hole (h+), which is a positive charge made up of empty electrons (Figure 2).

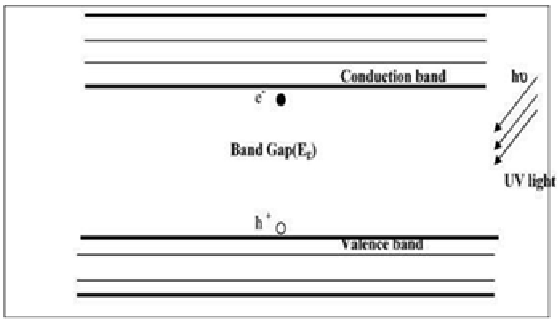


Figure 2: Band-gap diagram of semiconductor material

CATALYSIS

Catalysis is an interesting field of study because it has many applications in our daily lives. Catalytic processes are very important in four main areas of the world economy, as shown in Figure 3: making oil and energy, making chemicals and plastics, making food, and cleaning up waste. A lot of people are interested in the idea of using semiconductor-based photocatalysis, which is also called heterogeneous photocatalysis, to clean up trash and make hydrogen fuel from sunshine, which is a clean and plentiful energy source.

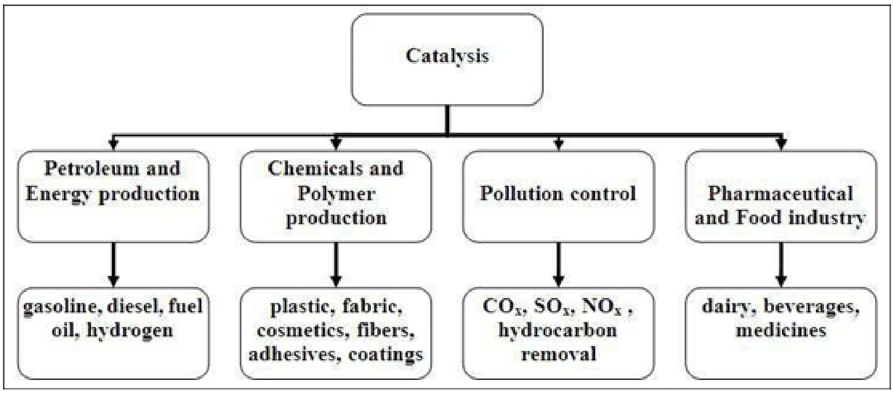


Figure 3: Four areas which involve catalytic process

CATALYTIC REACTIONS

In a chemical reaction that is thermodynamically sustainable, a catalytic reaction happens when a small amount of a chemical substance speeds up the process of reaching chemical balance without changing the substance itself. What is known as a trigger is something that speeds up a process. What makes catalysts work is another process that uses a lower-energy transition state. As a result, as shown in Figure 4, the catalytic process has lower activation energy than the reaction that doesn't have a catalyst.

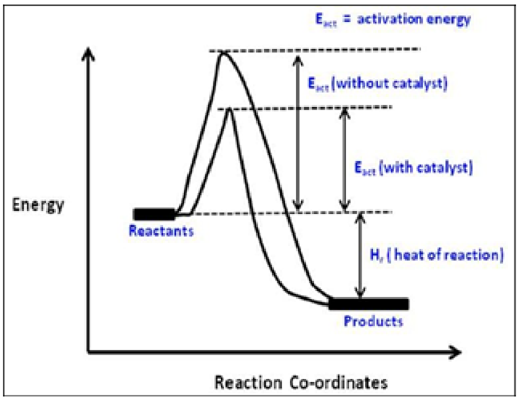


Figure 4: Activation energies of exothermic catalytic and non-catalytic systems

PHOTOCATALYSIS

The word "photocatalysis" has been used a lot since it was first used in science writing in 1930. This is what the International Union of Pure and Applied Chemistry says a photocatalytic reaction is: "a catalytic reaction involving light absorption by a catalyst or a substrate." In the 1980s, Salomon identified two main types of photocatalysis: photon catalytic and photolysis catalytic. In photon catalytic, the process creates photons, while in photolysis catalytic, it does not. Catalysis that is caused by light involves both the substrate and the catalyst in the ground states during the thermodynamically spontaneous (exoergic) phase. For catalysed photolysis, on the other hand, either the substrate or the theoretical catalyst needs to be in an excited state, or both.

What are photocatalysts or catalysts? They are solid substances that meet certain conditions. Some of these situations are:

- Molecules sticking to the surface of particles;
- The molecule moves across the reaction surface and goes through a number of chemical changes.
- The intermediate or product molecule is then adsorbted into the gas or condensed phase.

There has to be an equilibrium between the strength of the reactant molecule's contacts with the photo catalyst's surface site for bond breaking and bond forming to occur throughout the residence duration of the intermediate(s), as well as for desorption and adsorption to take place.

In order to expedite the process, the catalyst may interact with the substrate(s) in either their ground or excited states, or with the catalyst's primary product, depending on the photoreaction mechanism. In conclusion, photocatalysis refers to the action of light on semiconductor surfaces to cause catalysis. The three main steps in photocatalysis are photo-induced charge carrier excitation, bulk diffusion, and surface transfer. The electrical structure, surface structure, and bulk structure of semiconductor photocatalysts all play a role in these processes.

Many chemical processes may be accelerated by using semiconductors as catalysts. Various examples include oxidation, hydrogenation, hydroxylation, and so forth. The electronic activities taking place inside and on the surface of semiconductors have a direct correlation to their catalytic characteristics. The nature and electrical state of the object dictate it. Another factor that affects the activity is the presence of impurities in the semiconductors.

The application of semiconductors to heterogeneous photo catalysis is a relatively young field of study. The activation mechanism is the sole difference between photocatalytic reactions and conventional catalysis. Other than that, the two are identical. Light, rather than heat, is used to activate the reactants in photocatalysis. It is still unclear why semiconducting materials are such effective photocatalysts. Substances with conductivities that are intermediate between those of insulators and metals are known as semiconductors. As you can see in Figure 5, their band gap (E bg) is in the middle of what metals and insulators have. This is the energy level difference between the conduction band, which is the lowest band that isn't being used, and the valence band, which is using the most energy.

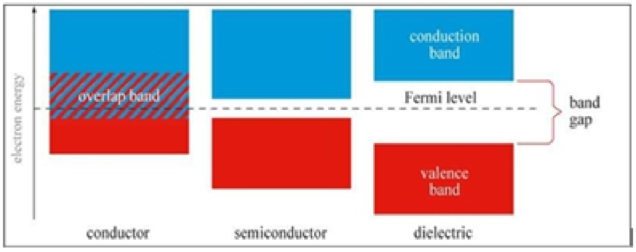


Figure 5: Band Structure of metals, semiconductors and insulators

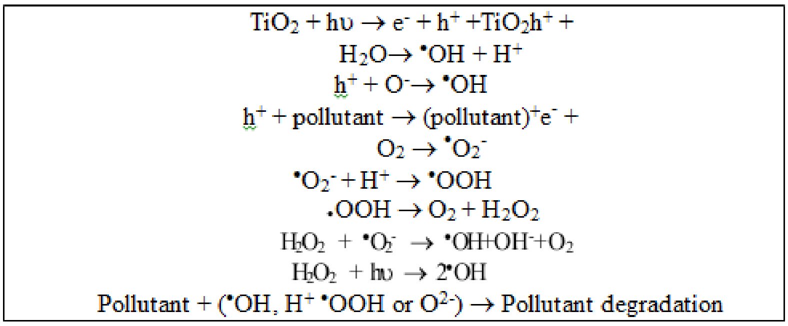
PHOTOCATALYTIC REACTIONS

Heterogeneous photocatalytic reactions require three components: a photon with the right wavelength, a surface that acts as a catalyst (typically a semiconductor material), and a powerful oxidising agent (often oxygen). Since absorbed photons are a nonmaterial reactant, their presence is essential for a reaction to occur, as stated by Pasquali et al. (1996). There are many levels in a semiconductor that are full of electrons and a set of levels that are mostly empty. These are called the conduction band and the valence band, respectively. It is called the "energy gap" because the two bands have different amounts of energy. A photon with energy equal to or greater than the photocatalyst's band gap energy (Ebg) hits its surface and sets off the molecules inside. This starts the heterogeneous photocatalytic process.

After molecular excitation, the lower energy valence band (Evb) of a catalyst forms positive holes while the higher energy conduction band (Ecb) forms mobile electrons. A catalyst, such as a semiconductor, speeds up a reaction compared to its equilibrium state, allowing it to achieve equilibrium more quickly. Thermodynamically favoured but kinetically slow reactions may be accelerated by catalysts via interactions with reactants that choose a lower energy pathway. Once the reaction is complete, the catalyst may be returned to its initial state and concentration.

There can be changes in the Gibbs free energy of this process that are both positive (during photosynthesis) and negative (during photocatalysis). Most of the time, a semiconductor photocatalyst will respond with particles that are between micrometres and nanometres in width and are made up of groups of nano crystals. These particles can be stacked on top of each other to make a powder or a thin film that is usually 100 to 10,000 nm thick.

Making an electron pair is the first step in the photocatalytic process. In the second step, a number of chemical events happen. So, oxidation reactions use the electron hole (h+), reduction processes take the electron (e-), and oxygen can make hydrogen peroxide and superoxide anions. The process is not very effective because electron and electron hole recombination happen at the same time, wasting the photon's energy. Recombination of electrons and holes is one of the main things that makes photocatalytic processes less effective. In order for mixed photocatalytic processes to clean water and air, it is important to stop electron and electron-hole recombination. The heterogeneous photocatalytic process is made up of a series of steps, which are shown in Scheme 1.1. TiO2 is turned on by light, which makes an electron and an electron hole.



$$TiO_2 + h\upsilon \rightarrow e^- + h^+ + TiO_2h^+ +$$
$$H_2O \rightarrow {}^{\bullet}OH + H^+$$
$$h^+ + O^- \rightarrow {}^{\bullet}OH$$
$$h^+ + \text{pollutant} \rightarrow (\text{pollutant})^+ e^- +$$
$$O_2 \rightarrow {}^{\bullet}O_2^-$$
$${}^{\bullet}O_2^- + H^+ \rightarrow {}^{\bullet}OOH$$
$$\bullet OOH \rightarrow O_2 + H_2O_2$$
$$H_2O_2 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}OH + OH^- + O_2$$
$$H_2O_2 + h\upsilon \rightarrow 2{}^{\bullet}OH$$
$$\text{Pollutant} + ({}^{\bullet}OH, H^+ {}^{\bullet}OOH \text{ or } O^{2-}) \rightarrow \text{Pollutant degradation}$$

Scheme 1.1: Photodegradation of pollutants by semiconductors

OH• radicals are very reactive, so they go after pollution molecules and break them down into natural acids like water and carbon dioxide.

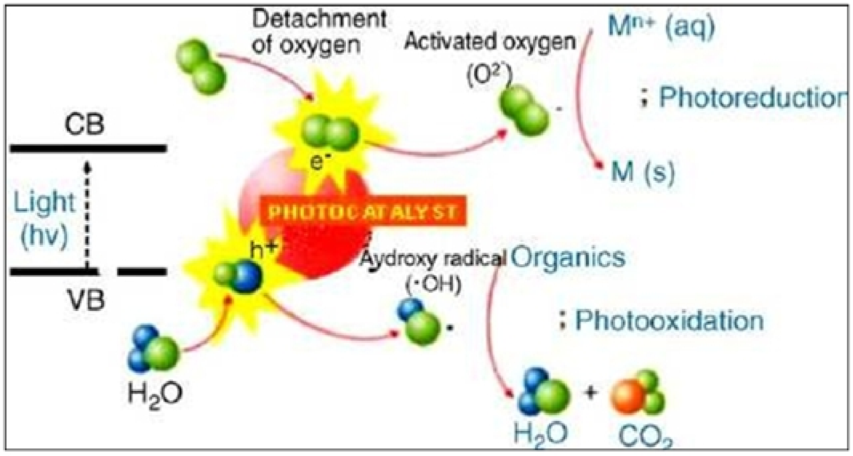


Figure 6: Photochemical reaction in presence of a photocatalyst

The creation of electron-hole pairs by a semiconductor particle is shown in Figure 6.

EFFECT OF FUNDAMENTAL PARAMETERS ON PHOTOCATALYSIS

To get photocatalytic oxidation (PCO) to work, you need to figure out the best process factors. Some toxins break down better in alkaline media, others may do better in neutral or acidic media, etc. Because different pollutants go through PCO through different chemical pathways, process factors have different effects on each type of pollutant. So, for each type of pollution, it is usual to look into the effects of the most important operating factors and do a lot of research on a particular PCO system to find the best treatment options.

CHARACTERIZATION TECHNIQUES

The characterisation procedures were crucial in understanding the materials' properties, which were then used in a variety of technological applications. In this part, we see examples of the many kinds of instruments used for characterizing nanomaterials and nanocomposites.

X-ray Diffraction

There is a robust relationship between the structure and characteristics of nanomaterials. Because of its dependability, X-ray diffraction is an effective and non-destructive technique for determining structural characteristics such as crystalline/amorphous, phase, lattice constants, bond length, and space group.A comparison between the XRD characterisation results and the JCPDS Fundamental data may validate the presence of certain components or reveal the existence of novel compounds or materials.

The fundamental idea behind XRD is the interaction of monochromatic X-rays with crystalline materials, which leads to the creation of interference patterns according to Bragg's rule. The structural properties of the materials can be uncovered by employing a PANalytical X-Ray diffractometer equipped with CuKα radiation (λ=1.548 Å) and a scanning speed of 0.02/sec within the 2θ range of 10˚-100˚.

Raman Spectroscopy

A key component of the Raman effect is the inelastic scattering interaction that occurs when vibration phonons from materials interact with incoming light photons. As a result, molecular identification using Raman vibration spectra is commonplace. Any kind of defect or sublattice disorder introduced during synthesis may be extrapolated from the Raman spectra in terms of band location, intensity, and shift as well as Full Width and Half Maximum (FWHM).

X-Ray Photoelectron Spectroscopy (XPS)

The X-ray photons that come from the magnesium or aluminum Kα lines at 1253.6 eV or 1486.6 eV are used to create the photoelectric effect, which is the fundamental basis of the XPS method. This effect involves the ejection of electrons from the surface of the material, at depths ranging from 3 to 10 nm. It is possible to determine the oxidation states and surface chemical compositions of materials using XPS analysis, however this information is not available via the equation.

$$E_{binding} = E_{photon} - E_{kinetic} - \varphi$$

where, $E_{binding}$ - Emitted electron (from the material) energy

E_{photon} - X-ray photon energy

$E_{kinetic}$ - Emitted electrons kinetic energy

φ - Work function of the spectrometer

The distinctive binding energy peaks of an element may be used to determine its identity and valence state. Different compounds exhibit the similar phenomenon of spin orbital splitting at the core level of an element, which is caused by the separation of two peaks. Additionally, the chemical potential of a substance may vary, leading to chemical shifts (a change in binding energy) that help us comprehend the material's chemical states.

Field Emission Scanning Electron Microscopy (FESEM)

In the micro to nanoscale domain, field emission scanning electron microscopy (FESEM) is an effective and non-destructive imaging method for studying surface characteristics (topography) and particle size or shape (morphology). Instead of using light, it operates on negatively charged electrons. The field emission source scans the materials in a zigzag pattern with its released electrons. When compared to traditional scanning electron microscopy (SEM), FESEM produces surface analysis pictures that are three to six times more detailed, clear, and electrostatically distorted. FESEM pictures are supplied by a Japanese instrument called JEOL JSM 7001F, which has an accelerating voltage of 20 kV.

Transmission Electron Microscope (TEM)

To analyze the structure and morphology of materials, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) rely on the idea of transmitted electrons rather than scattered electrons. TEM is an innovative method for determining the exact chemical make-up of materials. Materials were loaded for TEM examination onto carbon-coated copper grids.

Diffuse Reflectance UV- Vis Spectroscopy

In order to capture the materials' reflectance properties between 200 and 800 nm, the diffuse reflectance spectrophotometer is outfitted with an integrating sphere. The reference material has been barium sulfate. A formula has been developed to assess the basic optical absorption of crystalline semiconductors close to the band edge:

$$\alpha h\gamma = A\,(h\gamma - E_g)^n$$

Photoluminescence Spectroscopy

Bandgap energy, exciton migration, impurity levels, and exciton separation efficiency may be better understood in order to comprehend electron-hole pair creation. at ambient temperature A non-invasive and non-destructive technique that has shown promising results is photoluminescence (PL) emission spectroscopy. Electrons in materials undergo photoexcitation when light hits them, causing them to jump from lower energy levels to the allowed excited ones. When these electrons regain their equilibrium states, they release the energy they have received by radiative or non-radiative means, a process known as photo-emission.

Photocatalytic Activity Experimental Setup

In Figure 1.11, you can see a homemade photo reactor made of glass that was used to test the photocatalytic activity of the synthesised samples. Water that was moving around the experiment kept it at room temperature. A photocatalytic reactor setup that was made at home was used for the photodegradation tests. To do this photocatalytic experiment, 75 mg of the photocatalyst that had already been made was added to 50 mL of a 10 ppm methylene blue dye solution in water. The mixture was kept in the dark and stirred with magnets for 30 minutes to find the balance between adsorption and release.

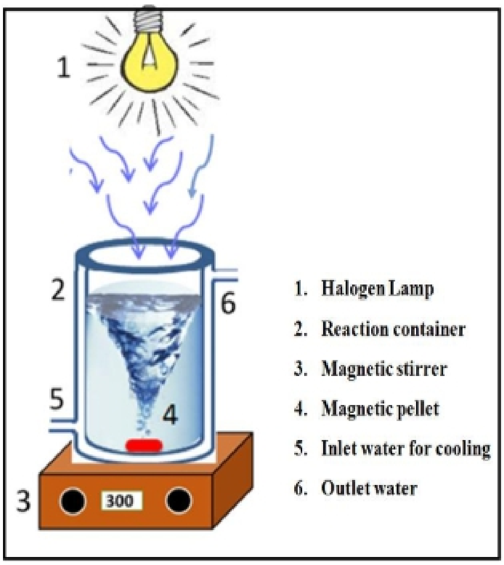


Figure 7: Photograph of Phocatalytic reactor

So that the solution with the photocatalyst in it could be exposed to radiation, a 500 W halogen lamp was put about 25 cm above the tank. Three millilitres of the fluid were centrifuged at regular times during the experiment. The samples were then looked at with a UV-Visible spectrophotometer, starting with the wavelength at which MB absorbs light the most, which is about 664 nm. The Beer-Lambert rule says that the absorption of a solution is directly related to its quantity. So, UV-Vis spectroscopy can be used to find out how concentrated a solution is.

$$\eta(\%) = \frac{(A_0 - A)}{A_0} \times 100$$

where, A_0 - The absorbance of the MB solution without photocatalyst and irradiation,

A - The absorbance of the MB solution with photocatalyst after the irradiation of light for the time of t.

CONCLUSION

Nanocomposite materials have demonstrated remarkable potential in the realm of photocatalytic degradation of organic contaminants under visible light irradiation. Through synergistic combinations of distinct nanoscale components, nanocomposites exhibit enhanced photocatalytic activity, paving the way for efficient environmental remediation. The diverse array of nanocomposite architectures, coupled with tailored synthesis approaches, enables fine-tuning of photocatalytic properties to meet specific application requirements. However, challenges such as stability, scalability, and recyclability still need to be addressed to facilitate the practical implementation of nanocomposite-based photocatalytic systems. Future research endeavors should focus on optimizing nanocomposite design and fabrication processes, as well as elucidating fundamental mechanisms governing photocatalytic activity. By harnessing the potential of nanocomposites, we can advance towards sustainable solutions for mitigating organic pollutant contamination and preserving environmental quality for future generations.

References

1. Berradi M, Hsissou R, Khudhair M, Assouag M, Cherkaoui O, ElBachiri A, Harfi E, A (2019) Textile finishing dyes and their impact on aquatic environs. Heliyon 5(11):e02711

2. Chiang K, Amal R, Tran T (2002) Photocatalytic degradation of cya- nide using titanium dioxide modified with copper oxide. Adv Environ Res 6(4):471–485

3. Durmus Z, Kurt BZ, Durmus A (2019) Synthesis and characterization of graphene oxide/zinc oxide (GO/ZnO) nanocomposite and its utilization for photocatalytic degradation of basic fuchsin dye. ChemistrySelect 4(1):271–278

4. Kanakaraju D, Chandrasekaran A (2022) Recent advances in TiO_2/ ZnS-based binary and ternary photocatalysts for the degradation of organic pollutants. Sci Total Environ 868:161525

5. Khan SR, Jamil S, Bibi S, Ali S, Habib T, Janjua MRSA (2020) A versatile material: Perovskite Bismuth Ferrite Microparticles as a potential Catalyst for enhancing fuel efficiency and degrada- tion of various Organic Dyes. J Inorg Organomet Polym Mater 30(9):3761–3770

6. Li Z, Sheikholeslami M, Shafee A, Haq RU, Khan I, Tlili I, Kandasamy R (2019) Solidification process through a solar energy storage enclosure using various sizes of Al_2O_3 nanoparticles. J Mol Liq 275:941–954

7. Nasseri S, Omidvar Borna M, Esrafili A, Rezaei Kalantary R, Kakavandi B, Sillanpää M, Asadi A (2018) Photocatalytic degradation of malathion using Zn^{2+}–doped TiO_2 nanoparticles: statistical analysis and optimization of operating parameters. Appl Phys A 124(2):1–11

8. Oyekunle JAO, Adekunle AS, Adewole AM, Elugoke SE, Durodola SS, Oyebode BA (2021) Determination of organochlorine pesti- cide residues in some evaporated milk samples in nigeria using gas chromatography-mass spectrometry. Chem Afr 4:349–366

9. Rogozea EA, Petcu AR, Olteanu NL, Lazar CA, Cadar D, Mihaly M(2017) Tandem adsorption-photodegradation activity induced by light on NiO-ZnO p–n couple modified silica nanomaterials. Mater Sci Semiconduct Process 57:1–11

10. Srivastava N, Mukhopadhyay M (2014) Biosynthesis of SnO_2 nano- particles using bacterium Erwinia herbicola and their photo- catalytic activity for degradation of dyes. Ind Eng Chem Res 53(36):13971–13979

11. Subhiksha V, Kokilavani S, Khan SS (2022) Recent advances in deg- radation of organic pollutant in aqueous solutions using bismuth based photocatalysts: a review. Chemosphere 290:133228

12. Zaytseva O, Neumann G (2016) Carbon nanomaterials: production, impact on plant development, agricultural and environmental applications. Chem Biol Technol Agric 3(1):1–26

13. Zhang LH, Zhu Y, Lei BR, Li Y, Zhu W, Li Q (2018) Trichromatic dyes sensitized HKUST-1 (MOF-199) as scavenger towards reactive blue 13 via visible-light photodegradation. Inorg Chem Com- mun 94:27–33