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PHOTOCATALYTIC DEGRADATION OF INDUSTRIAL HEAVY WATER USING ZINCOXIDE NANOPARTICLES – A REVIEW

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Abstract

Due to the increased demand for clothes by the growing population, the dye-based sectors have seen fast growth in the recent decade and also the industrial waste water. This waste water contains heavy metals such as cadmium, mercury which raises the stakes for the environment. The numerous sources of heavy metal in wastewater and their effective treatment procedures are addressed in the current review. Even among nanoparticles, photocatalytic materials, such as TiO2, ZnO, and Fe3O4 have shown greater potential for photocatalytic degradation of heavy metals such as cadmium and mercury. Such nano-sized metal oxides are the most ideal materials for the removal of water pollutants, as these materials are related to the qualities of flexibility, simplicity, efficiency, versatility, and high surface reactivity. The use of nanoparticles generated from waste materials to remediate heavy metals is highlighted in the present research.

Keywords: Photocatalytic, Nanoparticles, Heavy Metals, Zinc oxide, Pineapple peel

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1 Introduction

Graph theory is a field of mathematics that Wastewater, sometimes known as sewage, it is a result of numerous water-related activities. There is industrial waste, domestic usage like showering, washing, laundry, and of course toilet flushing. Furthermore the businesses utilize water for a variety of functions including operations, goods, and part washing or rinsing. After being utilized the water enters the wastewater stream and goes to the wastewater treatment facility [1]. When individuals visit a treatment facility for the first time, it is generally not what they expected. These wastewater treatment plants are complicated facilities that produce high-quality effluent.

To safeguard the environment and public health from the industrial waste, we must eliminate wastewater contaminants [2]. When our civilization uses water, it becomes tainted with pollution. These contaminants would have a harmful impact on our water ecosystem if they were not treated. Organic materials can deplete oxygen levels in lakes, rivers, and streams. This biological breakdown of organics has the potential to cause fish deaths and bad smells. Waterborne infections are also avoided when wastewater is treated properly. When wastewater is adequately handled, waterborne illnesses are also prevented. The flow and pollutant intensity of industrial effluent varies substantially. As a result, assigning fixed values to their components is impossible. In general, mineral and organic particles, as well as suspended, colloidal, and dissolved substances, can be found in industrial wastewaters [3]. Furthermore they may be extremely alkaline or acidic with low or high quantities of the colorful materials. These wastes may comprise inert, organic, or poisonous substances, as well as dangerous germs. These wastes may be released into the sewage system if they have no negative impact on treatment efficiency or are not harmful to the sewer system. It may be essential to pretreat the wastes before releasing them into the municipal system, or it may be necessary to process the wastes completely if they are to be released directly into the ground or surface waters. Heavy metal which contains high atomic weight and atleast has the five times the density of water that is occurring naturally in the environment. The extensive dispersion in the environment has resulted from their numerous industrial, residential, agricultural, medicinal, and technical applications, raising worries about their possible consequences on the human's health and environment [4]. The toxicity is determined by the different parameters, including the exposure path, chemical species, gender, genetics, nutritional state, dosage, and the age for those who have been exposed. The heavy metals which has high toxicity in the priority list are arsenic, cadmium, chromium, mercury and lead [5].

H_2S gas is the byproduct of the anaerobic decomposition of the sulphur-containing organic materials. It also forms the gaseous contaminant from geothermal fluids during the sulphate by microorganisms in anaerobic reduction condition. H_2S may be present in waste from the chemical facilities, tanneries, textile and paper mills [6]. The ion nitrite, NO_2, is found in the waste water as an intermediate oxidative stage in the nitrogen's oxidation state. Nitrite is used in various industrial operations to prevent the rate of corrosion; nevertheless, amounts higher than 0.1 mg/l are rarely seen in drinking water. Some industrial wastewater includes ion sulphite and SO_2.

In humans, lead causes acute poisoning produces significant malfunction in the kidneys, reproductive system, liver, neurological system, and brain. Mercury is present as a trace component in many minerals, with continental rocks holding an average of roughly 80 ppb, or somewhat less [7]. The main commercial mercury ore is cinnabar which is red mercuric sulphide. In electrolytic chlorine gas production, metallic mercury is used as an electrode, laboratory vacuum apparatus and other applications.

2.Various forms of pollutants:

Some of the major heavy metals causing pollutants to the environment are

2.1 Inorganic Pollutants

Inorganic pollutants are chemicals formed from inorganic byproducts such as radiant radiation, noise, heat, or light. Fluorides, cadmium, lead, mercury, chromium, nitrites, nitrates and aluminium are the examples of inorganic pollutants.

2.2 Cyanide

The cyanide ion C N-, is most likely the significant inorganic species in the wastewater. In water the cyanide is a highly toxic chemical that occurs as HCN, a weak acid. The less deadly ferrocyanide with iron[8]. The very hazardous HCN that is in the volatile condition used in the gas chamber in most of the countries. In industries, the cyanide is a frequently utilized, particularly for metal cleaning and electroplating [9].

2.3 Ammonia

The initial byproduct of the breakdown in nitrogenous organic waste is ammonia, and its presence frequently indicates the presence of such wastes. Some groundwater sources naturally contain it, and this is occasionally supplied to drinking water to lessen the taste and odour of free chlorine [10]. The majority of ions in water is NH_4^+ instead of NH_3 due to the PKA (minus log of the acid ionisation constants) of free ammonium ion, NH_4^+.

2.4 Other Inorganic Pollutant's

H_2S gas is the byproduct of the anaerobic decomposition of the sulphur-containing organic materials [11]. It also forms the gaseous contaminant from geothermal fluids during the sulphate by microorganisms in anaerobic reduction condition. H_2S may be present in waste from the chemical facilities, tanneries, textile and paper mills [12]. The ion nitrite, NO_2, is found in the waste water as an intermediate oxidative stage in the nitrogen's oxidation state. Nitrite is used in various industrial operations to prevent the rate of corrosion; nevertheless, amounts higher than 0.1 mg/l are rarely seen in drinking water [13]. Some industrial wastewater includes ion sulphite and SO_2.

2.5 Organic Pollutants

Effluent from the various industrial sources comprises a broad range of contaminants that includes the organic pollutants[14]. some of these contaminants are specially removed from the primary and secondary treatment in the sewage treatment procedures, notably the oxygen demanding, oil, grease, solids and chemicals such as salts, heavy metals and refractory organics are not successfully eliminated[15]. Detergents, soaps and related compounds are all the possible sources of the organic pollutants. The majority of the environment concerns now attributes to detergent are wetting properties of water. Poly-phosphates added with a complexly built calcium structure have the most worry among environmental contaminants[16].

2.6 Industrial Effluent

Continuous or intermittent efflux is are used. They may perhaps only be created for a few months. Pollution flows are formally recognized when the output is consistent[17]. However, because effluents in specialized programs are constantly changing and it is difficult to analyse them. Four types of effluent are

2.7 General Manufacturing Effluent

Most operations produce harmful effluents as a result of water coming into contact with gases, liquids, or solids[18]. Continuous or intermittent effluents are used. They may perhaps only be created for a few months out of the year. Pollution flows are usually known if production is consistent. However, because effluents are always changing, it is more difficult for companies working on specific campaigns to study them[19].

2.8 Special Effluent

Some of the effluents are segregated for a particular treatment process, and they recovered or retained in a tank that is ready to flow in treatment line by the case of weighted flow rate[20]. For example, wasted caustic soda, picking and electroplating baths[21].

2.9 Intermediate Effluent

These must not be overlooked; they can result from inadvertent product leaks during storage or handling, as well as dirty water and water from the floor washing, the latter which can cause a hydraulic overload[22]. Because of lactic fermentation or solicitation, the effluents are quite acidic (the pH range from 4 to 5). A wet approach extracts the starch, pollution by the evaporation of water which composed of fully volatile organic acids. The glucose shop might be a source of soluble protein pollution[23].

3. NANOMATERIALS AND THEIR TYPES

Nanomaterials have been effectively employed in numerous sectors, including catalysis, medicine, sensing, and biology, over the last few decades[24]. The nanomaterials in wastewater treatment and water contributes the major application particularly it has sparked the considerable attention to the researches[25]. The nanomaterials have high adsorption and the reactivity due to their tiny diameters and hence huge specific surface areas[26]. Furthermore the moment of nanoparticles in the solution is higher. Organic contaminants, heavy metals, inorganic anions, and microorganisms had been reported to be effectively removed by the various types of nanomaterials[27]. According to various research, nanoparticles have considerably used in wastewater treatment. The most intensively researched nanoparticles are mostly metal oxides and zero valent metal nanoparticles[28]. Nanomaterial's characteristics, such as optical, electrical, mechanical and magnetic properties. The change dramatically from the normal material because of exhibit catalysis, adsorption, and high reactivity. their nanoscale dimension[29]. A broad variety of nanomaterials.

3.1 Silver nanoparticles

The silver nanoparticles are very poisonous to the microorganisms. They offer potent antibacterial properties working against the wide varities of microbes, including fungus, bacteria and viruses[30]. The silver nanoparticles have been widely employed for water disinfection because they are an effective antibacterial agent. The mechanism of Ag NPs' antibacterial activities is not well understood and is still being debated. Ag NPs have been shown to combine the cell wall of the bacteria and then enter it causing changes in the structure and also in the cell membrane which increases its permeability rate[31] Furthermore, whenever silver nanoparticle comes into contact with bacteria, free radicals are produced. They had the power to trigger cell death by damaging the cell membrane[32]. Furthermore, because DNA includes a lot of phosphorous and Sulphur, and it interacts with the silver nanoparticles and hence damage it. This is yet another reason for Ag NP's induced cell death[33]. Furthermore, as silver NPs dissolve, antimicrobial Ag^+ ions are released, which can bind with thiol groups of many essential enzymes and then it is activated to disturb the normal cell functioning. In recent years the nanotechnology is widely advanced and the silver nanoparticles are effectively employed in the wastewater treatment[34].

3.2 Iron Nanoparticles

Various types of zerovalent metal nanoparticles such as iron, zinc, aluminum, nickel have piqued the interest of researchers in the field of water pollution remediation in the recent years. Nano-zero-valent Aluminum is thermodynamically unstable in the presence of water due to its exceptionally high reducing ability which promotes the development of hydroxides or oxides on the surface, inhibiting (totally) the passage of electrons from the metal surface to the impurities[35]. Ni has a lesser lowering ability than Fe because it has a weaker standard reduction potential with a negative sign. In redox-labile pollutants the standard reduction potential for nano-zerovalent iron or zinc is higher[36]. Despite its lower reduction capacity, iron has a numerous benefits over zinc for uses in the water pollution treatment such as superior adsorption qualities, oxidation and precipitation in the presence of dissolved oxygen and inexpensive in theie price[37]. As a result, the most intensively investigated by the zerovalent nanoparticles(metal) been zero-valent Fe nanoparticles. These properties contribute the most to its great effectiveness in pollutant removal[38].

3.3 Zinc Nanoparticles

Although zinc and iron were the subjects of the majority of studies on pollutant degradation in treating wastewater by zerovalent metal nanoparticles, zinc is believed to be a proposed alternative[39]. Zinc acts as a strong reductant than iron due to its lower standard reduction potential. As a result, the contaminant rate of degradation of zinc nanoparticles and quicker than n-ZVZ[40]. Even though various studies shown that contaminant reduction by n-ZVZ may be effective, its use is mostly confined to the degraded halogenated organic chemicals, particularly carbon-tetrachloride. Other types of pollutants have seldom been treated by n-ZVZ in the past[41]. As a result, full scale or pilot scale uses a number of ZVZ in polluted field locations have yet to be accomplished.

3.4 TiO2 Nanoparticles

Photocatalytic degradation has received a lot of interest as a new and promising

Technique [42]. An electrochemical photolysis of freshwater on semiconductor electrodes made of titanium dioxide was first observed by Honda and Fujishima[43]. The photocatalytic degradation technique has been used effectively in the breakdown of contaminants in water and wastewater in recent years[44]. The contaminants can progressively oxidize into lower molecular weight with an intermediate products in the presence of catalyst and light and subsequently converted into water, carbon dioxide and anions[45]. The bulk of commonly used photocatalyst is sulphide semiconductor or metal oxide with titanium dioxide having received the most attention in recent decades. Titanium dioxide is the most outstanding photocatalyst to the date because of its higher photocatalytic activity with low cost, chemical, biological stability and photostability[46]. Titanium dioxide has a significant band gap energy of 3.2eV needs UV irradiation to produce charge separated inside the particles. When it is exposed to ultra-violet light, Titanium dioxide produces a reactive oxygen species that may destroy pollutants in a very short response of time[47]. Furthermore, because titanium dioxide nanoparticles have low selectivity, they may degrade a wide range of pollutants, including polycyclic aromatic hydrocarbons, phenols, dyes, pesticides, chlorinated organic compounds, arsenic, cyanide and heavy metals. Furthermore, the hydroxyl radicals produced by UV irradiation allow the nanoparticles to disrupt the structure and function of many cells[48]. TiO2 NPs' photocatalytic characteristics may destroy in a wide range of microorganisms including gram positive and gram negative bacteria as well as algae, virus, protozoa and fungus[49].

3.5 ZnO Nanoparticles

Apart from other nanoparticles, ZnO nanoparticles have proven as an efficient choice in treating wastewater due to their unique properties, which include a direct as well as broad banded difference in the near the area ultra violet spectral range, strong oxidizing ability, and improved photocatalytic function[50]. Zinc nanoparticles are ecologically advantageous since they are compatible with organisms, making them suitable for purification of water[51]. Furthermore because of their bandgap energy is almost identical, the photocatalytic performance of zinc oxide NPs is equivalent to that of TiO2 NPs. However ZnO nanoparticles are less expensive than titanium dioxide nanoparticles[52]. Furthermore zinc NP's may absorb a greater range of solar spectrum and light wavelengths than other semiconductors metal oxide[53]. A common method for improving the photocatalytic deteriorating effectiveness of zinc nanoparticles is metal doping. Cationic and anionic dopants, rare-earth dopants, and co-dopants were all evaluated [54]. Furthermore, multiple investigations have shown that linking with other semiconductor materials such as TiO2, Cadmium oxide, graphene oxide, Ceo2 and the proposed method to increase the photodegradation effectiveness of zinc oxide nanoparticles is reduced graphene oxide (RGO)[55].

3.6 Iron Oxides Nanoparticles

Due to their ease of use and availability, iron oxide nanoparticles are gaining popularity for heavy metal removal[56]. As nano adsorbents such as magnetic magnetite, magnetic maghemite, nonmagnetic hematite are commonly utilized. Nanosorbent particles are so small that separating them from contaminated water and recovering them from it is a substantial challenge for water treatment. With the use of an external magnetic field, magnetic magnetite and magnetic maghemite may be readily separated and retrieved from the system, respectively[57]. They have therefore been used successfully as sorbent materials to remove various heavy metals from water system. Hematite had regarded as stable and an inexpensive material for use in catalysis, sensors, and the environmental applications[58]. Additionally nano hematite is a superior adsorbent for eliminating the ion of heavy metals from industrial settings[59].

4. NANO MATERIALS BASIC PROPERTY

4.1 Surface effect

When a particle's size is reduced to a nanometer, its specific surface area grows rapidly, the number of atoms on it grows, its surface energy grows, and the particle's activity grows as well[60].

4.2 Small size effect

When the particle size is lowered to nanoscale size, the wavelength of the light source grows shorter, the de Broglie wavelength becomes smaller, the size of the single magnetic domain becomes smaller, and the critical size condition of the particle lattice becomes worse. There is a major shift in attributes as a result of emerging from an unstable condition[61].

4.3 Quantum size effect

When the particle size is lowered to nanometers, the continual combination of electronic activities modifies the electronic energy level structure, resulting in physical property changes[62].

4.4 Macroscopic quantum tunneling effect

Tunneling is the capacity of small particles (electrons) to enter and penetrate an obstruction. The tiny process of nanometer size will impact macroscopic physical characteristics such as magnetization and magnetic flux of microscopic particles[63]. The macro-quantum tunneling effect reduces the amount of time an optical disc preserves information and is bound to become a cornerstone in the field of microelectronics development, propelling the continued growth of science and technology toward shrinking [64].

5. APPLICATION OF NP's IN THE FIELD OF PHOTOCATALYSIS

Some of the major important application of titanium dioxide photocatalysts are

5.1 Removal of wastewater pollutants

Water holds a variety of contaminants includes phenols and hydrocarbons. The most dangerous of them are heterocyclic compounds[65]. It is challenging task to remove the contaminants from water and wastewater due to diverse makeup of the effluent[66].

5.2 Air purification

Today, air purification has always been a crucial concern of green growth. TiO2 is now significant in air purification since it decomposes air contaminants efficiently. TiO2 may be coated on the surface of different gadgets, utilized in steel bars, and even directly applied to pollution sources, which has played an important role in environmental governance[67].

5.3 Sterilization, Corrosion, and self-cleaning

TiO2 photocatalysis is employed in various parts of life since it can not only disintegrate germs but also sterilize and disinfect. Because of the difference in energy levels, it can protect the metal surface against corrosion[68]. It is beneficial for cleanliness and wellness. It has a good self-cleaning capacity when applied to difficult-to-clean objects. It also has an excellent cleaning and disinfection function, great practicability, and remarkable performance in antiviruses of everyday requirements[69].

6. ZINCOXIDE NANOPARTICLES(ZnO NP's):

ZnO NPs have been studied for their photocatalytic efficiency for their removal of contaminants from wastewater. It also have proven that their antimicrobial activity against gram positive and gram negative bacterial strains.Zinc oxide has been found to have natural antiseptic and antibacterial abilities. Other benefits include healing epidermal wounds, burns, rashes, skin oiliness and acne.

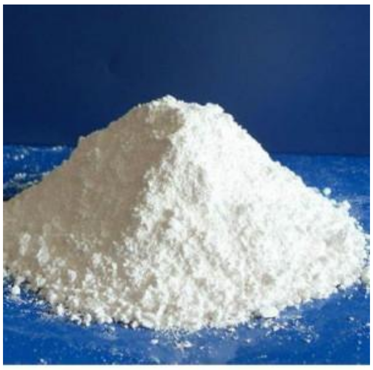

Fig 1 Zincoxide nanoparticle powder (0.1 M Zinc acetate + 0.01 M Sodium acetate)

7. PREPARATION OF ZnO NPs:

ZnO nanoparticles were prepared by refluxing precursor zinc acetate dihydrate (0.1 M) in diethylene glycol and triethylene glycol at 180 °C and 220 °C respectively. Reaction time varied for 2 and 3 h with and without sodium acetate (0.01 M). Before refluxing, the solution was kept on a magnetic stirrer at 80 °C for 1.5 h. After completion of reflux action, the samples were centrifuged at 8000 rpm for

15 min and washed with distilled water and ethanol for three times. Further, it was dried at 80 °C for overnight.

The reaction between zinc acetate dihydrate and DEG/TEG leads to esterification that forms (Zn-OH)2. Further dehydration of (Zn-OH)2 results into formation of ZnO nanoparticles.

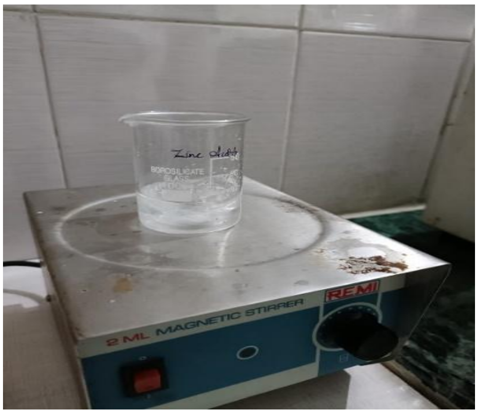

Fig 2. Zinc acetate and sodium acetate in magnetic shaker.

The basic approach for addition of sodium acetate was the addition of excess acetate ions that gives different particle morphologies than the particles synthesized in absence of sodium acetate. Sodium acetate causes a weak hydrolyzation, which controls the release rate of OH−.The sample shows the percentage of degradation efficiency of the wastewater.

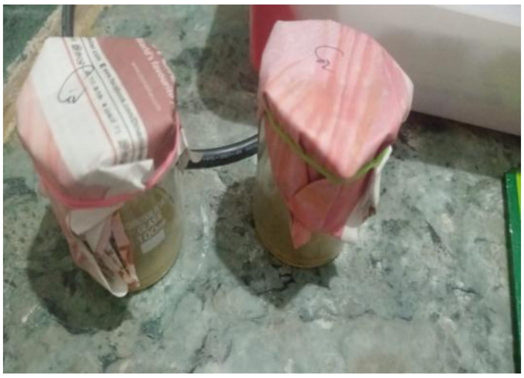

Fig 3 ZnO sample in beakers

Conclusion

Wastewaters from industries such as pharmaceutical waste and dye industry waste are mixed in river water which affects the living organisms and leads to acquiring of many diseases. This wastewater mainly possesses heavy metals. Heavy metals such as cadmium (Cd), chromium (Cr), mercury (Hg) etc., are insoluble in water and affect the environment. These heavy metals are degraded by using zinc oxide nanoparticles (pineapple peel). Our upcoming research is to treat the waste water using ZnO nanoparticles. The nanoparticles are abstracted from the pineapple peel by the photocatalytic activity. Some of the test conducted for the experiment is FTIR analysis is used to extract used for their synthesis was performed to find out the compounds involved in the formation of ZnO nanoparticles, the XRD patterns of bio-synthesized ZnO NPs from pineapple peel shows narrow and sharp curves. The sharp and intense peaks indicate that the structures of the synthesized ZnO NPs were highly crystalline. TEM analysis shows the increased rate of aggregation with temperature is similar to ordinary chemical reactions generally observed. At higher temperatures, the NPs come together to form nanoclusters, i.e. the average grain size increases with the annealing temperature and this was confirmed by XRD. In SEM analysis morphology is observed.

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