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REVIEW OF PHOTOCATALYTIC DEGRADATION TECHNIQUE OF GREEN SYNTHESIZED BISMUTH/ USING FOR DEGRADATION OF PESTICIDE

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Abstract:

Semiconductor photocatalysis is an effective green technology because it can completely decompose environmental pollutants under mild conditions. The applications of semiconductor photocatalysts have elicited much scholarly attention for use in the treatment of organic pollutants because these photocatalysts can transform solar energy into chemical energy.

Nanotechnology has emerged as a promising method for wastewater recycling.Photocatalytic degradation of organic dye by AOP's is an effective method to minimize water pollution. The semiconducting materials have a larger bandgap and difficult to fabricate in the form of 2 D-films.

KeyWord: Degradation Technique,Green synthesized Bismuth, Pesticide.

1. Introduction:

1.1 Role of Photocatalyst Demineralized:

1.1.1 General Mechanism for Photocatalytic Reaction:

A photo catalyst is utilised in photocatalysis. The pace of reaction is mostly determined by the crystal structure of the catalyst and the energy of the incoming photons of visible or UV light. Depending on the electronic structure of the materials utilised as a catalyst, they operate as a sensitizer for the irradiation of light-stimulated redox reactions. The filled valence and unoccupied conduction bands characterise the electronic structure.

If the catalyst's band gap is equal to or less than the energy of incoming light, electrons in the valence band absorb the photon and go to the conduction band. Holes have been left in the valance band. They are crucial because they oxidise donor molecules while also producing hydroxyl (a powerful oxidant).

In photocatalysis, a photo catalyst is used. The speed of the reaction is mostly governed by the crystal structure of the catalyst and the energy of the entering visible or UV photons. They work as a sensitizer for the irradiation of light-stimulated redox processes, depending on the electronic structure of the materials used as a catalyst. The electrical structure is defined by the filled valence and vacant conduction bands.

If the band gap of the catalyst is equal to or less than the energy of the incoming light, electrons in the valence band absorb it and go to the conduction band. The valance band has holes in it. They are important because they oxidise donor molecules while also creating hydroxyl (a strong oxidant).

1.1.2 Oxidation Mechanism:

When light is shone on the catalyst, an electron hole pair is formed due to the promotion of the valance electron to the conduction band. The hole formed on the catalyst absorbs water molecules and oxidises them into hydroxyl radicals, which have extremely powerful oxidising properties. If any organic contaminant is present, it will react with these hydroxyls and disintegrate. If the entire process is carried out in the presence of oxygen, then chain reactions occur between the intermediate radicals of organic molecules and oxygen molecules. In the case of organic pollutants, the final result is CO2 and H2O.

1.1.3 Reduction Mechanism:

The pairing reaction is used to reduce atmospheric oxygen. Because oxygen is easily reducible, it may be used instead of producing hydrogen. Conduction band electrons react with oxygen to generate superoxide ion. The anion can also bind to the intermediate in an oxidation process, creating peroxides and ultimately changing into water. When opposed to water, organic stuff may quickly undergo reduction. As a result, a high concentration of organic matter improves photocatalytic activity by raising the likelihood of the number of holes, which decreases the recombination rate of the carriers.

1.1.4 Material Selection for Nanomaterials as a Photo-Catalyst:

In photocatalytic reaction, oxidation and reduction reaction occur simultaneously. We need such kind of materials or those catalyst for photocatalytic reaction which support both oxidation and reduction reaction. In general, on the base of electronic properties, materials are divided in three basic categories conductor, insulator and semiconductor. In case of conductor, valence band and conduction band is overlap. For photocatalytic reaction necessary condition is oxidation and reduction simultaneously, but in conduction only free electron are available. Form conductor, we perform only oxidization reaction at a time not both reaction simultaneously. Best conductor are alkali, alkaline earth metals and transition metals. They have no suitable band gap or mostly they were overlap with each other in conduction and valence band. For catalytic activity they were not suitable for reaction. In case of insulator, they have high band gap then high energy required to perform oxidation and reduction reaction. We cannot split water molecule by using insulator as a catalyst or high energy is required. We need, that type of catalyst which activates in visible region or in the ultraviolet region. Moreover, insulator is deficient of free electron so no oxidation take place that's why insulator are not suitable for photolytic reaction. All gases in periodic like halogen and noble gases are insulator. Which were not suitable for the photocatalytic reaction. In case of semiconductor, which have moderate band gap and they have capabilities of oxidation and reduction perform or support simultaneously. When light falls, free electron hole pairs is generated. Necessary condition for a semi-conductor to be a photo-catalyst, is the low recombination rate. Moreover, those semiconductor whose absorption wavelength (350–700 nm) in visible region or band gap in (1.5–3.5 eV) suitable for photocatalytic activity. Because they perform catalytic activity in the visible.

Metal oxides are very important for different electronic applications and in photo-catalysis. They full fill all of our requirements as a photo-catalyst. Metal oxides have auspicious light absorption, electronic structure, band gap and carrier transportation, which makes them suitable for this job. Most important and fundamental property a photo-catalyst should have, is its band gap. Band Gap should be in the range of UV–visible range for low cost. Other properties are stability of the structure. Morphology, reuseability, high surface area etc. Metal oxides for example oxides of chromium, zinc, vanadium, cerium and titanium have all these properties. So they are used as photo-catalysts. When photo-catalyst is exposed to the visible light, it absorbs the photon and electron in valance shell is excited the upper conduction band creating an electron and hole pair. This e /h þ pair causes the redox reaction to occur on the surface of the metal oxide which decomposes the pollutants. That's why metal oxide is used mostly as photo-catalyst (Giannakis et al., 2017).

1.1.5 Application of Photo-Catalyst

Water Splitting:

Photo catalysis can be applied for the production of hydrogen gas which is a potential energy source. Hence the energy extracted by this method is low cost and also it produces no harmful side products which could possibly pollute our environment. That's many researchers are working on this method of obtaining clean energy. First time water splitting was discovered in 1972 by using TiO2 as a catalyst but that time gain less attention due to low efficiency, in 1973 oil crises and in 1979 energy crises in world cause lot of attention water splitting photocatalytic reaction (Boyjoo et al., 2017). When we discussed 21st century crises then energy is one of them, in present world we need such kind of energy resource which can be exchangeable with already available natural energy resources because number of problem with available energy sources most important in them is these resources are not long time available. Photocatalytic process is less energy consumption, long life and green process for hydrogen production. It work under the natural solar light and photo-catalyst.

1.1.6 Mechanism of photo-catalytic hydrogen production:

Generating hydrogen from the process of photo-catalysis primarily depends on the photo-catalyst. Mainly, we use semiconductor metal oxides as photo-catalyst e.g., TiO2, ZnO, Ag2O etc. Reaction basically starts from a photon striking activating the catalyst. It will excite it and produce a free electron-hole pair which will initiate the reaction. Creation of electron-hole pair requires some specific properties of photo-catalyst. But the most important one is the Band Gap represented by Eg. In semiconductors, electrons and hole reside in valance band when exposed to photons having energy equal to or more than the band gap, excitation takes place promoting electron to the conduction band.

1.1.7 Factors affecting photo-catalytic activity Band gap energy

Energy difference of conduction and valence band of Photo-catalyst or semiconductor metal oxide is represented by Band Gap (Eg). To make hydrogen evolution feasible, thermodynamic potential of conduction band should be higher than potential level of acceptor. Band gap is responsible for charge separation to reduce recombination rate and activity under a specific wavelength. General intentions are to decrease the band gap so that photo-catalyst can be activated in visible region. This will enhance the efficiency of hydrogen production. It is reported that doping (metal or non-metal) reduces the band gap into the visible region (Bafaqeer et al., 2019; Tahir and Amin, 2013).

Method:

a) **Sunlight-Driven Photocatalysts;**

For the past few decades, various metal oxide semiconducting-based nano assemblies have been designed and demonstrated as catalytic materials for water remediation applications under sunlight. Transition or d block metal ions have shown excellent efficiency in highly explored semiconductors for efficient photocatalytic materials (Wang et al. 2008).

The following factors affect the photocatalyst process:

1. **Dye concentration:**

   The concentration of the dye used in the photocatalyticreaction is an important factor. The catalyst should be able to degrade an average quantity of the dye. A quantity of the dye is adsorbed on the surface of the catalyst, which involves a photocatalytic reaction process under stimulated light conditions. The adsorption of dye on the surface of the photocatalyst is directly proportional to the original concentration of dye. The original concentration of dye is a significant feature that should be monitored carefully. Usually, the degradation percentage decreases with an increasing quantity of dye concentration, although the required quantity of photocatalyst should be maintained (Reza et al. 2017).

2. **Catalyst amount:**

   The amount of catalyst in the photocatalytic reaction alsoaffects the degradation of the dye. In a heterogeneous photocatalytic process,increasing the amount of photocatalyst in the reaction process also increases the percentage of photodegradation of the dye. More active sites can be produced in the photocatalytic reaction by increasing the number of catalysts, which promotes the creation of a greater number of reactive radicals in the photodegradation process. (Akpan and Hameed 2009).

3. **pH:**

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The solution pH also plays a vital role in the degradation process. It can either induce or suppress the photocatalytic reaction, depending upon the nature of the material and pollutant properties. By changing the pH of the solution, the surface potential of the catalyst (metal oxide nanoparticles) may vary. As a result, the pollutant adsorption on the surface of the photocatalyst could be altered, thus initiating a change in the photodegradation rate (Davis et al. 1994).

4. **Surface morphology of the photocatalyst:**

Surface morphology includes significant features to be measured for the photodegradation activity, such as particle size and shape. Each morphology is a direct relationship between the surface of the catalyst and organic pollutant(Kormann et al. 1988).

5. **Surface area:**

For better photocatalytic performance, materials with greater surface areas should be used. These materials are able to create a number of active sites on the photocatalyst surface, thus leading to the creation of more radical reactive species for efficient photodegradation activity (Ameen et al. 2012).

6. **Temperature-dependent reaction:**

To achieve efficient photocatalytic performance,the reaction temperature should be in the range of 0–80 _C. When the temperature exceeds 80 _C, the catalyst will promote the recombination of the electron-hole pair and suppress the photocatalytic activity. Hence, the reaction temperature plays a vital role in photocatalytic activity (Kazuhito et al. 2005;Mamba et al. 2014).

International Educational Applied Research Journal
A Multi-Disciplinary Research Journal
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7. **Nature of the pollutants and their concentrations:**

The degree of photodegradation can be determined by the concentration and nature of certain pollutants in a water matrix. Some photocatalysts, such as TiO2, are not able to disinfect the pollutant when the concentration of the pollutant is higher. It saturates the surface of the photocatalyst and does not allow the creation of active radicals, thus reducing the photocatalytic efficiency (Mills et al. 1993).

8. **Irradiation period and intensity of the light:**

The intensity of the incoming light and irradiation period are major factors affecting the photodegradation of pollutants. At high light intensities, the photodegradation percentage is inversely proportional to the intensity of light, because the creation of excitons is predominant at low light intensities and also hinders the recombination of electron-hole pairs. Alternatively, while increasing the intensity of the irradiation light, the recombination of electron-hole pairs occurs at the photocatalytic surfaces and thereby reduces the catalytic activity in the reaction medium (Asahi et al. 2001).

9. **Dopants on dye degradation:**

Various methods are available to fabricate TiO2 nanomaterials that can absorb photons at very low energy. These methods consist of band gap engineering by modifying and continuously altering valence and conduction bands by introducing metals and non-metals in the photocatalytic materials. Surface modification can be achieved by coupling with organic materials and semiconductors (Rajeshwar et al. 2008).

b) **Metal Oxides:**

Semiconducting metal oxide–based nanostructures have been used for photocatalytic applications to treat wastewater and produce hydrogen fuel by splitting oxygen and hydrogen, among others. The most important criteria for an efficient photocatalytic material are the required band gap, desired band edge position, large surface area, perfect morphology, chemical stability, and reusability capability. Among various metal oxide semiconductors, TiO2, ZnO, SnO2, Cu2O, and WO3 with these characteristics have identical photocatalytic properties, such as absorption of light. This excites photogenerated charge carriers with the creation of holes, which are able to oxidize organic substances (Maeda 2011).

c) **Metal-Doped Metal Oxides:**

The method of introducing impurity atoms into the lattice system of any semiconducting material is called doping, which was described by Neamen (Neamen 1997). The dopant atoms in semiconductor lattices influence and engineer the properties of the host material.

d) **Plasmonic Photocatalysis:**

Plasmonic photocatalysts have attracted great interest among researchers due to their enhanced photodegradation efficiency under visible light irradiation, wide range of sunlight absorption, and excellent charge transport properties (Xuming et al. 2013; Zhou et al. 2016; Liang et al. 2018; Dong et al. 2014; Yang et al. 2014). This kind of material architecture can be created by dispersing noble metal nanoparticles onto the semiconductors. In that way, two distinct features are achieved: localized surface plasmon resonance (LSPR) and a Schottky barrier (Xuming et al. 2013; Wang and Astruc 2014). These properties will help to separate and transfer the charge carriers effectively under visible light irradiation.

International Educational Applied Research Journal
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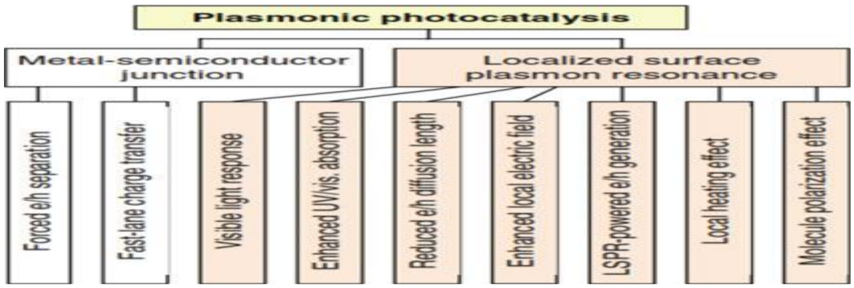

Figurer: Flowchart of plasmonic photocatalysis and its major effects (Xuming et al. 2013)

e) Carbon Family:

Carbon nanomaterials have been studied extensively in recent times for their unusual physiochemical, structural, optical, and electronic properties (Zhu 2017). While keeping the favorable characteristics of carbon materials, nanocomposites can be developed for incorporation in conventional and stale photocatalytic materials for efficient light-derived water remediation applications (Hebbar et al. 2017; Jiang et al. 2016).

f) Z-Scheme in Photocatalysis:

The design and development of properly assembled metal oxide-based semiconducting photocatalysts are encouraging the use of nanomaterials to address environmental issues because of their ability to capture the visible range of the electromagnetic spectrum to cause numerous photodegradation reactions. Particularly, the development of the Z-scheme in photocatalysis has many advantageous processes, such as excellent harvesting capability of sunlight, rapid charge separation, the creation of active species for oxidation and

International Educational Applied Research Journal

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reduction reactions, and very good redox proficiency, which makes for better photocatalytic activity.

According to Merfat Algethami 2022, The study synthesized rGO@Bi/Bi2O3 as a bismuth-based nanocomposite by loading Bi/Bi2O3 on rGO surfaces. The nanocomposites were characterized using scanning electron microscopy and X-ray diffraction, and their photocatalytic activity was measured using cationic dyes methylene blue and rhodamine B. UV-visible spectroscopy determined the optical properties of the nanocomposites.

g) Cobalt Oxide:

An abundant form of inorganic metal oxides in nature are cobalt oxides. Cobalt oxides are highly stable, toxic-free, magnetic, incredibly resistant to corrosion and oxidation, and possess high mechanical strength, among other qualities that make them ideal for environmental applications (Hussain 2020, Gopinath 2022 and Rasheed, T 2019). At ambient temperature, they exhibit good conductivity and are p-type semiconducting materials [40]. Due to variations in oxygen vacancies, cobalt oxide can exist in a variety of oxidation states (Dharaskar, S 2021). The most prevalent oxidation states for cobalt are cobalt (II) oxide and cobalt (III) oxide (Dey, S. 2019).

Cobalt oxide has been synthesised using a number of techniques, including sol-gel, hydrothermal, and microwave-assisted techniques. Cobalt's varied oxidation states have made the particles useful in a wide range of fields (Asha, G. 2022). Cobalt oxide performs.A crucial role in a variety of applications, such as the detection of contaminants, the destruction of dangerous substances, medication delivery systems, supercapacitors, and storage devices (Navarrete, È ,2019, Jincy, C.S. 2022, Gaikar, P.S.2022, Lakra, R. 2022, Rakotonarivo, E.F. 2021, Jincy, C.S. 2020, Ni, Q. 2018, Feng, H. 2020 and Feng, H. 2022).

International Educational Applied Research Journal
A Multi-Disciplinary Research Journal
E-ISSN No: 2456-6713

h) Copper Oxide:

The numerous characteristics that copper oxides have make them widely applicable. In addition to nanowires, nanorods, nanotubes, and nanoparticles, copper oxides can also be formed into a variety of other forms [55]. They have significant catalytic and bactericidal action, are cheap, plentiful, and extremely stable [56]. Although there are several differaent oxidation states of copper oxides, cuprous oxide (Cu2O) and cupric oxide (CuO) are the most stable, whereas paramelaconite (Cu4O3) is metastable. Copper oxides have three different crystal forms, which are depicted in Figure 2 [57]. Cubic-shaped cuprous oxide (Cu2O), a p-type semiconductor, crystallises in nature.

Due to their powerful oxidation and reduction capabilities as well as compatibility with the environment, copper oxide semiconductors are recognised for their involvement in the cleanup of environmental toxins (Moghanlou, A.O,2021). Cobalt oxides are different from copper oxides in that they are more stable at high temperatures. Copper oxides are more widely used and easier to obtain than cobalt oxides, despite the fact that the precursor salts for cobalt oxides are more expensive (Vázquez-Vargas,2020). In the areas of sensors, antimicrobial activity, catalysis, coatings, polymers, and electronics, copper oxides have a wide range of potential uses (Maruthupandy, M.2017, Mohammed Ali,2017, Pourbeyram, S,2019, Nabila, M.I.;2018 and Kim, T.K. 2015).

i) Zinc Oxide:

The second-most prevalent metal, zinc oxide, has a variety of morphological sizes and shapes. It is an advantageous inorganic substance with multiple uses that has these qualities. Optoelectronics and transparent electronics are two significant domains that benefit from the optical and piezoelectric capabilities of zinc oxide. It is suitable for photocatalysis because it has a large band gap of 3.37 eV and a high surface area. Due to its antibacterial properties and the fact that zinc is regarded as a nutritional supplement, zinc oxides are frequently used in medical applications. Additionally, it has been stated that the size and form of zinc oxides, which are controllable during the manufacturing process, affect their antibacterial activity (Gupta, K.;2015, Bandeira, M.;2020, Darvishi, E.;2019, Sultana, K.A.;2020, Dkhil, M.A.;2020, Brindhadevi, K.; 2020, Dang, Z.; Sun, J.;2021 and Shankar, S.;2019).

j) **Iron oxide:**

Iron oxide nanoparticles' size, dispersion, and surface have a significant impact on their magnetic characteristics. Hematite has magnetic characteristics that are thermally induced, whereas magnetite and maghemite are minerals that are intrinsically ferrimagnetic. The primary characteristics of IONPs that make them so interesting in so many different disciplines include their superparamagnetic behaviour, high surface-to-volume ratio, non-toxicity, reusability, biocompatibility, high stability, and resistance to change (Ong, H.T.2020, Borges, R.;2021, Karaagac, O.;2022 and Al-Jabari, M.H.;2019).The aggregation of particles in aqueous conditions, which is unfavourable in water remediation applications, is the only drawback of IONPs. Therefore, surface modification, such as coating with surfactants and polymers, can further stabilise IONPs. For instance, a study functionalized iron oxide nanoparticles (NPs) with amine groups by coating them with chitosan (derived from chitin), which stabilised the particles and increased the number of binding sites accessible.

k) **Titanium Oxide:**

TiO_2, also known as titanium dioxide, is a naturally occurring element that provides favourable characteristics for applications in the fields of energy and the environment. Its chemical stability, biological and chemical inertness, and non-toxicity have all been shown to make it a suitable candidate for these purposes. TiO_2 is transparent to visible light and has a long endurance. It operates as a semiconductor with a band gap of about 3.2 eV and is active in UV light. Additionally, titanium oxide can be found in three different crystalline forms, with rutile being the most thermodynamically stable of the three: tetragonal anatase, tetragonal rutile, and orthorhombic brookite (Wei, Y.;2018, Bortamuly, R.;2021, Zhang, Y.;2018, Pérez-Jiménez, L.E.;2019 and Bayan, E.M.;2020).

l) **Magnesium Oxide:**

Magnesium oxide (MgO) is a multifunctional inorganic substance that is extremely important in technology. Magnesium oxide, often known as magnesia, has a rock salt-like structure that is comparable to simple NaCl., as seen in Figure 8. It has exceptional optical, thermal, electrical, mechanical, and chemical properties. MgO also has a high thermal stability, with a melting temperature of roughly (2852 °C), as well as a low heat capacity, making it a good insulator [138]. Because MgO is considered a necessary nutrient for plants and people, the particles are non-poisonous [139]. Magnesium oxides are widely employed in drug delivery systems and biological applications due to their biocompatibility and stability (Abinaya, S.;2021, Nagappa, B.;2007, Mehta, M.;2012, Abdulkhaleq, N.A.;2020, Saito, A.;2022, Sivaselvam, S.;2020, Alkhudhayri, A.;2022, El-Sawy, N.M.;2020, Zheng, X.;2019, Yang, S.;2021 and Nigam, A.;2021).

Conclusion:

The current review focuses on the green synthesis-based nanoparticles and their potential applications in energy and the environment. Plants, bacteria, and biomolecules are only a few of the raw materials used in green synthesis. The research presented here reveals precise information about the different types of green materials and methodology used in preparing nanoparticles, particle size, morphology and behavior.

Nanotechnology has great potential in the design of artificial photosynthesis systems to store solar energy and to reduce organic contaminants in the environment because of the unique properties of nanomaterials. The advent of green, accessible, and safe methods of producing these nanomaterials is necessary to address modern environmental concerns. Important aspects of green or biosynthesis solutions using biomass materials include a rapid reaction process, low temperature, and minimal usage of toxic substances. By mimicking photoactive green nanomaterials found in nature, we can create light-harvesting assemblies, new methods for synthesizing fuels, and tools to synthesize novel functional materials for solar cells, water-splitting units, pollution control devices, and more.

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