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Zinc Oxide Based Nanomaterials and Their Application in the Removal of Toxic Contaminants for Waste Water

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Abstract

The increasing global demand for clean water underscores the urgency of addressing environmental pollution, particularly through effective wastewater treatment. Rapid urbanization, population growth, and industrial expansion have significantly contributed to the degradation of water quality, making contamination a persistent and complex challenge. Despite numerous scientific efforts to develop remediation strategies, many existing techniques remain difficult to replicate or scale down effectively for widespread application. In this context, nanotechnology has emerged as a promising field, offering innovative solutions for environmental remediation. Among various nanomaterials, zinc oxide (ZnO) nanoparticles stand out due to their unique physicochemical and optical properties, which are substantially enhanced at the nanoscale. ZnO nanoparticles have gained considerable attention in material science, especially for their applications in photocatalysis, antimicrobial treatments, and environmental detoxification. However, their synthesis and functional performance are highly sensitive to several factors, including the pH of the reaction medium, calcination temperature, reaction time, stirring speed, the nature of capping agents, and

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the concentration of metal precursors. These variables critically influence the size, morphology, and surface activity of ZnO nanoparticles, thereby determining their effectiveness in water treatment applications. Understanding and optimizing these synthesis parameters are crucial for enhancing the reproducibility, efficiency, and scalability of ZnO-based nanotechnologies in real-world environmental contexts.

Keywords: Wastewater treatment; Environmental pollution; Zinc oxide nanoparticles; Nanotechnology; Water purification; Synthesis parameters.

Introduction

It is well known that water is considered globally to be an indispensable resource for any living being, lives cannot be sustained without water and so it must be consumed in a pure and hygienic state [1,2]. The rate at which water is being consumed daily cannot be over emphasized. There have been a grand environmental concern about the pollution of water bodies by effluent from industries, and this has been on the increase due to uninterrupted industrialization [3]. Wastewater is polluted water of low quality as a result in human utilization which may contain organic or inorganic pollutants as well as microorganisms depending on where it originated from. Water contamination is a form of environmental degradation which occurs when waste products are discharged into water bodies without adequate treatment to remove harmful substances [4,5]. Different conventional procedures have been used for the treatment of wastewater such as chemical [6], physico-chemical [7] and biological methods. These conventional treatments of wastewater habitually result in incomplete removal of pollutants [8], time consummation and high cost. Other techniques such as filtration [9], reverse osmosis [10], electrochemical treatment, distillation [11], ion exchange [12] and adsorption [13] have also been used for the remediation of wastewater, but these require much energy and high cost of operation. There is therefore a necessity to eradicate these deficiencies. With all these techniques, nanotechnology is seen as a viable technology that can eradicate these pollutants from water not including left over pollutants which is able to meet the requirements of untainted and disinfected water [14,15]. Since Nano-sized zinc oxide is cheap, readily available, non-toxic and can mineralize emerging pollutants in water and wastewater without leaving secondary pollutant, it can be used as a remedy for the treatment of wastewater. Zinc nanoparticles are used in coagulating suspended solids and removing impurities from contaminated water have been reported

[16]. The method is generally effective for water disinfection, simple, quite affordable and does not require high skill to operate [17]. Despite the opportunities presented by nanotechnology in this sector, very little is known about the application of zinc nanoparticles in Nigerian water treatment authorities. Millions of Naira are often needlessly spent on purchase of sophisticated and complex water treatment technology to make water available to the people. It is possible to address the problems associated with water quality at small scale using this approach because of the small size of the nanoparticles, which presents good reactive surface against the activities of microbial contaminants in the water. There is therefore the need to review the potentials of zinc nanoparticles as contaminated water treatment alternative. Thus, this review focuses on the potentials of zinc and magnetite nanoparticles as treatment agents for contaminated water for domestic, industrial and agricultural applications.

Nanotechnology

Nanotechnology is presently seen as a gigantic area of research in environmental science and with time scientist will be wrapped up in it because it has engrossed extensive awareness in the scientific neighborhood. Nanoscience refers to the handling of materials, systems and devices at atomic, molecular and macromolecular level, whereas, nanotechnology is the cluster of techniques involved in design, synthesis, characterization and application of structures, materials, devices and systems by manipulating shape and size at nanometer scale. At nanometer level, individual molecules and interaction between them becomes important in comparison with the macroscopic properties of the material or device. Control at nanometer scale and manipulation of fundamental molecular structure permits to regulate the bulk macroscopic chemical and physical properties of the material and device [18]. It is an advanced technology that deals with the method of applying, manipulating and breaking down of materials by an atom or a molecule to form new and unique materials at nano-sizes [19]. It is a multifunctional technology that has been adopted in the removal of toxic contaminants such as herbicides, pharmaceutical products, dyes, inorganic pollutants [20], aromatic hydrocarbons and organic pollutants; this is as a result of its high efficiency, afordability and reusability [21]. The present applications of nanotechnology in wastewater treatment are adsorption, photocatalysis, membrane processes [22], sensing and monitoring [23]. The particle size functionality possessed by

nanomaterials makes it a better technology for wastewater treatment. Nanomaterials have gained attention due to their special properties, and this has contributed to the extensive area of research by Nano-researchers [24]. It has been found out that materials on the nanoscale have some properties that the same material on a microscale do not have and this is attributed to its small size. With the development in areas of materials science, chemistry and engineering over the previous few eras' nanotechnology has remained exploited in all fields where insignificant size plays crucial part in determining fundamental properties.

Zinc Oxide

Zinc is a transition metal that blaze in air with a fame of blue-green coloration. It has an atomic number of 30, steady in dry air and becomes zinc oxide on reaction with moist air. It is a semiconductor as it belongs to the group II–VI due to the location of zinc and oxygen in the periodic table and exhibits both covalent and ionic bonding. Zinc is amphoteric as it can react with both an acid and base. Zinc oxide is known to be an inorganic compound, almost insoluble in water, whitish in color and powdery in form. The powdery form is extensively used as stabilizers in several materials such as cement, sealants, batteries and rubber [25]. It has a molecular weight of 81.37 and relative density of 5.607. It changes to yellow when heated and reverts to white on cooling. It possesses crystal structures of wurtzite which is most steady at ambient temperature in which, rock salt is produced at high pressure and zinc blende [26]. Zinc oxide nanoparticles constitute one of the important metal oxides materials that have been widely applied in materials science due to its unique physical, chemical, and biological properties such as biocompatible, environmentally friendly, low cost and non-toxic nature [27,28,29]. Owing to its exceptional properties, ZnO nanoparticles have been applied as a functional advanced material to solve different societal problems especially in the feld of catalysis for wastewater treatment and also as cosmetics and antimicrobial additives [29]. ZnO nanoparticles have several advantages which include unique chemical and thermal stability, robustness, and long shelf life over other metal oxides such as TiO_2, WO_3, SiO_2, and Fe_2O_3. Zinc oxide exists in the following phases: hexagonal quartzite, cubic zinc blende, and cubic rock salt [30]. The wurtzite structure is the most common due to its stability at ambient conditions, where every zinc atom is tetrahedrally coordinated with four oxygen atoms [31].

In each phase, zinc oxide nanoparticles (ZnONPs) are a semiconductor material with a direct wide bandgap of approximately 3.3 eV [32]. It has advantages such as stabilization on substrate especially the zinc blended form with a cubic lattice structure [33]. Food and Drug Administration (FDA) includes also zinc oxide as one of the safest metal oxides that can be used in food industries [34].

Many researchers have focused on the investigation of factors afecting the properties of sta ble zinc oxides- nanoparticles [35]. These factors include pH of the reaction mixture, synthesis and calcination temperature, reaction time, concentrations of precursors, solvent medium and surfactant concentration among others [36]. The aforementioned factors directly influence the particle size, morphology, phase and surface area of the zinc oxide nanoparticles [36,37,38]. Zinc oxide nanoparticles display some properties such as high chemical and thermal stability, unsaturated surfaces, and excellent adsorption behavior towards organic and inorganic pollutants in aqueous matrix. ZnO nanoparticles possess higher photon absorption efficiency, high surface area, and oxidizing power compared to the other semiconductors and are easily available, non-toxic, and cost-effective for the purification of wastewater [39]. These characteristics have encouraged many scientists in recent years to study the adsorptive potentials of ZnO nanoparticles for the removal of heavy metals from industrial wastewater [40].

Crystal Structures of Zinc Oxide Particles

Zinc oxide nanoparticles can exist in three forms, namely hexagonal-wurtzite, cubic zincblende, and cubic rock salt as shown in Fig 1. The shaded black and gray spheres represent oxygen and zinc atoms [41]. The wurtzite structure is most common and stable at ambient conditions due to its ionicity that resides exactly at the borderline between the covalent and the ionic materials [42]. The zinc blend ZnO structure can only be stabilized by growing on cubic substrates and the rock salt structure can be obtained at relatively high pressures, 10 GPa [43]. As found with most group II-VI elements, the bonding in ZnO is largely ionic with 0.074 nm for zinc ions (Zn^{2+}) and 0.140 nm for the oxygen ion (O^{2-}) as corresponding radii. This property is responsible for the preferential formation of wurtzite rather than zinc blend structure (Phillips), as well as its high piezoelectricity.

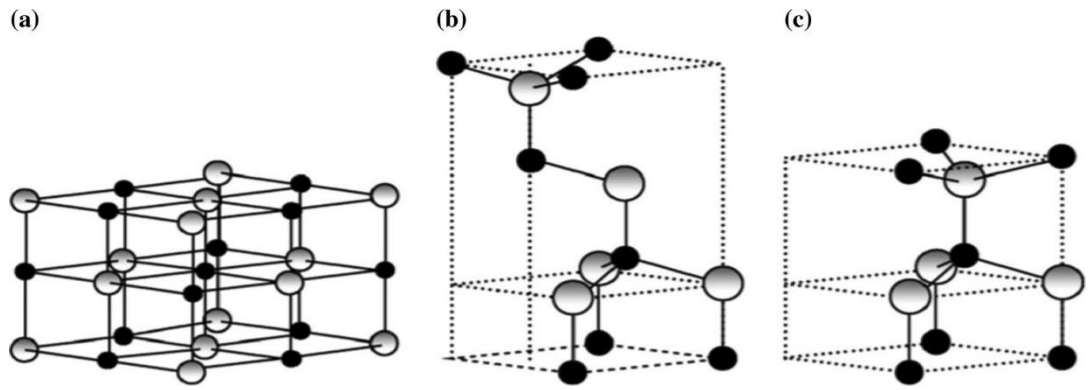
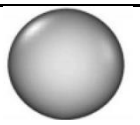


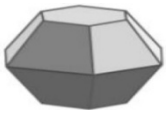
Fig 1:Different phases/network structures of ZnO nanoparticles (a) cubic rocksalt, (b) cubic zincblende, (c) Hexagonal-Wurtzite

Classification of Zinc Oxide Particles

Zno nanoparticles is classified based on the number of dimensions, which are not confined to the nanoscale range (<100nm). There are four main types of ZnO based on the dimensions and structures; zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials [44]. The table below gives a detailed description and morphological properties of the various types of ZnO.

Table 1: Different dimension and descriptions of zinc oxide nanoparticles

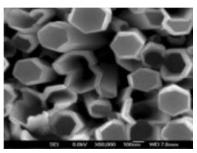
Dimensional	Description	Nanomaterial type	Morphology	References
Zero dimensional (0D)	All the dimensions (Length, breadth, and heights) are in existence in the nanoscale (< 100 nm), 0D nanostructures are the simplest building blocks that can be used to design and create 1D, 2D, and complex 3D nanostructures	Nanoparticles and nano-Dots		[45]
One dimensional (1D)	Two dimensions are in the nanoscale (1–100 nm) and the other one dimensions in macroscale	Two dimensions nanoma-terials have needles likeshaped such as nanowires,		[46]

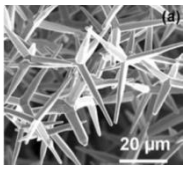
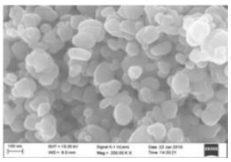
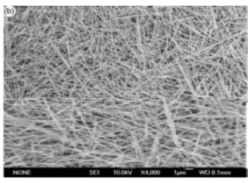
		nanofibers, nanorods, nanocapsule, nanowalls and nanotubes		
Two dimensional (2D)	In two-dimensional nanomaterial (2D), the two dimensions are outside the nanoscale	They exhibit plate-like shapes such as nanofilms, nanoplates nanolayers, and nanocoatings		[47]
Three dimensional (3D)	The three dimensions are not in nanoscale and all dimensions are in macroscale	Nanocomposites		[48]

Morphology of Zinc Oxide Particles

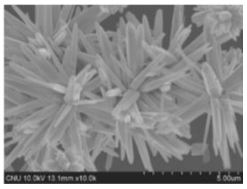
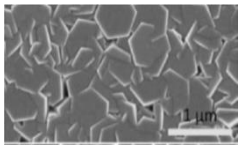
Various morphologies of zinc oxide nanoparticles have been reported by researchers due to the variation of the different process parameters. These morphologies include nanorods [49], nanowires [50], nanospheres [51], nanoflowers [52], nanotubes [53], nanotetrapods [54], nanoplate [55] and Nano tripods [56]. The formation of these different morphologies of ZnO nanoparticles depends on the applied synthesis conditions and methods in the laboratory. The formation of the desired shape of ZnO nanoparticles depends on the role played by synthesis parameters such as solution pH, template agents, reaction temperature and time, stirring speed, solvent types, calcination temperature and time, etc.

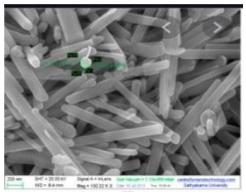
Table 2: Different morphology of zinc oxides methods and reaction conditions of ZnO nanoparticles

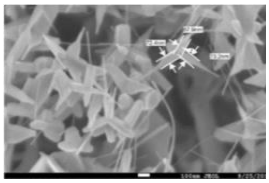
Nanomaterial	Method of Synthesis	Description	Morphology	References
Nanotubes	Chemical Precipitation	A nanotube is a tube-like structure that belong to one-dimensional (1D) nanostructure group (Erhard and Holleitner, 2015)		[53]

Nanotetrapod	Chemical vapor transport	Nanotetrapods are nanomaterial with four feet that belong to the dimensional structure. The advantage of nanotetrapods over other nanocrystalline geometric shapes of nanomaterials includes alignment with themselves spontaneously to the plane with one standard 'arm' (Marcus *et al.*, 2007). ZnO nanotetrapod legs are spatially distributed with an angle of 109.5° (Modi, 2015)		[54]
Nanosphere	Precipitation	The nanosphere is the simplest form of nanoparticle with only one adjustable geometric parameter (radius) exhibiting resonant responses under optical excitation (Ahmadivand *et al.*, 2016)		[57]
Nanowires	Hydrothermal	Nanowire is a solid rod-like structure having thickness or diameter constrained to tens of nanometers or less (1 nm = 10^{-9} m) that is similar to conventional wires (Waqar *et al.*, 2015). Nanowires are known as 1D material due to the large difference between their diameter and length (Nasrollahzadeh *et al.*, 2019). Nanowires have been reported to have fewer structural defects over their bulk counterpart (Erhard and		[50]

Holleitner, 2015)

Nanoflowers	Hydrothermal	Nanoflowers are nanostructure similar to plant flowers in a nanoscale range that is usually prepared in extreme conditions like 80–550°C (Shende *et al.*, 2018). Nanoflowers have also been reported to have a high volume-to-surface ratio which improve surface adsorption that can speed up reaction kinetics (Goryacheva, 2016)		[58]
Nanoplates	Hydrothermal	Nanoplate is a nanomaterial that has plate-like structure or have twodimensional nanostructures (2D) (Peng *et al.*, 2017)		[55]

Nanomaterial	Method of Synthesis	Description Morphology	References
Nanorods	Sol–gel	Nanorods are nanostructures that have rod-like shape. Nanorods have one dimension outside the nanoscale. Nanorods have unique advantage over other one-dimension nanostructure due to the fact that it can be made from most elements (metals and nonmetals) and compounds, and simple synthetic methods compared to nanotubes and nanowires (Ghassan *et*	 [59]

		al., 2019)	
Nanotripods	Hydrothermal	A nanotripod is a nanomaterial that is like a portable tee-legged frame or stand with a two-dimensional nanostructure with planar arms that appear as rectangular nanoplates (Al-Sarraf *et al.*, 2018). Zinc tripod is a two-dimensional (2D) nanostructure	 [56]

Synthesis of Nano-Sized Particles

Sol–gel method: This method entails four stages, namely hydrolysis, polymerization, particles development and formation of gel. It is one of the chemical methods for synthesizing metal oxides nanoparticles at low temperature in the range of 200–600°C. It also involves the use of chemicals that serves as the precursors for the gel. Sol–gel method of synthesis has the following advantages: simplicity of the procedure [60], production of smooth powdery structure of ZnO nanoparticles, molding of materials into complex geometrics [61], high purity of nanoparticles and control of the stability and phase formation of the precursors [62]. On the other hand, this technique has its shortcomings in that it leads to breakage while drying, difficult porosity control, introduction of toxic chemical agent for reduction of nanoparticle sizes and fragile bonding [63].

Co-precipitation method: This method is applied when synthesizing composites containing two or more metal element resulting in homogeneous compositions through precipitation reactions. This technique of synthesis is commonly used as it is cost-effective, has no complicated apparatus and can be produced on a large scale [64]. It also has its setbacks as the nanoparticles synthesized contain bulky amount of water molecules adsorbed which affects the properties of the nanoparticles synthesized [65], batch process, inconsistent particle size distribution and multiple agglomeration [66]. Over the years, various researchers such as [67], [64], [68], [69] and [70] have worked on the synthesis of n-

sized ZnO by co-precipitation method as a result of its high yield performance during synthesis, purity and its various applications.

Microwave method: This method is a simple and fast way of synthesizing nanostructures of different morphologies such as spherical, ring-like, flower-like, fake-like and rod-like. It is cheap [71], does not require high pressure or temperature, decreases particle size and enhances nanoparticle yield and purity. The disadvantage of this procedure is the choice of the precursor which must possess high microwave absorption.

Precipitation method: This method entails the addition of an insoluble substance in an aqueous medium to form a precipitate. This technique is simple, cost-effective [72], convenient, and scalable size of particles can be achieved [73]. It also has its disadvantage as nanoparticles synthesized via this method absorb water molecule which will require further drying.

Hydrothermal method: This method is used to synthesize single-crystal nanomaterials which are dependent on high temperature and solubility of the aqueous solution. Nanoparticles synthesized via hydrothermal technique possess high crystallinity [74], controlled morphology [75] and less pollution due to its operating conditions. It is also prone to setbacks such as sluggish chemical reaction process at any temperature [76], high cost of autoclave, problem of monitoring reaction process due to the use of closed reactor [77] and safety problems [78].

Ultrasonic method: This method of synthesis applies the principle of sonochemistry to produce molecules during chemical reaction under dominant ultrasonic radiation which is in the range of 10 and 20 kHz. The principle behind the modification of structures in nanometer range is the acoustic cavitation's. This sonochemical technique is clean, efficient, decreases lengthy reaction time and temperature [79], improves the rate of conversion of precursors to nanometer size of n-sized ZnO [80] and can be used to prepare large variety of materials with managed properties.

Green synthesis method: This is a trending area that utilizes eco-friendly materials that are non-toxic and biosafe as a substitute for chemical and physical methods for synthesizing nanomaterials in the field of bio nanotechnology. The beauty of green synthesis is the availability of raw materials [81], effortless synthesis and environmental friendliness [82], but its side effect is the close contact with the tissues in the human being which leads to some malfunctioning.

Chemical vapor deposition: This is a vacuum deposition method that produces high value and high-performance solid materials. A volatile precursor (solid, liquid or gas) at room temperature put in a reactor is used in which the substrate is exposed to and this decomposes the surface of the substrate to produce the expected deposits. This method of synthesis is usually used for synthesizing complex structures of ZnO nanoparticles web-like and flower-like morphologies. Its setbacks are several steps for synthesis, powerful gadgets and high temperature which makes it difficult to study the reaction kinetics [83].

Electrochemical method: Electrochemical method of synthesis of nanoparticles has attracted the interest of researchers because of their easiness, low temperature procedure and feasibility for mass production of nanoparticles [84].

Factors influencing the synthesis of ZnO nanoparticles

pH of Reaction Mixture: The pH of the reaction mixture determines the types of ZnO nanoparticles formed [85]. The crystallite size, morphology, phases, and surfaces areas of ZnO nanoparticles depend largely on the amount of positively and negatively charge ions present in the medium during the preparation [86,87]. This is because the solution pH alters the electrical charge of molecules and such alteration will affect their reduction [88].

Reaction temperature: The physical methods mostly employed to synthesize nanoparticles require a higher temperature above 350°C, while chemical route used for the synthesis of nanoparticles can be carried out at room temperature [89]. The chemical method is the easiest way to synthesize ZnO nanoparticles [90]. It has been reported that higher temperature resulted to increase in reaction rate causing rapid consumption of metal ion and hence formation of nanoparticle of a smaller size [91,92].

Calcination temperature: Calcination involves heat-treating a material at a controlled temperature and in a controlled environment. During the calcination process, the particles fuse and enlarge its primary crystallite size [93]. This process is called particle coarsening, a phenomenon in solid (or liquid) solutions often used for the growth of larger crystals from those of smaller size and lead to reduction in the number of smaller particles while larger particles continue to grow. The particle coarsening phenomenon occurs due to the fact that the smaller nanoparticles are less energetic and unstable compared to the well-packed nanoparticle with a large crystallite size. This process can also take place at room temperature and however can be accelerated during heating process.

Reaction time: Reaction time is the time required for completion of all steps during the synthesis of nanoparticles including the reduction and formation of nanoparticles. Reports have shown that the formation of nanoparticles starts within minutes after the addition of the metal salt precursors and increases as the reaction time increases [94].

In conclusion, wet chemical processes of synthesizing n-sized ZnO such as sol–gel, precipitation, co-precipitation and hydrothermal are carried out at low temperature, simple to synthesize and scalable. In terms of cost-effectiveness, sol–gel, precipitation and co-precipitation are cost-effective except hydrothermal. Green synthesis technique is eco-friendly and the raw material is readily available. Ultrasound and microwave techniques can be used to produce n-sized ZnO in large scale at low temperature. In terms of reaction time, ultrasound and microwave technique undergoes slow reaction time. Chemical vapor deposition technique is very useful for synthesizing n-sized ZnO of complex structures such as flower-like, ring-like and web-like. Chemical vapor deposition and sol–gel methods require multiple steps of synthesis.

Application of ZnO Nanoparticles

Adsorption

Adsorption is an exothermic surface-based technique for the eradication of pollutants (organic and inorganic) from adsorbate which is fostered by low temperature. Various researches have shown the efficiency of adsorption in removing contaminants from aqueous solutions. [95] studied the effective adsorptive removal of amaranth (AM) and methyl orange (MO) dyes with zinc oxide nanoparticles. In addition, [96] studied the adsorption of methylene blue using activated carbon and activated carbon/ZnO in antibacterial capacities. Different concentrations of methylene solutions were prepared, followed by the addition of a known amount of each activated carbon (AC) and activated carbon/ZnO (AC-ZnO) in an orbital shaker. At the end of the shaking, the different solutions were filtered and analyzed with UV–visible spectrophotometer. The result shows that methylene blue equilibrium fits into Dubinin–Radushkevich model for AC (197.9–188.7 mg/g) and AC-ZnO (137.6–149.7 mg/g). Materials that are Nano-composited are good adsorbent for the removal in wastewater treatment. Also, Srivastava and co-team also conducted the removal of cadmium (II) from aqueous solution using synthesized n-sized ZnO. Different concentrations of cadmium solutions were prepared. The maximum

degradation of cadmium (II) achieved was 92%. The application of n-sized ZnO in the mineralization of cadmium (II) in wastewater shows that n-sized ZnO is an outstanding adsorbate. N-sized ZnO is one of the metal oxide nanoparticles that have gained attention due to its good electrical conductivity, high photocatalytic ability, chemical stability, non-toxicity and antimicrobial activity. The application of n-sized ZnO for higher degradation of pollutant in wastewater is generally achieved and has appeared to be a curative measure for water treatment as small quantity is required to convert the pollutant to CO_2 and H_2O which are essential for sustaining life. To shun unnecessary cost in the aspect of time consummation, reagents and equipment, n-sized ZnO can be applied to eradicate difficult pollutants as it reduces energy and can be synthesized effortlessly with no generation of waste

Adsorption technology

Adsorption is a mass transfer process that involves accumulation of substances at the interface between two phases, such as liquid–solid, liquid–liquid, liquid–gas, and solid–gas interface and becomes bound by physical or chemical interaction [97]. Adsorption is an effective and inexpensive process used for the treatment of wastewater [98]. The removal of pollutants usually occurs when an adsorbate in a solution comes into contact with the adsorbent, concentrates or accumulates on another surface. Adsorption process is often reversible, since the adsorbents can be regenerated by desorption process [99]. Adsorption can be classified into physical adsorption (physisorption) and chemical adsorption (chemisorption) and depend on the properties of both the adsorbate and the adsorbent [100]. The mechanism of adsorption involves the sorption of sorbate molecules on the surface of the sorbent through molecular interactions, and diffusion of sorbate molecules from the surface into the interior of the sorbent materials, either by monolayer or multilayer [101]. Adsorption process involves the binding of metal ions by physical (van der Waals forces) or chemical (ion exchange, chelation, precipitation, binding, complexation, and reduction). Various factors such as the nature of adsorbent, temperature, dosage, adsorption time, the reaction temperature, and the surface area played an important role in the removal of heavy metals by ZnO nanoparticle [102]. The adsorption of heavy metals from wastewater using ZnO nanoparticles could be complex depending on the nature of capping agents used during the synthesis of ZnO nanoparticles, because the capping agent may contain different functional groups that may greatly influence the removal of the heavy metals through metal ion exchange, chelation, precipitation, binding,

complexation, and reduction. The adsorption process may be simple or complex depending on the number of contaminants in the aqueous matrix.

Removal of heavy metals

Nanocomposites materials are materials that integrate nanosized particles and enhance the property of other materials for a better workability. Properties such as thermal stability, surface appearance, strength, fame resistance and electrical conductivity are greatly influenced. Different researchers have employed ZnO nanoparticles to remove heavy metals from simulated and industrial wastewater. For instance, [103] investigated the removal of Cd^{2+}, Cu^{2+} Ni^{2+}, and Pb^{2+} from aqueous solutions using ZnO nanoparticles as an adsorbent. The findings revealed that the adsorption of the heavy metal ions increases as the pH of the solution increases from acidic to alkaline. It was noticed that the pH of the solution played an important role in the adsorption of heavy metals by Nano adsorbents. This is expected because, at lower pH (acidity conditions), the hydrogen ions strongly compete with heavy metal ions in the solution [104]. Moreover, it was also observed that an increase in the absorbent dose (0.5 to 5 g/l) resulted to an increase in the removal efficiency of Cd^{2+}, Cu^{2+}, Ni^{2+} and $Pb2^{+}$ with Pb^{2+}, having the highest percentage removal of 81.5% at a dosage of 5 mg/g. The observed trend was attributed to the increase in the number of binding sites as the Nano absorbents increase [105]. Works done by various researchers on the application of ZnO nanoparticles as a Nano adsorbent for the removal of heavy metals from wastewater is presented in Table 3.

Table 3. The MCL Standards for The Most Hazardous Heavy Metals.

Heavy metal	Toxicities	MCL (mg/l)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.2
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Source: **[106]**

Effect of solution pH on removal efficiency of heavy metals

pH is one of the most significant control factors that directly influence removal of heavy metals during adsorption process. It can also influence the binding sites on the surface of the ZnO Nano adsorbent and also affect the degree of heavy metals ionization and chemical nature of the adsorbent [107,108]. For instance, [109] studied the effect of pH on the removal of heavy metals from an electroplating wastewater using ZnO nanoparticles as an adsorbent and found that at a pH below 7 (acidic), the solution was highly protonated (H+) resulting in a high positive surface charge on the surface of the adsorbent which repels the positively charged metal ions and subsequently low removal efficiency. However, due to dominant hydroxide ions (OH−) at a pH greater than 7, the adsorbent surface becomes negatively charged resulting to a high negative charge density that attracts more metal ions.

Photocatalysis

Photocatalysis is an energetic mechanism that is enhanced by light and catalyst for removing pollutants in wastewater. It is viewed as the most used techniques of advanced oxidation processes to remove organic pollutants from wastewater [110].The application of n-sized ZnO in the photocatalytic degradation of pollutant helps in breaking down pollutants to highly reactive radicals such as hydroxyl radicals (OH^-) and superoxide anions (O_2^-). The high photocatalytic ability attributed to n-sized ZnO decomposes organic pollutants to CO_2 and H_2O. , the work done by [111] revealed the biosynthesis of n-sized ZnO from Plectranthus amboinicus and its photocatalytic effect on domestic wastewater treatment. The synthesized n-sized ZnO was added to the collected wastewater from sewage treatment plant under sunlight for one-half hour; the COD of the wastewater before and after treatment decreases from 750 to 50 mg/l. This decrease in COD indicates that n-sized ZnO is a good catalyst for the removal of pollutants from domestic wastewater. The authors reported that the exposure of domestic wastewater under sunlight has little or no effect on the mineralization of domestic wastewater, but the addition of n-sized ZnO brought about 93.75% removal efficiency. [112] adopted the application of n-sized ZnO to the removal of methylene blue via sunlight and UV–visible. The n-sized ZnO was added to the methylene blue solution in duplicate. The result shows that 85% of methylene blue solution was degraded at 460 min under UV light, while 95% of methylene blue solution was degraded at 360 min under sunlight. The higher percentage of

degradation observed with UV light is as a result of one of the attributes of n-sized ZnO (highly photoactive) which helps in mineralizing pollutants in wastewater.

Degradation

Wastewater can undergo various degradation mechanisms depending on the type of pollutant that is needed to be removed. The most relevant one is discussed below:

Degradation by Photocatalysis

Photocatalysis is one of the advanced oxidation processes used as a problem solver in environmental issues relating to pollutant management [113]. It involves the use of reacting species such as OH radicals in mineralizing pollutants in wastewater with the establishment of a catalyst by photons. These methods of mineralization are in twofold, namely homogeneous photocatalysis and heterogeneous photocatalysis. In homogeneous photocatalysis, the pollutants and the photocatalyst exist as soluble in similar liquid phase, for example photo-Fenton process which engaged the use of Fe^{2+} and H_2O_2 in the production of hydroxyl radicals, while heterogeneous photocatalysis entails the existence of the semiconductor such as ZnO which act as a catalyst that is dependent on the pH of the pollutant in an insoluble form, and this makes it to be available in diverse phases which can be obtained easily after utilization. Zinc oxide is initiated by UV and visible light to generate electron hole pairs. Since ZnO is a semiconductor catalyst that absorbs light, there is excitation of electrons from the valence band to the conduction band and reacts with different organic pollutants and water, thereby generating a positive charged hole at the valence band and electrons at the conduction band. This positive charged hole oxidizes the organic pollutants to hydroxyl radicals (OH^-). The electrons at the conduction band reduce oxygen to superoxide anion (O_2^-). The reactant reacts with H+ to generate hydrogen peroxide, the electrons react with hydrogen peroxide to generate free hydroxyl radicals, the electrons react with hydrogen peroxide to generate free hydroxyl radicals. The organic pollutants react with hydroxyl radicals and mineralize it to carbon(IV) oxide, w\water and other mineralized products which are harmless when released to the environment [114].

Conclusion

In summary, the effects of different synthesis parameters on the textural, optical and microstructural properties of ZnO nanoparticles have been provided. The effectiveness of

zinc oxide in terms of high photocatalytic ability, non-toxicity, effortless synthesis, availability and antimicrobial activities has made it to be a good photocatalyst for the removal of pollutants in wastewater. The adsorptive behavior of ZnO nanoparticles for the removal of heavy metals especially at different solution pH has also been summarized. Based on the review, the following conclusions were drawn. Acidic medium favored the formation of smaller size of ZnO nanoparticles compared to alkaline medium. Several reports indicated a decrease in the crystallite size of ZnO nanoparticles as the pH increases from 7 to 12. Reaction time, reaction temperature and calcination temperatures influenced the crystallite size of ZnO nanoparticles. These findings indicated that these factors strongly affect the crystallite size and the morphology of the zinc oxide nanoparticles. The crystallite sizes with respect to each parameter also depend on the methods of synthesis of ZnO nanoparticles. There are still divergent views as reported by the researchers on the increase and decrease in the particle size of the ZnO nanoparticle. Optimization of all these parameters should be carried out to fully understand the mechanism of the synthesis of ZnO nanoparticles. Regeneration of the ZnO should be performed to evaluate the cost effectiveness of ZnO as an adsorbent. Future research should focus on the immobilization of ZnO nanoparticles on suitable supports for easy separation after usage

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