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## Insights on the advanced separation processes in water pollution analyses and wastewater treatment – A review

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## ABSTRACT

Globally, the problem of pollution is considered to be one of the main cause of water scarcity, as it is common to waste dumped in streams and rivers. This problem has resulted in high levels of toxic chemicals such as pesticides, micro-pollutants and heavy metals being found in water bodies. The unwavering natural surroundings of worldwide rareness of water is the topographical and sequential discrepancy between the demands for clean fresh water and the obtainability of it.

However, new and diverse technologies have been developed in order to achieve sustainable clean fresh water resources. The revolution in the development of novel technologies and materials such as nanomaterials is considered one of the most motivating and potential novel technologies for wastewater treatment. This review outlines the advancements of separation processes in treating polluted wastewater. Technologies such as phytoremediation, nanotechnologies and photo-catalysis were discussed.

### 1. Introduction

Water is the most abundant resource on the planet. It is said to comprise about 70 percent of the earth's mass (Harikishore, 2015). It also constitutes most of what we eat and helps in the digestive process of humans and animals. However, accessing clean water has been a problem for the world for a long time (Kumar et al., 2012; Ngene et al., 2021). A large portion of the planet's populace does not have access to clean and healthy water (Cisneros, 2011). Furthermore, the death rate from contaminated water has increased, over the years, as more and more people die every day from drinking unhealthy water (Wasewar, 2020). Water pollution, by definition, is the contamination of available water by pollutants or alien materials that lead to death and disease of livestock, aquatic life and humans (Abdulrazzak, 2020). It is a process whereby, the water that should be accessible, gets contaminated by foreign particles and once taken into the body, ends up causing harm to the internal system of the organisms in question (Muralikrishna, 2017). In addition, it may lead to the death or destruction of the surrounding organisms or the environment, in general (Saxena, 2012).

Looking at the significant of wastewater management at local and global level, the updated wastewater treatment, use and management is needed. Toshio et al. (2013) using data for 181 countries reported that

55 countries have no information on wastewater production, treatment and use, 69 countries have partial information while 55 countries have complete information on wastewater generation, management and utilization. Exall et al. (2008) found that 85km<sup>3</sup> of wastewater were generated in North America of which 61km<sup>3</sup> are treated. Large amounts of treated and discharged wastewater are a result of developed economies and the use of more fresh water in the domestic and industrial sectors. In Latin America (UN, 2012) reported that 20% of generated wastewater undergoes treatment because of the lack of well-developed wastewater collection and treatment systems in some Latin America countries. Seventy-one percent (71%) of the wastewater generated in Europe undergoes treatment, due to technology advancement and high public awareness regarding health and environmental protection (UN, 2012; OECD, 2008). Russian Federation generates 14km<sup>3</sup>/year of treated wastewater. About 28% of the waste is processed according to regulations, while the rest is discharged into aquatic bodies in an untreated state (Toshio, 2013). Only 51% of the sewage produced in the Middle East and North Africa gets treated, according to Qadir et al. (2010). WEPA-IGES (2012) discovered that in Asia 32% wastewater generated is treated as a result treatment plants inadequacy and the lack of financial resources. Only Senegal, South Africa, and the Seychelles have complete information on sewage water treatment, and usage in

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Sub-Saharan Africa, out of 48 nations in the region. In Sub-Saharan Africa, much of the sewage water goes unchecked, causing water contamination and the development of waterborne diseases including cholera and diarrhea (WHO, 2007, 2008).

There are several sources of water pollution, and typical types of pollutants associated with them. Sewage waste, which usually are domestic in nature and constitute wastes from the sinks, latrines, and other sources, when left untreated, are washed into waterways and thus, find a way to contaminate the available water (Lande, 2020; Elehinafe et al., 2020). Agricultural wastes, from pesticides, insecticides and fertilizers also when applied on the soil or left untreated, gets washed into the waterways and contaminate the available water. Plastics and garbage have arisen as some of the biggest contaminants of the available water and the seas have been plagued by them (Kumar et al., 2012). A lot of these, are as a result of human activities.

Several authors have highlighted different techniques for separating pollutants from available water sources, using a combination of modern technologies and some, combine some of the traditional methods in the process of water purity (Kumar et al., 2012). Historically, there have been methods that have been applied, in order to rid relatively smaller water environments of pollutants and contaminants (Arif, 2017). These methods have proved themselves effective in eliminating large molecules of contaminants, however, for the unseen contaminants, such as ions, organic and inorganic pollutants, the techniques, operated in their primary forms have proven to be ineffective against these. Some of the primary techniques include: distillation, decantation, filtration, boiling and some levels of sedimentations.

Distillation involves the separation of a target solute or solvent from a solution by the application of heat, while taking the difference in boiling points as the reference point or the property difference to be exploited (Harikishore, 2015). Distillation process is a separation technique that uses heat to separate mixed components in water. This process is established on the variances in boiling points of the discrete components. The characteristics of the boiling point is hinged on the concentrations of the components present in the mixture. Hence, the distillation process is dependent on the characteristics of the vapor pressure of liquid mixtures. The simple principle described how the input of heat energy raises vapor pressure. Once the vapor pressure gets to its contiguous pressure, the liquid mixture boils and distillation takes place as a result of the variances of volatility in the mixture. Nonetheless, as simple as this method is, organics of large molecules with boiling points lower than 100 °C cannot be effectively eliminated and can in fact become concentrated in the product water. Subsequently, a carbon filter system must be inserted in the process to actually make water safe to drink. However, the carbon filters regularly need to be changed as they can speedily become breeding grounds for bacterial growth (Sharma and Bhattacharya, 2017).

Decantation process occurs under the effect of Earth's gravity. Hence, decantation requires a distinct and clear difference in both appearance and weight of the components in the mixture. This process can be employed to separate solid particles from a liquid or two immiscible liquids of diverse densities (Berk, 2009). In this process, the top layer of the mixture is poured and collected in another container or beaker (Abdulrazzak, 2020). Decantation is also a simple process, however, one limitation of this process is that it does not give room for a perfect separation of mixtures of components. The is due to the fact that a small quantity of one component could be lost in the course of collecting other component, otherwise, the collection moves too far and the collection gets contaminated with the second equipment. Hence, the process does not make available precise or pure product (Helmenstine, 2021).

The filtration process operates in a rather similar manner but with a slightly different technique and with a different apparatus. Here, solid particles in the mixture are trapped and removed with a sieve or filter bed while liquid is allowed to pass through. The process is also simple, none the less, the widely known limitation of filtration is that it

eliminates useful minerals present in the liquid. Conversely, it doesn't eliminate all the harmful particles present in the liquid. In addition, the filters can't be reused again; hence, have to be discarded at the end of the filtration process (Sulaiman, 2022). In the same vein, filter can retain contaminants through the thickness of the filter and on the surface of the filter in the course of liquid filtration (Onur et al., 2018).

For boiling process, this is usually targeted at organisms that cannot survive at certain temperatures. The water is heated at that temperature, for a period of time, and then the resulting product is deemed fit for usage and free from bio-pollutants and their harmful effects. The boiling process is similarly a very simple process of water disinfection. In this process, the wastewater to be treated will be heated to a high temperature, such as 100 °C in order to kill most of the pathogenic organisms, especially, viruses and bacteria as they are the cause of waterborne diseases (Kumar et al., 2012). However, this method can only globally treat small amount of water, with a predictable 1.2 billion people utilizing it as a means of household water treatment (Brown and Sobsey, 2012).

Sedimentation process is a process that enables particles that are suspended in water to settle out of the suspension using the influence of gravity. Particles that settled out from the suspension are known as sediment; however, in water treatment they are known as sludge. The continuous settling of the thick stratum of sediment is known as consolidation. When mechanical activities are used to assist the consolidation of sediment, or sludge, the process is known as thickening. In water treatment, sedimentation could be employed for the reduction of particles concentration in suspension prior to the application of coagulation. This is done to reduce the quantity of coagulating chemicals needed, or after coagulation and, possibly, flocculation. The purpose of the application of sedimentation after coagulation is usually to reduce the concentration of solids in suspension for the subsequent filtration to function most effectively (IWA, 2022). One of the disadvantage of this method is connected to the sedimentation tank. The mechanical drive unit and shaft bearings unit of sedimentation tank need continuous maintenance (Ramzi, 2020). In addition, the process is very slow because it requires more time and it also depicts pollution trend in some precise districts over time (Dream Civil, 2022). Furthermore, the intrinsic heterogeneity of sediment in this process makes it problematic to describe with regards to bulk sediment physicochemical parameters like the total organic carbon content, the distribution of particle size and surface area. Thus, the management of sediments and the control of sediment contaminants in this process are among the most challenging and complex problems encountered in using this process (Luthy, 2004).

Hence, the problem with these techniques, in their primary form, is that there is no real guarantee of the absolute effectiveness and efficiency that they offer, even in a combination of each other. In addition, these techniques are hardly ever tested with standard techniques to be able to ascertain if it (the product and final water sample obtained) can be universally accepted as totally free of both organic and inorganic pollutants. Furthermore, these techniques are only able to handle a limited amount of water (Kumar et al., 2012). The inefficiencies of the above techniques resulted in researchers making use of techniques such as denitrification (Du et al., 2014; Xu et al., 2020), biological degradation (Thanave et al., 2020; Mishra et al., 2021), nanotechnology (Agboola et al., 2021; Poornima et al., 2022) and photocatalysis (Liu, et al. 2020; Ren et al., 2021) at advanced levels to be able to be more effective. The objective of this review is to identify the modern separation techniques that aid in the treatment of polluted water. In addition, the separation techniques are critically looked at, to determine the extent to which their efficiencies guarantee the highest level of purity that can be attainable while employing each process. The impact of the techniques, the amount of water and the health benefits are confirmed.

## 2. Advanced separation processes in water pollution analyses and wastewater treatment

As mentioned in the introduction, the old methods, operated in their primary forms, have proven themselves to be non-effective in eliminating large molecules of contaminants, and unseen contaminants, such as ions, organic and inorganic pollutants due to their shortcomings. Some of the primary techniques include: distillation, decantation, filtration, boiling and some level of sedimentation. In addition to the argument provided in section 1 on distillation, distillation process resulted to some limitations such as the consumption of a massive volume of energy with respect to cooling and heating requirements. Furthermore, some pollutants might move into the condensate, careful maintenance to ensure purity is also required (Sharma and Bhattacharya, 2017). Furthermore, for the argument provided in section 1 on decantation, the process also results in limitation such as not being able to separate liquid or solid that dissolves in a mixture, not being able to separate salt and impurities such as chalk powder from water, and finally not being able to remove small-size and microscopic impurities (Aakash, 2022). Based on the argument made for filtration, openly disposing of the filters used for filtration could lead to further harm to the milieu and the surroundings, as a result of the harmful nature of the particles filtered out. Sedimentation also has a shortcoming of time consumption as a result of slow process and pollution trend in some particular areas over time. Though advances in analytical techniques ensures possibility of measuring the smallest quantity of anthropogenic contaminants present in sediment. However, the capability of relating sediment concentrations to the quality of water, biological availability, and toxicological impacts are stalled by insufficient understanding of the binding and contaminants release in sediment (Luthy, 2004). Hence, the reasons for advanced methods which are hereby reviewed in this section.

### 2.1. Phytoremediation

Phytoremediation is an evolving technology that employs green plants for the relieve, stabilization and management of an extensive range of environmental pollution challenges; this includes the clean-up of soils, polluted surface water and groundwater as a result of hydrocarbons and other harmful substances (Das and Preethy, 2011). Other

crops have the ability to assimilate and process nutritional and organic contaminants, while certain other crops may trap and immobilize metal pollutants. Multifarious relationships and reaction interphase amid soil, plants, microbes and pollutants allow several phytoremediation processes possible (Laghlimi et al., 2015) for large sites with low residual levels of pollution by nutrients, organic or metal pollutants, where pollution have no impending hazard and only “polishing treatment” is needed, phytoremediation can be cost-effective. In addition to that, phytoremediation can also be cost-effective where vegetation is utilized as a concluding plug and site closure (Schnoor et al., 1995). Hence, the benefits of phytoremediation are low budget, esthetic advantages, and prolonged and extended usage. Additionally, the utilization of phytoremediation as a secondary or polishing in situ treatment step reduces land disruption and eradicates transportation and costs liability connected to the offsite treatment and disposal (Das and Preethy, 2011). Phytoremediation approach involves different mechanisms; illustrated in Fig. 1.

#### 2.1.1. Plant root architecture

For plant root architecture, the root zone has a distinct importance in phytoremediation. It can capture pollutants, store or process them within the plant tissue. Another phytoremediation technique is the decomposition of toxins in the soil by plant enzymes secreted from the roots. Drought morphological adaptation is characterized by an increase in root diameter and constricted root elongation in accordance to the dried soil's reduced penetrability (Merkel et al., 2005). Root plants release substances that stabilize, neutralize, and bind pollutants in the soil structure, lowering their bioavailability. The phytostabilization process is the name given to these systems. Toxins in soil and groundwater are immobilized in the phytostabilization process via incorporation and aggregation in plant tissues, adhesion onto roots, or precipitation inside the root zone, inhibiting mobility in the soil as well as erosion and compression (Erdei et al., 2005; Erakhrumen and Agbontalor, 2007). Hence, some types of plant species are utilized for the immobilization of contaminants in the soil and groundwater via absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone (Tangahu et al., 2011).

The roots of plants have the capacity to impact on heavy metal phytoavailability (Elekes, 2014) through the modification of the soil properties in the rhizosphere (Brown et al., 2003). The plant enzymes

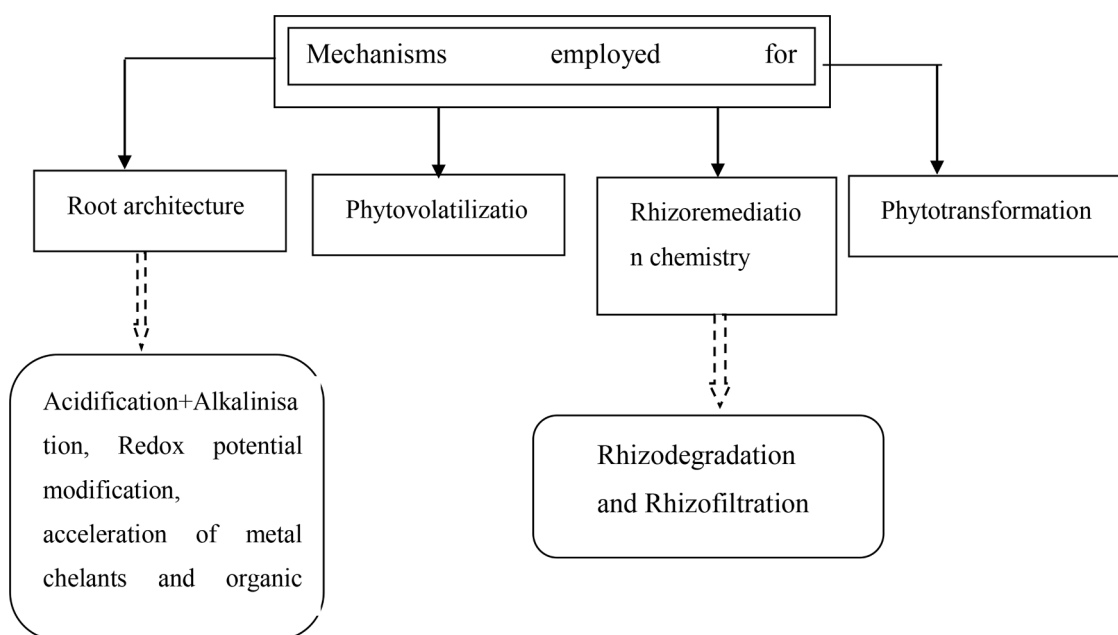


Fig. 1. Different mechanisms utilized for phytoremediation.

radiated from the roots have a crucial role to play in the alteration and chemical speciation of metals in soils as this will accelerate their uptake by plant (Degryse et al., 2007; Mallmann et al., 2014). Acidification/alkalinisation, redox potential modification, acceleration of metal chelants and organic ligands are the activities of plant root that possess the potential to upsurge the solubility of metal and could also alter heavy metal speciation (Wenzel et al., 2003; Jones et al., 2004). Nonetheless, studies have shown that the process of root secretion and composition of efflux is still not well understood for most of the environmentally pertinent heavy metals (Mahmood, 2010). This is as a result of root contact, which is a main constraint on the practical application of phytoremediation. Pollutants must come into touch with the base of the crops during agricultural remediation. Either the crops' base must be able to reach the pollutants, or the polluted material must be put within reach of the crops (U. S. Environmental Protection Agency, 2000). If the contamination is limited to shallow pollution inside the root system of remediated crops, the site's surface layer may need to be adjusted to prevent flooding or degradation (Mwegoha, 2008).

Furthermore, the interactions amid root exudates and microorganisms in the rhizosphere have been documented to be an acute component of plant growth in phytoremediation (Badri et al., 2009). In the study of Mavrodi et al. (2021) on root exudates altering the expression of diverse metabolic, transport, regulatory, and stress response genes in rhizosphere pseudomonas; they focused on the molecular dialog between eight well-characterized beneficial strains of the *Pseudomonas fluorescens* group and *Brachypodium distachyon*, as a model for economically important food, feed, forage, and biomass crops of the grass family. In this study, bacteria, screened of by Biolog Phenotype MicroArrays showed that many of these metabolites offer carbon and energy for the *Pseudomonas* strains. RNAseq profiling of bacterial cultures modified with root exudates showed modifications in the expression of genes encoding many catabolic and anabolic enzymes, transporters, transcriptional regulators, stress response, and preserved hypothetical proteins. Hence, root exudates could serve as metabolic substrates for the promotion of As-tolerant microorganisms' growth, which therefore results in an alteration in the microbial community, which is in favor of As migration, transformation and bioavailability in rhizosphere (Shenton et al., 2016). Jiang et al. (2023) studied the increase in arsenic (As) mobility by root exudates and altered microbial community in paddy soils. The study was done for the purpose of investigating the impact of diverse concentrations of root exudates on soil physicochemical properties, the impact of As speciation and mobility in paddy soils and to examine the microbial mechanisms of how root exudates affect As biotransformation. The results obtained suggested that investigating how root exudates impacted the mobility and transformation of As in paddy soils was useful for systematically understanding the biogeochemical cycle of As in soil-rice system, which is of pronounced importance in reducing the health risk of soil As contamination.

### 2.1.2. Phytovolatilization

Phytovolatilization is the process of a plant absorbing and losing a toxin by evaporation, followed by discharge of the toxin or a modified version of the toxin into the environment. Following the biotransformation of pollutants into minute hazardous forms, this process occurs. However, because of the possibility of re-deposition of the released chemicals (in less harmful forms) surrounding the locations, this strategy was not considered a comprehensive cleanup solution (Ali et al., 2013). Phytovolatilization happens when developing vegetation soaks up moisture along with the pollutants. Some of these pollutants can pass through the crops to the leaves and spread into the environment at moderately low concentrations (Erdei et al., 2005; Erakhrumen and Agbontalor, 2007). The following are the steps in the phytovolatilization process: (1) Adsorbed toxins (organic or inorganic) are transported to plant tissues through the root, where they are transformed into small hazardous forms. (2) The changed chemicals' translocation to the

leaves. (3) The changed molecules are discharged into the atmosphere by the transpiration or evaporation processes in leaves. According to Muthusarayanan et al. (2020), phytovolatilization of toxic substances is not ideal for cities with high concentration of people and regions with changing weather patterns since it increases the likelihood of volatilized pollutants resettling.

Hence, plants have the capacity to interrelate with a range of organic compounds, which have impact on the fate and transport of several environmental contaminants. Volatile organic compounds could be volatilized from stems or leaves; this is known as direct phytovolatilization, or from soil due to plant root activities, known as indirect phytovolatilization (Limmer and Burken, 2016). Thus, the pollutants are adapted by the roots, translocated to the shoot and volatilized in atmosphere via the stomatal leaves (Tollsten and Muller, 1996). Moreno et al. (2008) investigated the phytofiltration potential of Hg by *Brassica juncea* plants with a view of treating Hg-contaminated wastewater to address a previous work which reported Hg losses from the plant-soil system by Hg(0) volatilization. The study showed that *Brassica juncea* grown hydroponically removed up to 95% of Hg by both phytovolatilization and plant accumulation. Guarino et al. (2020) assessed the phytoremediation capabilities of *Arundo* exposed to very high concentrations of As (up to 20.0 mg/L) which was also supported by an As tolerant bacterial consortium (BC) previously isolated. Their study further investigated whether the amendment of the DNA methylation status of *Arundo* could be an epigenetic mechanism involved in the response to As pollution. After the trial plant biomass, As concentration were measured and it was found that plants did not show any noticeable signs of toxicity; instead, the leaf and stem biomass to some extent, increased in the presence of As and/or PGPBs. Furthermore, though the Bioaccumulation Factor was double in the presence of BC, the total values of As accumulation in the *Arundo* plants appears to be very low in both the presence or absence of BC. This was only detectable in the presence of the maximum As dose (20 mg/L of As). Nugroho et al. (2021) aimed to comprehend the metals uptake and removal rates by vetiver for the purpose of evaluating vetiver as a possible phytoremediation agent. Water, roots, and shoots were periodically collected by employing Atomic Absorption Spectrometry (AAS) for the determination of Cr and Ni contents. Their results depicted that vetiver (*C. zizanioides* L.) was able to eliminate 61.10% Cr and 95.65% Ni on metal-contaminated water. The highest uptake rates for Cr and Ni were respectively 127.21 mg/kg/day and 15.60 mg/kg/day, while the elimination rates for Cr and Ni respectively tend to slow 1.09 mg/kg/day and 12.24 mg/kg/day. However, in spite of the series of toxicity symptoms, the vetiver was found to be well adapted, indicated with the growth of roots and new individuals in the Cr and Ni treatment. Hence, the ability of plants to absorb large quantities of metals and decrease their toxicity is an important factor for the remediation process. Thus, this demonstrated that vetiver has a high prospect as phytoremediation agent.

### 2.1.3. Rhizoremediation chemistry

The degradation of pollutants is established by plant enzymes in the course of phytoremediation; while, in the course of natural attenuation or bioaugmentation, the (indigenous) microbial population accomplishes the degradation. A significant contribution to the degradation of pollutants in the literature is attributed to the presence of microbes in the rhizosphere of plants, employed in the course of phytoremediation or of plants which are evolving as natural vegetation on a contaminated location (Kuiper et al., 2004). Rhizodegradation is the breakdown of toxins in the soil by the action of living organisms aided by the appearance of the root zone. Microorganisms are used in the Rhizodegradation mechanism to consume and process chemical compounds for nourishment. Several chemical substances, such as sugars, are formed of carbonaceous fuel and include nutrients for microbial activity while also constructing a sturdy crop-base structure capable of receiving large amounts of water. The majority of the time, this process is utilized to eliminate organic chemical pollutants from the soil (Prasad and De

Oliveira Freitas, 2003). Rhizosphere microorganisms are occasionally the primary factors that influence the decomposition process. A crop can be thought of as a solar-powered biological pump and treatment system that draws water in with its crop root, accumulates water-soluble pollutants in the rhizosphere, and then degrades or trans-locates the pollutant (Erickson, 1997).

Rhizofiltration is a type of rhizoremediation. Rhizofiltration is a green technology that uses a built wetland to bind or precipitate pollutants in liquid close to the crop-based zone onto crop roots, or to integrate pollutants into and sequester them in the crop's base (Erdei et al., 2005; Erakhrumen and Agbontalor, 2007). For the purification of groundwater, Rhizofiltration is used. Crops are produced in greenhouses in water instead of in the earth in this method. The plants are acclimatized to their environment using contaminated water from the area. The crops are then placed in a polluted subsoil system, where the crop's base absorb the aqueous solution and pollutants. Plants are taken together with the roots as immediately the crop's base is inundated with the pollutants (Abdullahi, 2015). Heavy metals like cobalt, lead, copper, cadmium, arsenic and uranium are considered too low for effective elimination via the use of conventional methods; however, they can be effectively eliminated via rhizofiltration technique. This technique is practically profitable and sustainable because it embroils the utilization of plant roots for the absorption and concentration of heavy metals from unclean aqueous streams (Srivastava et al., 2021). Ure et al. (2019) developed a fast system for the remediation, recovery, and possible recycle of phosphate from agricultural wastewater by employing tomato plant roots as an ensnare matrix and carboxymethyl cellulose (CMC) was used as an eluent and booster of phosphate precipitation. Their study showed that by adding CMC, the precipitation of phosphate with a clearance of 97.2% was improved as contrasting 33.3% when devoid of CMC. The on-site tests depict an average elimination of 226.5 µg/L per day which corresponds to a 71% phosphate removal rate.

Literature has it that some investigation inoculated PGPR strains in the rhizosphere to enhance the growth of plant under contaminated conditions. Xun et al. (2015) investigated the effect of plant growth as a promoting bacteria (PGPR) and arbuscular mycorrhizal fungi (AMF) inoculation on oats in saline-alkali soil contaminated by petroleum to enhance phytoremediation.

The study depicted that the degradation rate of total petroleum hydrocarbon in the course of treatment with PGPR and AMF in moderately contaminated soil attained a maximum of 49.73%. Hence, the study showed that *Avena sativa* (common oat) growing in oil-contaminated soil and inoculated with an *Acinetobacter* PGPR strain displayed an upsurge in dry mass and stem height in comparison to controls, together with a higher rate of decontamination. Yaashikaa et al. (2020) studied the isolation and identification of metal resistant bacteria to grow on medium together with the concentration of copper ion (1500 mg/L). *Pantoea dispersa* was identified as the resistant isolate by a 16S rRNA sequencing. At the 125 mg/L concentration of Cu(II) ion in soil, the bioaccumulation of Cu(II) ions in plant was high. This study demonstrated that pyrolysis is an encouraging technique for the conversion of metal ion contaminated plant residues from phytoremediation into useful products.

#### 2.1.4. Phytotransformation/phytodegradation

Phytotransformation, also termed phytodegradation, is a process of breaking down organic contaminants confiscated by plants through metabolic processes contained in the plant or by using the influence of compounds like enzymes, produced by the plant. The organic contaminants are degraded into modest compounds that are incorporated with plant tissue. This will subsequently stimulate the growth of plant (Hawaii, 1998). The success of phytotransformation is dependent on collaborating associations among plants, microbes, soil and water. The plant is responsible for the provision of surface area for microbes to inhabit around the root and to shoot in order to upsurge the microbial activity for degrading carbon substrates. For example, Al-Baldawi et al.

(2018) discovered that the underwater crop *Azolla pinnata* can absorb Methylene blue dye from water when used as an organic matter media. The dye amounts employed in the experiment were 5, 15, and 25 mg/L, using 3 g of *Azolla pinnata*. Their findings revealed that the optimum decolorization of Methylene blue was 85%, indicating that natural biomass media from a floating plant (*Azolla pinnata*) is capable of converting and mineralizing the dye. As a result, *Azolla pinnata* can be used to efficiently cleanse dye-contaminated water. Apart from the enzymatically process, plants also play a crucial role mechanically, by decreasing runoff that facilitates adsorption of compounds on to root surface and stimulate evapotranspiration (Sri Lakshmi et al., 2017). Therefore, phytotransformation of green plant is considered an important means employed in managing waste that are characterized in line with vegetative control techniques of pollutants, that is used to manage contaminated groundwater plumes and soil.

Phytoremediation as described above make use of plants for the extraction, degradation and control of pollutants and contaminants in the soils and bodies of water (Gerhardt et al., 2017). Literature has recorded several researches in this area and several plants with excellent Phytoremediation potential have also been recorded. These plants include, Indian Mustard (*Brassica Juncea* L), Willow (*Salix* Species), *Salvinia Molesta*, Poplar tree (*Populus deltoides*), Indian grass (*Sorghastrum nutans*) and Sunflower (*Helianthus Annus* L). There are several advantages when it comes to applying the phytoremediation process (Cameselle and Gouveia, 2019). They are used in the recovery of several metals, such as Zn, Fe, Se and Ni. In combination with biofortification process, they improve the nutritional value of grains (Imadi, 2016) and the maintenance cost is usually low (Nakbanpote, 2016). When not controlled, the plant can be of danger to aquatic life as it can cause clogging of the rivers and as such, then prevents growth of plants and other organisms from thriving (Harikishore, 2015; Elehinafe et al., 2020; Kumar et al., 2012).

Munfarida et al. (2020) worked with *Salvinia Molesta* found out that it absorbs pollutants, but does not stop light from interacting with the water environment and thus, allows room for organism growth and existence. Munfarida et al. (2020) used polluted river water for two different treatments, with one sample without *Salvinia Molesta* in a polluted river water and one with *Salvinia Molesta* in a batch reactor with both the media and the phytoremediator placed together, for a period of time, with the expectation to obtain a final product. The system was expected to experience some level of loss in its overall nutrient content as a result of the activities in the entire process. The amount of *Salvinia Molesta* utilized was 150 g and 6 L of the polluted river water during the experimentation phase. The parameters considered were dissolved oxygen (DO), total dissolved solids (TDS), total solids (TS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). It was discovered that *Salvinia Molesta* was effective in treating polluted water and very good phytoremediator, that grows very fast and stretches over a good amount of space and survives with little nutrients required.

Jaiswal and Pandey (2019) investigated dissolved oxygen (DO), which is the measure of the amount of oxygen in the water sample and the effect of either an addition or reduction process on the oxygen content in a sample polluted water from a water body. The DO, at the start of the experiment was measured at 2.7 mg/L, and saw an increase in control of 2.7 mg/L. The general assumption that was made, by Munfarida et al. (2020), revealed that the increased oxygen level is as a result of dissolved oxygen being increased via the process of photosynthesis carried out by the *Salvinia Molesta*. This is a positive indicator of pollutant nullifying, as the presence of oxygen in the water would be a space organic life can continue its activities, regardless of the counter-effect of pollutant activity (Roy et al., 1986).

At several contaminated regions, there are mixtures of different contaminants with different properties. This could result in extra complications and hence, added costs. Thus the attempt of using advanced technology such as of electric field for the improvement of

phytoremediation. Chirakkara and Reddy (2015) made an effort to improve the phytoremediation of soil contaminated with naphthalene, phenanthrene, Pb, Cd, and Cr with the utilization of an electric field in the course of the phytoremediation with oat plant and sunflower. Contaminants and toxic materials in soil were found to be significantly reduced as a result of the findings. Despite the fact that the crops exposed to the electric current produced more carbonaceous fuel, there was no clear improvement in toxic substance phytoextraction or polycyclic aromatic hydrocarbon (PAH) decomposition as a result of the application of the electric current. The time and frequency of the electric potential application are proposed to be increased to have obvious impacts in heavy metal uptake and PAHs degradation. Cameselle and Gouveia (2019) investigated the feasibility of improved phytoremediation using electric current as a viable approach for soil stabilization with mixed pollutants (polycyclic aromatic hydrocarbon and metals). The type of electric current (alternating current; AC, direct current; DC) and manner of approach (periodic, continuous, and polarity inversion) were investigated in order to determine the ideal circumstances for improving the plants' restorative abilities. Several crop variants were examined for their potential to flourish in polluted soil after they adapted to the soil and climatic conditions. According to the findings of their research, AC appears to be the appropriate electric current for numerous applications. The spread of the electric current in the earth is affected by the layout of electrodes. Several different layouts of electrodes were evaluated, and it was determined that complementary anodes and cathodes on the earth's topsoil are the best configuration for field applications. Pollutants can be concentrated around the developing plant or transported from deep soil strata to the rhizosphere by other methods.

## 2.2. Nanocomposites for wastewater treatment

Nanocomposites were developed as a consequence of research into increasing composite material qualities. Because they are made up of at least one phase with dimensions in the nanometer range (1 nm = 10<sup>-9</sup> m), nanocomposites are enhanced materials with unusual pairs of attributes and different configurations (Roy et al., 1986; Camargo et al., 2009). As demonstrated in Fig. 2, different kinds of nanomaterials have varying sizes. When materials' dimensions approach the nanometre scale, their activities at phase interfaces improve dramatically, which is critical for improving material properties. Considering this, the surface area/volume ratio of reinforcing agents used in nanocomposites synthesis is critical to understanding

their structure–property correlations (Camargo et al., 2009) for different applications. For this reason, a great interest has been drawn in the direction of using nanocomposite for wastewater treatment. Numerous studies have used different types of nanocomposites materials for wastewater treatment because of its effectiveness, especially when the nanocomposites materials are hybridized for water purification.

The qualities of nanocomposites are dependent on the separate constituents, the system's structure, the volume and shape proportion of the filler, and the characteristics of the inter-phase between the components' interfaces (Osman et al., 2005). If there is appropriate contact and good distribution between the matrix and the nanoparticles, then these qualities can be improved (Opoku et al., 2017). Because of the nature of the matrix, nanocomposite materials can be classified into separate classes based on their matrix materials, as shown in Table 1.

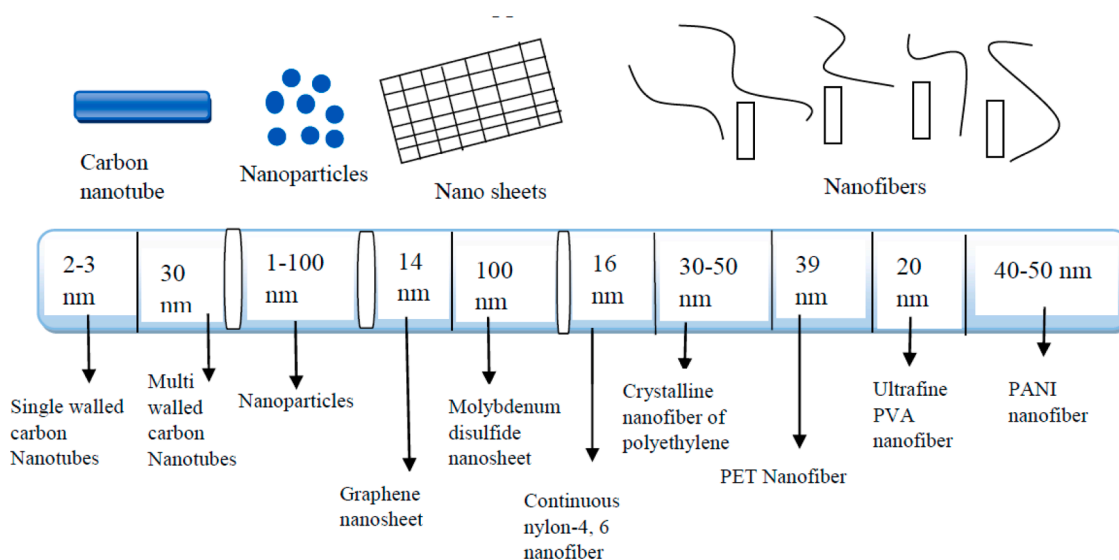
### 2.2.1. Metal nanocomposites for wastewater treatment

Metal matrix nanocomposites also known as reinforced metal matrix composites are composites materials that can be categorized as continuous and non-continuous reinforced materials. They are substances made up of a ductile metal with minuscule reinforcing material inserted in it. Metal matrix nanocomposites substances have both metal and ceramic properties, such as ductility and toughness, as well as high strength. As a result, metal matrix nanocomposites are well suited to the manufacture of systems with good shear/compression strength and high service temperature capacities (Camargo et al., 2009). They therefore have the demonstration of an amazing prospect for different applications such as wastewater treatment. Metal nanocomposites are often employed as photocatalysts, adsorbents and sensors to combat the problems of environmental pollution. The benefit of being at nanoscale provides high surface area and high reactivity that makes them highly

**Table 1**

Classes of nanocomposites based on their matrix materials (Camargo et al., 2009).

Classes of nanocomposite materials	Examples
Metal nanocomposites	Ni/Al <sub>2</sub> O <sub>3</sub> , Al/CNT, Mg/CNT, Fe-Cr/Al <sub>2</sub> O <sub>3</sub> , Fe-MgO, Co/Cr,
Ceramic nanocomposites	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> /SiC, Al <sub>2</sub> O <sub>3</sub> /CNT, SiO <sub>2</sub> /Ni,
Polymer nanocomposites	Thermoplastic/thermoset polymer/layered silicates, polyester/TiO <sub>2</sub> , polymer/CNT, polymer/ layered double hydroxides



**Fig. 2.** Schematic representation of different nanomaterials and their diameters (Agboola et al., 2021).

effective for water purification and timely sensing of pollutants (Hu et al., 2013; Lateef and Nazir, 2017). Among all metal nanocomposites, iron nanocomposites constructively linked with nanostructures have exhibited highly promising characteristics for sewage control.

Diagboya et al. (2015) studied the adsorption of mercury by using synergistically iron oxide nanoparticles functionalized with graphene oxide. The nanocomposite adsorption efficiency is 5 times more than that of pristine graphene oxide sheets, according to the research. By contrasting the adsorption capacity of mercury at different temperature ranges (20 °C, 30 °C, and 40 °C), the study also demonstrated that a temperature increase has a significant impact on the process. Marini (2015) developed new hybrid nanocomposites and investigated their potential for removing contaminants from stormwater. By hybridizing uncoated iron oxide nanoparticles and attaching them to graphene oxide nanosheets, the nanocomposites were created. The findings of magnetic measurements and magnetic separation at the end of adsorption trials show that these nanocomposites may be efficiently removed at the end of their uses by simply applying a magnet. Depending on the type of toxic substance handled, different removal efficiencies were achieved. Lead had a higher removal effectiveness than chromium and nickel among the heavy metals eliminated. Huang et al. (2018) prepared amino-decorated Zr-based magnetic Metal-Organic Frameworks composites (Zr-MFCs) through the utilization of a facile and efficient strategy. The nano-sized  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core (around 15 nm) was coated with a shell of Zr-MOFs (roughly 5 nm) through in-situ growth. The Pb (II) and methylene blue adsorption efficiency of the hybrid composites were exhibited. Ge et al. (2018) created a Fe@MgO nanocomposite that made use of the significant magnetism of nZVI and the high adsorption efficiency of MgO. Batch adsorption tests revealed that the nanocomposite had optimal removal capabilities for Pb (II) and methyl orange (1476.4 and 6947.9  $\text{mg}\cdot\text{g}^{-1}$ ). This shows that the composites are good for wastewater treatment.

All these studies have shown that metal nanocomposites hold unlimited prospects for heavy metals removal from wastewater as a result of their easy separation property. Nonetheless, the compatibilities of these metal nanocomposites with other nanomaterials should be considered for a further research. This is due to the fact that the compatibilities of these nanocomposites will have effects on the broad application prospects in wastewater treatment.

### 2.2.2. Ceramic nanocomposites for wastewater treatment

By including a ductile metal phase into the matrix, several efforts were made to create ceramics suitable for use in the Engineering industries. As a result of the relationship that exists between separate stages, framework, and supports, at the phase borders throughout the material, mechanical properties such as hardness have improved. In order to understand the structure–property connection in ceramic matrix nanocomposites, the surface area/volume ratio of the reinforcement materials is critical (Camargo et al., 2009), this will afford ceramic nanocomposite materials with exceptional catalytic, electronic and optical properties and excellent mechanical characteristics. This will enhance their use for engineering applications. Furthermore, some research has discovered that the crack-bridging function of the nano-scale supports, influences the strengthening technique of ceramic nanocomposites (Zhang et al., 2003). As a result of the incorporation of high potency nanofibres to ceramic matrix, improved ceramic nanocomposites with great toughness and durability are now possible (Kruis et al., 1998; Awasthi et al., 2019)

Most of the ceramic-based nanocomposites used for environmental applications are shown in Table 1. Ceramic composites with the integration of carbon nanotubes have shown improved results in environmental applications (Tjong and Wang, 2004). Intapong and Raksudjarit (2012) prepared porous ceramics filter by sintering of hydroxyapatite (HA) and silica composite nano-powder. The studies were done for agricultural wastewater. The studies showed that the sintered ceramic filter at all studied temperatures reduced the TDS, TS, conductivity, and

arsenic (As) content. Shirgholami et al. (2018) made a hybrid nanocomposite with multi-wall carbon nanotubes and used it as an adsorbent to remove anionic acid red 37 from its solutions. The study's ideal circumstances were a pH of 4.2, 90 min of contact, and an initial concentration of 24 mg/L with 1.6 g of the hybrid adsorbent. At this condition, a 97% adsorption efficiency was achieved, and the optimum adsorption capacity of the suggested hybrid adsorbent was determined to be 45.6 mg/g. Pranoto and Fathoni (2018) used model reactions study to combine clay and andisol composition to test for the performance of a hybrid adsorbent for the separation of Cd by adsorption maximum adsorption conditions were 200 °C activation temperature, 60 min contact time, and a clay:Andisol adsorbent mix of 60:40. By constructing transparent glass–ceramics containing piezoelectric crystals, Singh et al. (2020) investigate piezocatalytic dye degradation. Glass–ceramics in various proportions of  $\text{LiNbO}_3$  crystallites were present in the produced ceramic nanocomposite, which contained  $30\text{SiO}_2\text{--}35\text{Li}_2\text{O--}35\text{Nb}_2\text{O}_5$  (in mol percent). The ceramic nanocomposite is optically transparent and has promising activity for decomposing cationic and neutral dyes. Their research showed that piezocatalysis may be used to clean water using transparent ferroelectric glass–ceramics.

### 2.2.3. Polymer nanocomposites for wastewater treatment

Materials made of polymer have found interest by researchers because they are considered promising materials for separation processes. The progress made so far in the area of fabrication and utilization of polymer has led to substantial advancements in wastewater treatment technologies. Researchers have successfully prepared and utilized numerous functional and advanced materials based on polymers to enhance the separation and purification processes with regards to contaminant elimination efficacy, the condition of operational, cost of implementation and operational process; and environmental friendliness (Geise et al., 2010). An upsurge in the utilization of different range of polymers for elimination of contaminants and particulate matters in wastewater treatment processes persists. Regardless of all advancements made in the applications of polymer in the field of separation and purification, selection of appropriate polymer from an extensive variation of polymers and polymer-based products is somewhat difficult (Khadakarami and Bagheri, 2021).

Furthermore, one of the primary reasons for the hybrid material's exceptionality is the exhibition of unique physicochemical properties that are impossible to achieve when separate constituents work independently. This is due to the large boundary layer thickness that exists between polymers and nano-fillers. As a result, polymeric materials are multiphase materials in which supporting fillers are injected into a copolymer material; the resulting material has complimentary qualities that are impossible to achieve with a single component (Agboola et al., 2021). Polymer nanocomposites combine the advantages of both nanofillers and polymers due to their remarkable structural capabilities and compatibility, as well as distinct physicochemical properties. However, the qualities of copolymer supports are typically a factor in their selection. Another aspect that should be carefully studied is the selection of biological organisms, which includes the balance of Biochemical functions (Sinsawat et al., 2003).

Based on the above advancements in polymeric nanocomposites materials, several researchers have used polymeric nanocomposites materials for the removal/separation of contaminants from wastewater. For example, polymeric nanocomposites materials have been used as adsorbents for wastewater treatment and removal of dye. Due to the requirement for substances with improved assimilation and elimination properties of several toxic pollutants, polymer nanocomposite research was presented. The materials used in these composites were classified principally by their source. They are further divided into three groups based on their structure-property (linear, branching, and crosslinked polymers) (Berber, 2020).

Clay minerals have the potential to improve the efficiency of polymeric compounds. Clay minerals and polymers together are being

considered as potential reinforcements for the manufacture of clay-polymer nanocomposites with improved qualities that will aid in the removal of contaminants. Exfoliated nanocomposites, intercalated nanocomposites, and phase-separated micro-composites are the three most common types of nanocomposite clay-polymers. Clay layers from microporous nanomaterials are equally distributed throughout the matrix material. They're made up of one-nanometer clay layers that are shattered within a polymer chain. The intercalated nanocomposites' silicate crystalline layers are implanted into the polymeric chains to create a submicron clay-polymer composite. This polymer nanocomposite has extraordinary properties, including self-extinguishing behavior (Amari et al., 2021). Rytwo (2012) proposed nanocomposites for wastewater treatment (due to a cost-effective clay minerals and organic molecules). This material provided a highly successful preparation for reducing TSS and COD at the same time. The nanocomposites used in the study were made from the clay mineral sepiolite and the cationic polymer poly-DADMAC. The researchers proposed employing nanocomposites made comprised of a bonding particle and a polymer as "coagflocculants" to effectively and quickly decrease TSS and turbidity in sewage with a significant number of organic pollutants. By lowering the potential of colloidal matter while also bridging across them and docking them to a heavier particle (the clay mineral), such materials take full advantage of the qualities of a coagulant and a flocculant, promoting precipitation. In a single treatment period, a very quick and effective pretreatment was achieved. Essomba et al. (2021) recently investigated the elimination of direct yellow 12 dye by employing clay/polymer nanocomposites in batch reactor and fixed column experiments based on several parameters. The results obtained depicted that there was an upsurge in the amount of dye removed with an upsurge in contact time.

Polymer nanocomposites that are based on carbon are used for environmental applications because they offer important physico-chemical characterizations. Recently, carbon-based polymer nanocomposites used for the treatment of wastewater are carbon nanofibers-polymer nanocomposites, carbon nanotubes-polymer nanocomposites, graphene-polymer nanocomposites and their derivatives such as fullerenes, nano-diamond together with other nano-sized carbon allotropes. Using a new technique combining mussel influenced chemistry and SET-LRP established for the synthesis of exceptionally sorbents (CNTs), Xie et al. (2015) synthesized poly(sodium-p-styrene sulfonate) enhanced macro carbon nanotubes. These CNT-based polymer nanocomposites were investigated for their adsorption potential in the separation of a cationic dye (methylene blue) from a liquid. Methylene blue has an optimal adsorption capacity of 160 mg/g. This demonstrates that the composite's functional CNTs have excellent methylene blue adsorptive properties. To achieve carbon nanotubes/poly (sodium 4-styrene sulfonate), Zhang and Xu (2014) enhanced carbon nanotubes enfolded with poly (sodium 4-styrene sulfonate) (sodium 4-styrenesulfonate). The findings suggested that the modified hybrid material might accept -electrons from the conjugated system of CNTs with the help of  $\pi$ - $\pi$  electron-donor-acceptor interactions and  $\text{SO}_3$  groups. As a result, CNTs in the fusion absorbed methylene blue via  $\pi$ - $\pi$  interactions and aided electrostatic attraction between poly (sodium 4-styrene sulfonate)  $\text{SO}_3$  groups and dimethylamino groups of methylene blue.

Hosseinzadeh et al. (2018) investigated the possibility of using value-added macro carbon nanotubes as an efficient adsorbent for the removal of cationic dyes in a variety of applications. The magnetic carbon nanotube composites with magnetite nanoparticles were made via surface reversible addition-fragmentation transition of chain co-polymerization of acrylic acid and N-isopropyl acrylamide. The study showed that the composite adsorbent exhibited extraordinary adsorption capacities. The composite was reusable as it offers easy recovery; thus, resulting to a good choice of adsorbent for the treatment of wastewater.

Polymeric nanocomposite membranes are a new type of membrane made from natural and artificial copolymer materials at the nanoscale.

When compared to traditional membranes, they are thought to have improved performance (Kango et al., 2013). Inorganic materials are made of ceramics, glass and metals while organic substances are made of polymers or hybrid composite substances (Ulbricht, 2006). Of these two types of materials, polymeric membranes are of greater importance in industrial usage. The main reason for selecting polymeric membranes embedded with nanomaterials for different environmental applications is based on their high selectivity, being able to manipulate membrane structures and characteristics to suit an application, easiness in fabrication; management of the pore generation and the low-cost effect of the polymer (Hilal et al., 2015). Therefore, innovative membranes advancement that possess tremendous penetrability, outstanding retention, selective transfer of chemical species, and exceptional anti-contamination property is vital for the neutralization of water (Yin and Deng, 2015). For these reasons, several authors have fabricated polymeric nanocomposites membranes for the treatment of wastewater.

Shao et al. (2017) assembled few-layered graphene oxide onto the surfaces of polyamide thin film composite membrane via a spin-coating method in order to address the challenge of improving chlorine resistance of polyamide (PA) reverse osmosis membranes. Their study observed that the pH values have great impacts on the performance of the membrane which also includes maximizing water flux at a pH value of 6 to 7. All the modified membranes demonstrated a good suppression of membrane degradation in salt rejection exposed to chlorine, and the extent of resistance to chlorine was improved with the upsurge of the number of graphene oxide stratums. Kusworo et al. (2018) fabricated nanohybrid PES/nano-ZnO membranes through non solvent-induced phase separation methods followed by surface modifications using UV irradiation and thermal annealing treatment to evaluate membrane performance. Filtration tests exhibited that the flux increased up to 18% and rejection of TDS improved up to 15% with less foulant deposition on the membrane surface. Zaman et al. (2018) investigated membrane performance in diluted and concentrated salt solutions using a synthetic polyimide (PI)/graphene oxide (GO) hybrid polymer produced at various GO/PI concentrations. The results showed that the hybrid polymer has nanofiltration capabilities, with extraordinary water permeability and outstanding salt rejection (99%) in diluted conditions, regardless of the filtration pressure used in the experiment. With the increase in GO content, there was an increase in water and permeate permeability. By exploiting the UV light (3–5%) present in the solar radiation, Zioui et al. (2020) demonstrated that  $\text{TiO}_2$  nanoparticles immobilized on an enhanced membrane can be an effective mechanism for the breakdown of oil in wastewater in a solar photoreactor. The photocatalytic efficacy of the nanocomposite membranes was demonstrated by the breakdown of greasy wastewater: after seven hours of solar irradiation, colourless water was obtained.

### 2.3. Photo-catalysis for the treatment of wastewater

Photocatalysis process has its place in the cutting-edge oxidation technology for the elimination of persistent organic compounds and microorganisms from wastewater. This technique has a lot of promise; it's a low-cost, ecologically responsible, and long-term management system that complements the water/wastewater industry's "zero" garbage system (Bodzek and Rajca 2012). As far back as the 1970s, there has been a lot of research that has gone into the process of photo-catalyst action on water environments to be able to rid bodies of water of pollutants that plague the waters of the planet. Modern research has come a long way as this technique has received much more attention than in previous years, because of the growing demand for better and more efficient water purification techniques (Li, 2021). The process requires that light energy be converted into chemical energy, required to breakdown organic compounds in the water pollutants, in order to create a safer environment for organisms to thrive without the threat of harm by the toxic waters (Sakar, 2019).

Li (2021) identifies the different structures that constitute the overall



material molecule of photo-catalysts, which include: high energy conduction band that forms part of the core of the material (photo-catalyst), low energy valence band that plays a huge role when it comes to energy capture and electron synthesis, and band gap between them. The action of photocatalysts breaks down the organic content in pollutants, according to Li (2021). When the material receives a certain amount of sunlight that trumps the energy of the band gap, then the electrons that are present in the low energy valence band will go into a process of transitioning into holes. The combination of these holes and the available electrons will go into a process with water material molecules and available amount of oxygen on the material's surface. Further chemical processes will take place, allowing for the breakdown of organic materials present in the contaminants that afflict water bodies, and thus the eradication of the pollutants and the deleterious effects they have on animals and humans alike. Photo-catalyst materials that are very prominent include,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{ZnS}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{WO}_3$ , and  $\text{Bi}_2\text{M}_2\text{O}_6$ .

The primary technological challenges that prevent its complete commercialization remain on the post-recovery of the catalyst particles at the conclusion of water treatment, which must be overcome by a small number of systems (Bodzek and Rajca 2012). This shows there is still more research to be done with the wealth of literature reporting the utilization of photocatalysis for the treatment of wastewater. With experiments that are usually done at bench-scale, studies have the tendency to over-represent the prospects and under-represent the restrictions confirmed by the technology when used in the field. An overemphasis on the design of material and systematic assessments has resulted in some hubris in the academic literature with regards to the realism of photocatalysis, perpetuating the gap between academic research and industrial application. From many restrictions identified, low photo-conversion efficiency stands to be the main challenge (Loep et al. 2018). However, stimulated by progress in materials science and nanotechnology, progressively more portion of research has tried to find means to developing improved catalyst materials.

The rutile (bandgap 3.0 eV) and anatase (bandgap 3.2 eV) phases of large bandgap semiconductors like  $\text{TiO}_2$  are usually studied, and  $\text{TiO}_2$  sensitivity to UV light has not only led to photocatalysis research (Ibhadon et al., 2008; Ibhadon and Fitzpatrick., 2013); additionally, investigation of  $\text{TiO}_2$  super-hydrophilicity and its use in environmental remediation has been done extensively. Charge reaction happens after bandgap activation of  $\text{TiO}_2$ , followed by sifting of electrons and holes by surface adsorbed entities (Ibhadon and Fitzpatrick., 2013). The usual mechanism of toxic organic compound degradation through

nano-photocatalysts is shown in Fig. 3 (Yaqoob et al., 2020). It has been reported that  $\text{TiO}_2$  photocatalysts have the capacity to efficiently decompose organic contaminants in water as a result of a strong oxidizing ability generated when the  $\text{TiO}_2$  is irradiated by a suitable band gap illumination (Ibhadon et al., 2008). More consideration is being given to heterogeneous solution-phase catalysis for the purpose of developing an environment-friendly technology for the purification of polluted water devoid of electricity or other energy consuming sources (Ibhadon and Fitzpatrick., 2013).

Umar et al. (2015) used the sol-gel method to synthesize nano-crystalline  $\text{ZnO}$  materials complexed with various amounts of molybdenum (Mo) and manganese (Mn) in the range of 0.2–1.0 percent and investigated their performance for catalytic efficiency for the color removal of two different chromophoric dyes in the presence of atmospheric oxygen using a 500 W halogen linear lamp in the presence of atmospheric oxygen as a function of Irradiation time. When they compared the catalytic performance of  $\text{ZnO}$  with additive amounts of 0.60% Mo and 0.80% Mn to the other additive amounts for the color removal of azo dye and anthraquinone dye, they found that  $\text{ZnO}$  with additive amounts of 0.60% Mo and 0.80% Mn had the highest catalytic performance. In the instance of azo dye, 84% dye removal was achieved in 390 min, however in the case of anthraquinone dye, 66% dye removal was achieved in 390 min using 0.60% Mo. Liu et al. (2016) used a simple ultrasonic dispersion process to make mpg- $\text{C}_3\text{N}_4$ /anatase  $\text{TiO}_2$  hybrids with activated {001} facets. Under UV and visible light irradiation, photocatalytic tests revealed that the mpg- $\text{C}_3\text{N}_4$ / $\text{TiO}_2$  composites had much higher photocatalytic activity than pristine  $\text{TiO}_2$  and mpg- $\text{C}_3\text{N}_4$  for the breakdown of methylene blue (MB). Raliya et al. (2017) investigated the breakdown of an azo dye, methyl orange, in a simulated industrial effluent using a variety of oxide nanomaterials (Titanium dioxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), and graphene oxide (GO) as photocatalysts under the effect of visible light. These oxide nanoparticles were used to remove the dye by adsorptive and photocatalytic means. In addition, the photocatalytic performance of nanocomposites of the three components (GO- $\text{TiO}_2$ - $\text{ZnO}$ ) was investigated. For dye degradation, the  $\text{TiO}_2$ / $\text{ZnO}$ /GO combination was the most efficient. The degradation rate increased as the proportion of  $\text{ZnO}$  to GO in the nanocomposite increased. These studies have shown that combined materials have great potential than they do when used alone due to electron/hole pair recombination. Ibrahim et al. (2021) also prepared mesoporous silica supported  $\text{ZnO}$  photocatalyst (MS/ $\text{ZnO}$ ) using the direct and indirect methods of impregnation in solvent media and grinding method in solvent free media. These methods depict that the dissemination of  $\text{ZnO}$

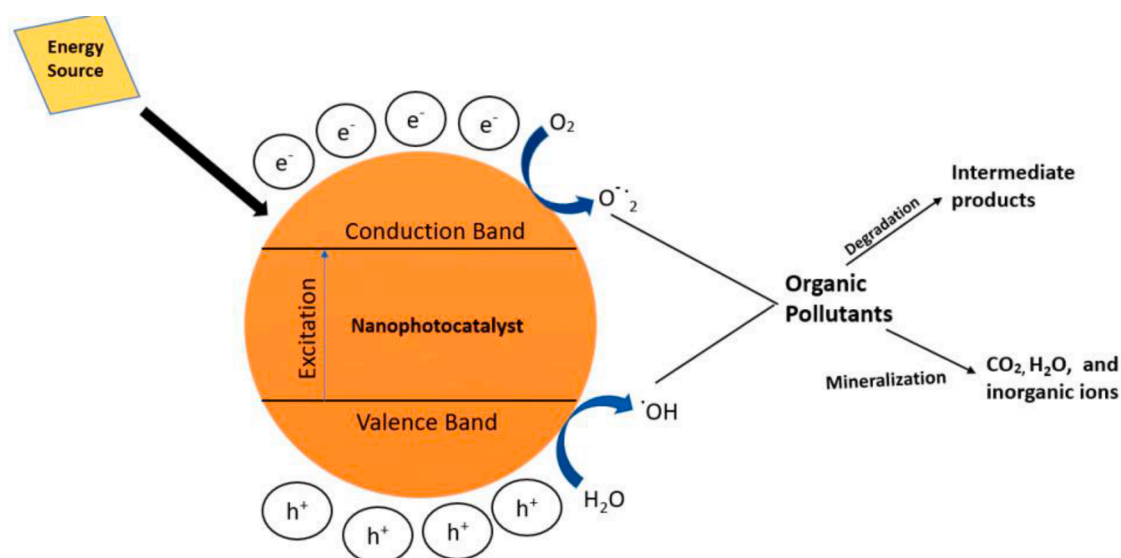


Fig. 3. Usual mechanism of toxic organic compound degradation through, nano-photocatalysts (Yaqoob et al., 2020).

nanoparticle over mesoporous substrates is in connection with the creation of a secondary phase of ZnO crystalline on the mesoporous materials. From their study, it was observed that the synthesized photocatalysts made using the method of grinding attained the best efficiency when compared with the synthesized photocatalysts made using the method of impregnation. Conclusively, their study confirmed the merits and flexibility of the grinding method in preparing MS/ZnO photocatalyst for an efficient removal of solvent. Hence, Nano-catalysts composites are effective for the elimination of contaminants from wastewater as a result of their distinctive physical and chemical characteristics.

Photocatalysis process for the treatment of wastewater has been enhanced using green technology due to the toxic chemical and stabilizing agents employed for the synthesis of photocatalysts using both physical and chemical methods; and they are not cost effective. Literature has reports that stated that biological synthesis has proven to be nontoxic or less toxic against cell lines (Vimala et al., 2014; Madhumitha et al., 2016). Prasad et al. (2019) synthesized biogenic zinc oxide nanoparticles (ZnO NPs) through a green synthetic strategy, by employing *Abelmoschus esculentus* (okra) mucilage for selective degradation of cationic dye pollutants. It was observed that the ZnO NPs have capability to selectively photodegrade the target cationic dyes, where 125 mg of the catalyst removed 100% of the methylene blue solution (32 mg/L) within 60 min. Vasantharaj et al. (2021) synthesized ZnO NPs by employing *R. tuberosa*, a common weed that belongs to the Acanthaceae family. This weed is generally known as Minnie root and snapdragon root in India. The synthesized ZnO NPs were further subjected to antibacterial activity test, photocatalytic degradation of dyes and the viability to utilizing it as a coating material on textile fabrics for the prevention of bacterial contamination. ZnO NPs exhibited higher antibacterial activity against Gram negative bacteria, especially *Escherichia coli*. Furthermore, ZnO nanoparticles respectively degraded 94% and 92% of methylene blue (MB) and malachite green (MG). Rambabu et al. (2021) studied a scalable and effective fabrication technique for DP-ZnO—NPs by employing date pulp waste (DPW) and the prospective utilization of the DP-ZnO—NPs for the treatment of synthetic wastewater. The photocatalytic degradation of hazardous MB and eosin yellow dyes by employing DP-ZnO—NPs, exhibited swift decomposition rate with an efficiency of 90% degradation. Furthermore, DP-ZnO—NPs proved a significant antibacterial effects on several pathogenic bacteria with regards to the zone-of-inhibition measured via disk-diffusion technique. Karthik et al. (2022) recently studied the biosynthesis of ZnO and Cu-doped ZnO NPs in the presence of dopant concentration varied from 1 to 9 wt% and *Synadium Grantii* leaf extract for the photocatalytic removal three different organic pollutants such as Methylene blue (MB), Indigo Carmine (IC), and Rhodamine B (RhB). The green synthesized ZnO NPs depicted improved photocatalytic performance, demonstrating that bio-synthesis can be an exceptional method of developing versatile and environmental products.

### 3. The propensity of the discussed methods and the suggestions to improve their efficiency towards the removal of contaminants

The pollutants that mostly contributes to numerous cases of water pollution are raw wastewater and ineffectively treated wastewater effluents from industries and domestic homes. Hence, the preposition of advanced separation techniques. Though these techniques are advanced and effective; they however, have some limitations that can be overcome. For example, phytoremediation is restricted to the depth occupied by the roots. In addition, slow growth and low biomass that need a continuing commitment are also its short comings. Again, adaptation to a variety of environmental conditions such as soils that lacks good nutrients (Gerhardt et al., 2017), is also phytoremediation short coming. In order to overcome these short comings, the following approaches can be developed via adjusting and refining certain traits of plants used for phytoremediation to guarantee their capability for effective

phytoremediation.

- Plants could be selected for their root depth; for instance, poplars could be employed for remediation of soil to a depth of 5 to 10 feet. The effect of the roots could elongate deeper into the soil; however, this depends on the conveyance of root exudates to lower soil depths (Sharma and Pathak, 2014).
- Plant hybridization or the formation of transgenic plants are utilized to either advance growth rate and biomass of hyper-accumulator or to bring together hyper-accumulation traits in order to fast growth, high biomass plants (Yan et al., 2020; DalCorso et al., 2019).

The growing interest with regards to the development of efficient wastewater treatment technologies using nanocomposite materials is due to its unique properties. Nano materials possess a high surface area, small size, and has the ability of good adsorption of potent toxins making them a good candidate for the elimination of pollutants from water (Umar et al., 2022). However, the use of nanocomposite materials has its own limitations. One of nanocomposite material limitation is the tendency of the nanomaterial to accumulate; hence, the cohesion of these particles in solution, which will reduce the efficacy of adsorption and separation (Fan et al., 2012; Mousavi et al., 2020). Furthermore, the presence of some materials in the environment that have the capacity to easily adsorbed nanoparticles (like phosphate) will possess an adverse influence on the adsorption of heavy metals owing to the competition in the occupation of active adsorbent sites (Fan et al., 2012; Mousavi et al., 2020; Amari et al., 2021). In order to overcome these limitations, for example, the possibility of using selective reactivity of iron nanoparticles with different functional groups should be explored. Furthermore, in order to enhance the stability of nanocomposite materials, the surface of the nanocomposite materials should be modified to make selective adsorption on these particles (Hosseini and Salari, 2021). Different types of stabilizers, polymers and electrostatic surfactants have been proposed to improve the structure and stability of iron nanoparticles (Mousavi et al., 2020; Amari et al., 2021).

Literature has reported several studies on the use of photocatalysis for degradation of organic pollutants of contaminants of emerging concern (CECs). Nevertheless, degradation of organic pollutants could lead to the formation of by-products, which could be more toxic than the parental contaminants. Hence, the toxicity of wastewater treated by photocatalysis has now become an interesting issue (Rueda-Marquez et al., 2020). Hence, a toxicity assessment is of vital importance when photocatalysis is been used to treat wastewater, especially if the whole mineralization of contaminants is not an objective (Rueda-Marquez et al., 2020). In addition, photocatalysis also has some drawbacks that have restricted the application of this method on a large scale as a result of the technical challenges that ensue when photocatalyst should be separated from water for further reuse. To overcome the limitations of reuse, strategies such as the exposure to ultraviolet (UV) in aqueous media or air (Wang et al., 2015); the oxidation of by-products bounded to the surface by H<sub>2</sub>O<sub>2</sub>/UV (Miranda-García et al., 2014) and alkaline treatment (NaOH and NH<sub>4</sub>OH) (Miranda-García et al., 2014) should be explored. Therefore, photocatalysis can be considered a promising method of treating wastewater should these strategies be taken into consideration for the degradation of organic pollutants in raw wastewaters and/or wastewater detoxification, especially from the view of practical application.

### 4. Conclusions

Clean water is an unavoidable need in human life; hence, extensive development has been made to upsurge access to clean water and sanitation. The main sources of clean water are surface and underground water. Nonetheless, the increasing growth in population, expansion and industrial activities made several sources of water polluted; hence the demand for clean water, food and agricultural products together with

other natural resources. In addition, the change in climate and too much utilization and depletion of the supply of water, water pollution caused by human beings have resulted in concern of globally making clean water available. Conventional methods have been in existence for the treatment of wastewater; however, they possess a lots of short comings which was argued for proposing advanced methods of treating wastewater in order to safeguards ecosystems and public health. For these reasons, advanced separation processes such as the ones discussed in this review will certainly play abundant roles in solving issues relating to water shortage and water quality in sectors that have relevance in the treatment of wastewater. Hence, the transformation in the development of advanced separation processes, such as phytoremediation; nanocomposites materials; photo-catalysis are among the most inspiring and innovative separation processes that offer great prospects for wastewater treatment. Granted that these advanced treatment processes play important role in wastewater remediation, they however, possess their short comings. Hence, the propensity of the advanced methods of treating wastewater was reviewed and the suggestions to improve their efficiency towards the removal of contaminants were also discussed. Therefore, it can be suggested that these methods can be used for the degradation of organic pollutants in raw wastewaters and/or wastewater detoxification, especially from the view of practical application; should the strategies of combating the few limitations be taken into consideration.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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