

Wastewater Treatment Technologies



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Abstract Access to sustainable drinking water remains a serious challenge both in rural and urban areas due to population explosion, pollution of various water systems through natural and anthropogenic activities such as industrial activities, agricultural practices, urbanisation among others. Although, water and wastewater treatment was early discovered in history, however, took several years before people understood that adequate judgement for quality water is not by human sense. The earliest water treatment includes filtration and removal of pathogens carriers of typhoid, cholera and dysentery among other diseases. Different treatment techniques such as membranes filtration technologies, thermal technologies, biological aerated filter technologies, advanced oxidation technologies are available for the mitigation of organic, inorganic, heavy metals, microorganism, suspended solids and emerging persistent pollutants from water. This chapter review different technological of advanced oxidation processes wastewater technologies especially their efficiencies, cost implications, durability among others. Of all the advanced oxidation processes, photoelectrocatalysis has been found more suitable for the treatment of wastewater than conventional methods.

Keywords Physico-chemical parameters · Classification · Conventional methods · Advanced oxidation processes · Photoelectrocatalysis · Photo-fenton · Photocatalysis

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1 Introduction

Despite the importance of water to human life especially for drinking, household chores, agricultural and industrial purposes, the quality of water has been compromised through the release of different pollutants into water system [127]. Some of these pollutants are release either through domestic waste or industrial waste or both. Some of these domestic and industrial wastes are highly toxic to living beings and our ecosystem. They have caused our water systems to experience different colours, high turbidity, bad odours, suspended solid matters, heavy metals, inorganic and organic and micro-organisms [125] which led to water pollution.

In 2019, United Nations reported that water pollution has cause loss of many lives more than any other form of violence dues to several diseases such as water borne diseases (i.e. Diarrhea), type B and type C hepatitis virus and human Immune deficiency virus among others. One of the most significant disease's burdens among many groups of lives is waterborne diseases, especially in developing countries. In Nigeria, the ratio of those that suffered from diarrhea is 1:25 among children below age five [126]. Thus, poor management of solid and liquid waste has resulted to spread of many diseases [101].

Also, in 2007 World Health Organization estimated that yearly patients between 8 to 16 million type B hepatitis virus, 2.3 to 4.7 million type C hepatitis virus and 80,000 to 160,000 HIV (human immune deficiency virus) always exist which all result from poor waste management systems [117]. WHO further estimated that annual death of approximately 829,000 which translate to 54–65% caused by diarrhea in low- and middle-income countries are due to consumption of unconventional water [90]. It was discovered that around 13% of acute infections which translated to about 370,000 deaths in 2016 was linked to inadequate access to safe drinking water [90]. The use of sewage wastewater in agriculture for irrigation may also result in disease transmission [126]. In 2016, malaria cases reported were 217 million with over 451, 000 deaths equivalent to 90% in sub-Saharan Africa alone [128]. World Health Organization [126] reported that the population of the world is expected to grow by 33% (7.2 to 9.6 billion) between 2014 and 2050 with increase in urban population by 61% (3.9–6.3 billion) in Africa and Asia. Climate variability and climate change are also pilling pressure on water supplies due to drought and flooding [27]. Due to the problem of water pollution and water shortage, there is a need to retreat, reuse and recycle wastewater obtained via different wastewater treatments.

2 Physico-Chemical Assessment of Wastewater

In this section, physico-chemical parameters used to evaluate the quality of water are discussed. This will help the reader to understand some important parameters to known if water was polluted. Some of the physical and chemical parameters used to determine the quality of wastewater are explained as follows.

2.1 Physical Characteristics

(I) Colour

Colour is one of the essential water quality parameters that indicates the period of time of exposure. Generally, fresh wastewater always appeared grey while after a long period, the wastewater is always black due to the decomposition of bacterial via anaerobic conditions [17]. It has been found that blacken colouration of wastewater, normally occurs since there is generation of various sulphides such as ferrous sulphide or hydrogen sulphide via reaction of with divalent metals such as iron under anaerobic conditions [138].

(II) Odour

Odour determination is becoming more important, as the public is becoming more concerned. Odour is usually produced via gases during decomposition process of the organic matter [132]. There is distinctive but not offensive for fresh wastewater which is less objectionable compare with septic wastewater odour dues to several odorous compounds release during biological decomposition through anaerobic conditions [32].

The sources of different unpleasant odours generated by industrial wastewater are identified in the Table 1.

(III) Temperature

Wastewater temperature is always greater than the temperature of fresh water dues to the activities of aerobic bacteria which lower the presence of oxygen thereby increase the water temperature [109]. Temperature of wastewater is very important since there are some treatment schemes for wastewater such as biological processes which depends on temperature [15]. Though there are some factors causing variation in temperature such as seasons, geographic location among others, it has been observed that wastewater temperature is always higher than the fresh water [136]. In the Equatorial regions, its temperature varies from 13 to 24 °C while in Polar region, temperature of wastewater varies from 7 to 18 °C [82].

Table 1 Odour sources in selected industries wastewaters

Industries	Sources of odours
Cement work	Dibutyl sulphide Amines, Mercaptans, SO ₂ , H ₂ S
Food	Fermentation produces, sulphides, amines, mercaptans
Rubber	Mercaptans, sulphides
Paper pulp	Sulphur dioxide, hydrogen sulphide
Pharmaceutical	Fermentation produces
Textile	Phenolic compounds
Organics compost	Sulphur, ammonia compounds

(IV) Total Solids

Wastewater total solid comprises soluble compounds and suspended or insoluble solids dissolved in water. The content of the insoluble solid is the dried residue removed through filtration process [116]. The volatile solids burned off as a result of ignition of residue. Several organic matters are volatile solids in nature, though some organic matter cannot be ignited while at high temperature, some inorganic salts break down [58]. The following are the organic matters; fat, carbohydrates and proteins which constituted around 40–65% of the solids in the average suspended wastewater. Settled solids are those solids that can be removed by sedimentation [105]. 60% of the suspended solid in municipal wastewater are settled solid which are been expressed as Millilitres per litre [9].

2.2 Chemical Characteristics

(I) Phosphorus and Nitrogen

These elements can be determined through the measurement of phosphorus concentration and nitrogen concentration present in the water respectively [81]. One of life essential nutrients is Phosphorus, which can be derived from fertilizers, animal waste and phosphate detergents. When the concentration of phosphorus is high, orthophosphate will affect the quality of the water by increasing algae growth and further lower the volume of oxygen needed for the aquatic animals and eventually led to their death whereby pollute the water [129]. Orthophosphate will also cause odours and tastes in the water.

Nitrogen is another essential nutrient that is very important to plants in ecosystem [134]. The major sources of nitrogen include; animal waste and fertilizer while the other sources are; atmospheric deposition and septic systems. When application of nitrogen such as through fertilizers is higher than the amount that can be ingested by the plants or released into the atmosphere via denitrification, then the nitrogen concentration will increase [67]. When nitrate is in excess, it is not toxic to aquatic life though increase in nitrogen concentration may lead to overgrowth in algae which reduce the content of oxygen of the water thereby kills or damage aquatic species such as fish and pollute the water [74].

(II) Chemical Oxygen Demand

The chemical oxygen demand (COD) is an essential parameter used to determine the water quality through the measurement of the amount of oxygen to oxidize particulate and soluble organic matter [118]. Similar to biological oxygen demand (BOD), COD provides an index to assess the effect of wastewater discharged. When the COD level is high, the level of dissolved oxygen reduces and can lead to anaerobic conditions and deteriorate the aquatic life [68]. It can be measured using COD analyzers and it has a shorter length of testing time compared to Biological Oxygen Demand.

(III) Dissolved Oxygen

This is the determination of the amount of oxygen present in a sample of water or wastewater at the time of collection and it is very important for respiration of aquatic life such as fish and other organisms [68]. This dissolved oxygen get access into the water system through by- product derived from photosynthesis of plants and from atmosphere diffusion. The dissolved oxygen concentration in the epilimnion of the waters bodies continue to equilibrate with concentration of atmospheric oxygen as it is 100% dissolved oxygen saturated [37]. The oxygen diffusion rate to the atmosphere is lower than the photosynthesis rate when the algae growth is in excess and over saturates the water with dissolved oxygen. When the dissolved oxygen is low there is no mechanism to replace the consumed oxygen via decomposition and respiration which will lead to death of aquatic animals [43].

(IV) Biological Oxygen Demand

This is referred to as the estimation of organic matter amount that is unstable in the water. It estimates the required amount of oxygen needed by the microorganism to degrade the available organic matter into simplest forms such as carbon (IV) oxide, water and ammonia [5]. Though it helps to establish unstable organic matter characterization, it takes a much longer period of time compared to chemical oxygen demand.

(V) pH

The potential hydrogen (pH) is the measurement of the basicity or acidity of a water body [79]. The scale of pH is in logarithm form which commonly ranges from 14 to 0. When the pH value of a solution is 6, it is ten times more acidic than a solution with pH value of 7 [108]. The pH value of sachet water is 7. which is neutral, when the pH value of Water is said to be less than 7, it is considered to be acidic and when the pH value of water is said to be greater than 7, it is considered to be alkaline or basic [3].

(VI) Conductivity

Conductivity of water is an expression of its capacity to transfer electric current in an aqueous solution [43]. It is estimated in micro siemens per centimetre ($\mu\text{s/cm}$) or micromhos per centimetre ($\mu\text{mhos/cm}$). The conductivity of distilled water is said in the range of 0.5–3 $\mu\text{s/cm}$. This ability depends on the mobility, presence of ions, valence, their total concentration, relative concentrations and on the temperature of the liquid [43]. The following solutions are relatively good conductors such as salts, bases and inorganic acids among others.

(VII) Alkalinity

Alkalinity is a measurement of the total components present in the water that tend to neutralize acidity [43]. This is carried out by determining various levels of radicals. Such radicals are hydroxides, phosphates, bicarbonate and carbonates present in the water which is measured in terms of milligram per litre of calcium, carbonate (that

is ppm of CaCO_3). This also determined the ability of water to resist the change in pH. The organisms are being affected directly due to the change in the pH values caused by the presence of some pollutant toxicity in the water system [95].

3 Classification of Pollutants in Wastewater

There are two classes of pollutants to be discussed in this section; they are: Organic Pollutants and Inorganic Pollutants.

3.1 Organic Pollutants

(I) Dyes

Generally, dyes are organic compounds which been classified into cationic, anionic and nonionic dyes. These dyes are highly toxic and potentially carcinogenic which are related to various diseases in humans and animals [147]. Dyes are also related to environmental degradation such as recalcitrant in aerobic environments [8] whereby responsible for its bioaccumulation which further entered the water system [63]. There are some of these dyes that degraded partially in the presence of anoxic sediments like in the case of azo-type compounds which occurs during reduction and further release dangerous aromatic amines [63] and in some cases, the dyes undergo direct combination with intermediate substance to produced carcinogenic or mutagenic compounds [63]. The effects of recalcitrant and xenobiotic nature of the dyes end on impacting the functioning and structure of the ecosystem [53]. In long period exposures, some dyes with a longer half life of 2–13 years always bring profound unfolding such as to human health or to aquatic biota as it is with metal-complex dyes [94].

(II) Pesticide and Pesticides Residue

Pesticides are categories as herbicides, molluscicides, fungicides, rodenticides, nematocides insecticides and plant growth among others. Globally, it has been widely used to control the pests which cause various diseases and increase the yield of crops yield. However, according to several studies, pesticide has been proved to inflict adverse effects on human health and our environment [4].

These pesticides are designed and produced with the view to kill insect pests generally and not site-specific. The applications designed of these pesticides are expected to operate in contact or systemic approach with the target pest in order to kill and to avoid the non target living things. However, some of these target pests are simply species animals that have similar characteristics to other animals such as susceptibility to certain toxins. Therefore, a chemical that is toxic to an animal may also be toxic to other animals. It has been reported by some researchers that larger

dose of some pesticides can kill humans while the normal does require to kill some pests can further affect human health such as sex hormones disruption and lowering of reproductory system performance among others [104]. These pesticides can act as a xeno-hormones whereby mimicked the action of endogenous hormones, hence it has been proved and categorized as endocrine disruptors [10].

(III) Pharmaceutical Pollutants

Pharmaceuticals and their metabolites have been generating serious issues in the ecosystem especially in the aquatic environment and have become a major concern to researchers in the area of environment chemistry [69]. Till date, majority of articles published to address the presence of drugs in the effluent of the sewage. Exposures to these drugs are associated with some risks which are significant to the natural environment [98]. In countries where reuse of water is practice, public's concern is more focused on exposure to human health [20].

(IV) Volatile Organic Carbons

The following are the examples of volatile organic compounds: toluene, benzene, xylenes, trichloroethylene, trichloroethane and dichloromethane are common pollutants present in soil [143]. In commercialized areas, one of these sources of these pollutants is leakage of underground storage tanks. Improper release of solvents and landfills are also significant sources of volatile organic carbon in the soil [6]. Some of these organic substances are classified as priority pollutants namely; polycyclic aromatic, polychlorinated biphenyls, formaldehyde, acetaldehyde, 1, 2-dichloroethane, dichloromethane 1, 3-butadiene and hexachlorobenzene among others [46].

Several industrial wastewaters generated from industries contain heavy metals. For instance, electroplating industries produce qualities of heavy metals in its wastewater. The following are these heavy metals released during their operations and application; zinc, chromium, copper, platinum, cadmium, lead, nickel, vanadium, silver and titanium among others [131]. This application includes; milling, electroplating, anodizing-cleaning conversion-coating and etching [131]. Another source of these heavy metals is the wastes of printed circuit board industry. Nickel, Tin and Lead solder plates are commonly used resistant over plates [100], the products of inorganic pigment industry which is pigments contain cadmium sulphide and chromium molecules [135]. All these generated large quantities of wastewaters with residues and hazardous sludges [122].

3.2 Inorganic Pollutants

(I) Anionic Pollutants

Fluoride, chromium and arsenic are the most commonly found anionic pollutants in wastewater. Fluoride is one of the species present in aqueous media. In Arsenic

species, there are Arsenate (As(III)) and Arsenate (As(V)) which were more toxic than organic matters [103]. Arsenate is said to be predominately much on the surface of water while Arsenite is dominant in ground water system [61]. Arsenite is in negative ionic form (H_2AsO_3^-) under the condition of pH while at pH value of 2.2 As(V) is present as H_3AsO_4 , at pH value of 2.2–6.98 As(V) is present as H_2AsO_4^- , at pH value of 6.98–11.5 As(V) is present as HAsO_4^{2-} and at pH 11.5 As(V) is present as AsO_4^{3-} [51]. Chromium is of two different forms in the environment; Cr(III) and Cr(VI) with the latter considered more toxic than the former [31]. The predominant species of Cr(VI) is HCrO_4^- at low pH but when the pH value increases, there is a shift to CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$. However, in anionic pollutants, the surface charged is negative as the solution pH value increases which weakening the forces of electrostatic attraction between negatively charged anionic pollutants and the adsorbent, thus reduced the efficiency of the adsorbent [92]. Moreover, when there is an increase in pH value, the anionic pollutants compete with OH^- especially at level of higher pH.

(II) Cationic Pollutants

Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Hg(II) and Zn(II) are the generally known cationic pollutants present in wastewater [56]. Any cation with atomic mass greater than 23 is referred to as heavy metal [120]. Several of these heavy metals such as Mercury, Lead, Chromium and Cadmium among others are dangerous to human health and ecosystem. Lead and Zinc can lead to corrosion and are harmful to humans. Heavy metal cannot deteriorate unlike organic pollutants, thus it is difficult to treat via remediation.

There is three mechanisms of adsorption which determined metal ion adsorption. They are ion exchange, electrostatic and complex formation [45]. Graphene oxide sheets have abundant oxygen groups which can be used to bind ions via ion exchange, electrostatic and coordinate approaches. For those cationic pollutants, when the pH value is high it easy adsorption process dues to the competition of $-\text{O}-$ and $-\text{COO}-$ on the sites between metal ions and proton in acidic conditions which lower adsorption capacity. When there is increased in the solution pH value, $-\text{O}-$ and $-\text{COO}-$ will be converted to $-\text{OH}$ or $-\text{O}-\text{H}$ and generate electrostatic interactions that is favourable to adsorb cationic species. Different categories of constituents wastewater are illustrated in Fig. 1.

4 Water Treatment Technologies: Operational Principles and Limitations

In this section, our consideration will be on two types of water treatment technologies which are; conventional water treatment and advanced water treatment. The conventional water treatment is as follows: physical process which is always referred to as primary or preliminary treatment method, chemical and biological process which are

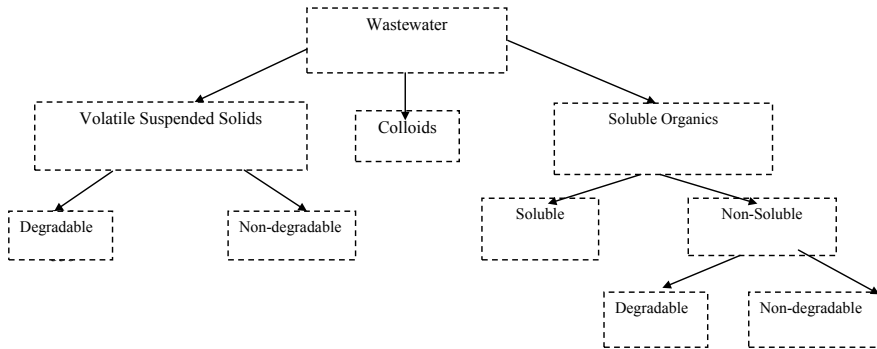


Fig. 1 Organic constituents partition of wastewater

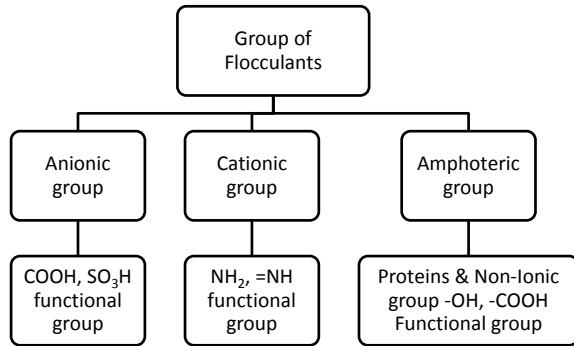
also referred to as secondary treatment methods while the advanced water treatment is refers to as advanced oxidation process called tertiary treatment method. This section gives the reader best understanding of the recent trend on different water treatment technologies. Let's consider these different types of water treatment technologies.

4.1 Conventional Water Treatment Methods

4.1.1 Coagulation and Flocculation

Part of the constituents of most water systems is suspended solids. The purpose of coagulation and flocculation is to separate the suspended solids from the water bodies. Before separation can occur, coagulation reaction must take place by destabilization of colloids through neutralizing their intermolecular force when coagulants are added to the water bodies. There are some factors that are expected to be considered in choosing a coagulant such as particle size, shape, charge, composition and density among others [88]. When particles carry like charges, repulsion occurs and remains suspended in the water. Therefore, the application of the coagulant brings the suspended together to form aggregates in size and settle. The following are several coagulants used for coagulation; iron (II) sulphate, alum and iron (III) Chloride among others [88]. Since the primary aim of coagulation are based on suspended particles and hydrophobic colloids, researchers have tried to improve coagulation for the removal of both insoluble and soluble substances through the grafting of sodium xanthogenate group and it is referred to as amphoteric polyelectrolyte [21]. The pH is one of the main factors to considered through coagulation since when the water pH value is acidic, the negative charges of colloidal substances will be coagulated while there will be removal of cationic ions. When water pH is high, there is a decrease in the turbidity removal which increases the cationic ion's removal. Though coagulation has been helpful in the area of water treatment especially in developing and

Fig. 2 Groups of Flocculants



under-developing countries, this method is still associated with shortcomings such as formation of sludge which becomes secondary pollutant, high concentration of aluminium residue from the coagulants (i.e. aluminium based) present in the treated water. The presence of aluminium residue is associated with some challenges such as; loss in hydraulic capacity, increased turbidity, reduced disinfection efficiency and potential adverse effects like alzheimer [137]. Though, it can be controlled through adjustment of the pH value to acidic regions. This approach is not generally accepted since it required increase in pH value for the control of corrosion in post treatment in water distribution network which makes the process costly [14].

Flocculation is when polymer act as a bridge between the flocculants and the particles bind into large clumps or agglomerates. Immediately the flocculated suspended particles are formed into larger particles, separation can take place through floatation, straining, or filtration. There are many different types of flocculants namely; polyacrylamide and polyferric sulphate. However, flocculation cannot successfully remove heavy metals directly from wastewater via flocculants. Therefore, researchers have developed macromolecule heavy metals flocculants such as mercaptoacetyl chitosan among others and have been proved to remove heavy metals and also remove turbidity in wastewater (Fig. 2). Apart from heavy metals, differences in the particle's properties are other challenges that make it impossible to use universal flocculant. There are different groups of flocculant; Anionic group contain $-\text{COOH}$, $-\text{SO}_3\text{H}$ functional group, Cationic groups contain $-\text{NH}_2$, $=\text{NH}$ functional group, Amphoteric group (both anionic and cationic groups) contain proteins and Nonionic group contain $-\text{OH}$ and $-\text{COOH}$ functional groups as it is shown in Fig. 2.

Generally, coagulation-flocculation is not enough to treat wastewater completely especially with heavy metals [65]. Therefore, there is a need for other treatment techniques to be applied after coagulation and flocculation in order to achieve complete removal.

4.1.2 Chemical Precipitation

One of the most commonly used wastewater treatment techniques is chemical precipitation which its operation is simple with low cost. This involves the removal of suspended solids, inorganics such as metal, greases, fats, oils and organic substances which will later be separated through filtration or sedimentation. This method is usually used for mitigation of pollutants from the wastewater which contains heavy metals of high concentration but always have low efficiency when there is low concentration [35]. This can result in production of sludge of metallic that need further disposal, making the process of recovery of the metal difficult [60]. There are two types of chemical precipitation namely; Hydroxide and sulphide precipitation.

(I) Hydroxide Precipitation

This is one of the most commonly used chemical precipitation since it is very relative simple, ease pH control and with low cost [36]. The solubility of hydroxides of metals is controlled within the pH values of 8 to 11. Several hydroxides have been applied to precipitate metals from wastewater, since hydroxide precipitation has a low cost and ease of handling, one of the preferred choices of base is lime used in the settings of industrial wastewater [55].

(II) Sulphide Precipitation

This is another form of chemical precipitation which is said to be an efficiency process in removal of toxic heavy metals. Sulphide precipitation is advantageous to hydroxide precipitation because the solubility of its metal sulphide precipitate is lower than the precipitate of hydroxide and its nature is not amphoteric. Therefore, the process of sulphide precipitation was able to achieve more degree of removal of metal ions for a wide range of pH values than hydroxide precipitation. The sludge of metal sulphide also exhibit better characteristics such as dewatering and thickening than the sludge of corresponding hydroxide metals [97]. However, the use of sulphide precipitation comes along with different shortcomings such as production of heavy metal ions and sulphide precipitants in acid conditions whereby sulphide precipitants resulted in evolution of toxic H_2S fumes. It is necessary that sulphide precipitation performed in alkaline or neutral ranges of pH values.

4.1.3 Ultra-Filtration

This is one of membrane filtration techniques used for separation, based on size exclusion mechanism. The separation membrane pore size is within the range of 1–5 μm [148] and falls between nano-filtration and micro-filtration. This method can be used to remove substances of high molecular weight namely; colloidal material, inorganic and organic polymeric molecules. The purpose of these membranes in this technique is to fractionate or separate the wastewater into more useful or less polluting streams but cannot degrade into simpler substances [12]. In view of the above, Ultra-filtration has been increasingly applied in treatment of wastewater. One

of the limitations of ultra-filtration is fouling of the membranes which significantly increase trans-membrane pressure and reduced the lifespan of the membrane [7]. There are other several factors that can lead to destruction of the chemical structure of membrane material and membrane fouling such as; concentration polarization, formation of filter cake layer and blockage of membrane pore. Natural organic matter (autochthonous biopolymers and humus) is considered the main culprit for membrane fouling [7].

4.1.4 Reverse Osmosis

The reverse osmosis process is one of the wastewater treatment techniques which involves the use of a pores semi-permeable (that is, cellophane-like) membrane to separate treated water from the wastewater. This technique is capable of removal of dissolved species in a wide range from water which gives more than 20% desalination capacity of the world [19]. There are two sides to this technique namely; treatment side and dilute side. On the treatment side, there is need for the use of pressure on the wastewater forcing the treated water into the dilute side then removed the impurities and washed into the rejected water. Reverse osmosis has been reported for its application in different industries wastewater treatment such as mining, petrochemical, food processing and textile industries [123]. The Membranes with smaller pores size was able to prevent pollutants with larger molecular particle sizes from entering the treated water. However, hazardous chemicals like herbicides, pesticides, insecticides with smaller molecules size than water were able to pass with the treated water [71]. Hence, there is need to incorporate carbon filter with the use of reverse osmosis [71]. There are several challenges associated with reverse osmosis such as been too slow in operation compared with other alternative water treatments, it has high consumption power, its membranes are subjected to decay which leads to poor quality of treated water and also its membrane has shortened life due to treatment of hard water.

4.1.5 Nano-Filtration

This is another membrane filtration technique which is usually an intermediate technique between ultra-filtration and reverse osmosis. Nano-filtration is a promising technology for the treatment of wastewater by removing some pollutants such as dyes, small molecules, nanoparticles and heavy metal ions like copper, chromium, arsenic and nickel among others [115]. There are many benefits associated with Nano-filtration such as reliability, operational ease and comparatively low consumption energy [25]. Nano-filtration application is highly requested for the removal of dyes in wastewater since most dyes average molecular weights is in the range of 100–1000 Da [145]. However, its membranes have pores with low connectivity and low porosity, hence at low pressure the flux is low and the pores block easily [146]. Several researchers had made further studies to improve nano-filtration membranes flux through the properties and structures of the supporting and barrier layers [146].

It has been proved that the application of nano-fibre membrane as a supporting layer should be a good potential candidate for the removal of pollutants.

[33] reported the studies of two commercial nano-filtration namely N30F and NF90 for the removal of pentavalent Arsenic from synthetic water with Arsenic feeds. He further reported that when there is a decrease in the operating temperature with an increase in pH values, the two membranes remove higher concentrations of Arsenic. Feed concentration is one of the parameters which affected Arsenic rejection. [72] also investigated the use of Nano-filtration membrane for the removal of heavy metal ions. He reported that there is rejection of nickel ion through the application of thin-film composite polyamide Nano-filtration membrane. The maximum rejection of nickel was further reported to be 92 and 98% when the initial concentration of the feeds is 250 mg/L and 5 mg/L respectively [72]. He also reported the investigation of binary heavy metals (cadmium and nickel) and the maximum observed solute rejection of cadmium and nickel was 82.69% and 98.94% respectively when the feeds initial concentration is 5 mg/L [72]. There are several reports on heavy metal removal through reverse osmosis membrane and Nano-filtration. [24] used Nano-filtration and reverse osmosis for recovery process copper from wastewater. [59] also studied the efficiency of reverse osmosis membranes and nano-filtration in the removal of metals in the effluent of metallurgical industry. He reported further that the reverse osmosis and nano-filtration desalination satisfied the state reutilization qualification but in industrial large-scale, nano-filtration process would be more suitable.

4.1.6 Solvent Extraction

Another name for solvent extraction is called liquid-liquid extraction. This is a method used in separating different compounds based on their solubility relationship into two different immiscible liquids, usually organic solvent and water. It is also referred to as an extraction process whereby a substance is extracted from one liquid phase to another liquid phase due to differences in its solubility [16]. This can be achieved through application of partition coefficient or poor solubility of two incompatible solvents. It has been widely applied in chemical, food, metallurgical and other industries for its continuous easily operation, perfect process, enhanced economic and superior productivity [142].

Triethylamine belong to the family of amine and its molecular formula is $(\text{CH}_3-(\text{CH}_2)_2)_3 \text{N}$ and possess high basicity [142]. Triethylamine has the ability to generate complex anions and to gives back-extraction through its combination with metal ions which can easily recover organic acids from aqueous solution [142]. It has many benefits such as high extraction capacity, good extraction kinetics and negligible solubility in the aqueous phase among others [142]. Thus, it was commonly applied in the recovery process of much precious metal and organic acid.

4.1.7 Electrolysis

Electrolysis is one of the treatment techniques used in metals removal in wastewater. This process involves the generation of current from electricity and passes via aqueous medium which contains an insoluble anode and cathode plate. This electricity process can be produced through movement of electrons from an element to another. When electrochemical process is used for heavy metal removal in wastewater, it precipitates in neutralized or weak acidic hydroxides. Electrochemical treatments in wastewater includes; electro-coagulation, electro-deposition, electro-oxidation and electro-flotation [40]. Electro-coagulation process is formed through electrolytic oxidation of an appropriate material of anode. In this process, the removal of charged metal species from the wastewater is allowed by reacting with the effluent anion. The advantages of this process are; no required use of chemicals, reduction in the production of sludge and ease of operation [40].

4.1.8 Adsorption Technology

This is a technique that involves accumulation of solutes that is liquid or solid on the site surface of an adsorbent (liquid or solid) to generate an atomic or molecular film [76]. The nature of adsorption operation is more of a biological or chemical or physical system that is commonly applied industrially for water treatment and activated charcoal among others. Due to its low cost and simplicity, adsorption has been considered suitable techniques required in treatment of wastewater [4]. This technology has been widely used for the removal of heavy metal ions from different industrial wastewaters [1]. One of the most commonly applied adsorbents is Activated carbon. This adsorbent has been confirmed by many authors due to its highly porous and amorphous crystalline solid nature. Other commonly used adsorbents are clay minerals [77] zeolites, industrial solid wastes and biomaterials [140]. Certain waste from the operation of agriculture or natural materials is one of the low cost adsorbents used. Generally, most of these materials are locally available in large quantities as waste and contributed to pollution of the ecosystem. Therefore, they are very cheap. However, regeneration of the adsorbents after usage remains a challenge facing adsorption technology.

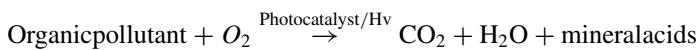
4.2 *Advanced Oxidation Processes*

4.2.1 Photocatalysis

Photocatalysis process is a chemical reaction that involves radiation of catalyst material using photon [85]. When the catalyst and the system are in the same phase, it is referred to as homogeneous photocatalysis while when the catalyst and the system

are in different phases, it is referred to as heterogeneous photocatalysis [11]. Photocatalytic technique is the formation of hole-electron pairs through the absorption of light of photocatalyst; the radicals include hydroxyl, hydroperoxyl and superoxide are been formed through the photogenerated charges [119]. These radicals react via reduction and oxidation reactions, reducing the organic compound and inorganic ions and oxidizing the organic compounds [75]. There are several other ways whereby photocatalysis is applied such as; environmental surfaces and medical devices [102], environmental cleaning [18], coating for hard surfaces in hospital environment [23], self-disinfecting catheters [93], percutaneous implant [107], metal implant [22], intraocular lenses [44], dental implant [26], dental adhesives [106], antimicrobial healthcare surfaces [2] among others.

In the process of heterogeneous photocatalysis, the semiconductor employed as a photocatalyst is very important. The most suitable photocatalyst are metals of oxide or metals of sulphide which have band gap energy suitable to transit electrons by the source of irradiation [84]. Some of these semiconductors include TiO_2 , ZnO , WO_3 , CdS , SiO_2 and Fe_2O_3 among others. There is formation of a positive empty site when an electron leaves the valence band to conduction band. This empty site is referred to as hole (h^+). The recombination of the electron-hole pair photogenerated occurs either through material surface or bulk, whereby moves to a state of initiation and dissipate the heat (energy) [91]. Also, it can further react with the compounds adsorbed on the surface of the photocatalyst by donating or accepting electrons or trapped in the metastable surface state. It is advantageous that the material for photocatalyst can be excited through cheaply available sources like sun radiation. Several researchers have reported mineralization of the toxic organic compound present in the wastewater into water, carbon dioxide and simple inorganic acids [111]. Therefore, photocatalytic method can break down dangerous and toxic compounds like phenol, biphenyl, pesticides, solvents, dioxins and dyes among others to generate non-toxic mineral species namely carbon (IV) oxide and water.



Reaction mechanism of photocatalysis process

Photocatalysis principle involves photocatalyst excitation when exposed to light radiation namely Ultraviolet light or visible light. During photon's action, the photocatalyst generate highly oxidizing free radicals which further involves breaking of the chemicals adsorbed on its surface [70]. The photocatalyst converts from chemical energy to photon energy via reduction-oxidation reaction which results in the nanoparticle activation and degradation of the present molecular chemical. This degradation process involves the succession of radical oxidation initiated via oxidants like OH^\bullet which is directly produced via the light degradation of water molecules adsorbed on the photocatalyst active site. The followings are some of the parameters considered in the photolysis of organic compounds by a semiconductor;

- i. The water content and the nature of the formation of hydroxyl radicals and concentration of pollutants.
- ii. The intensity and nature of irradiation of the source of light.
- iii. The numerical value of incident rays to the nanoparticle activation.
- iv. The reaction medium is determined by the amount of the active site on the nanoparticle.

The processes can be summarized into four levels:

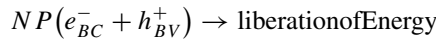
A. Nanoparticle (NP) activation

This level is associated with activation process through the illuminating of the nanoparticle which generates the hole-electron pair.



B. Electron and Holes separation

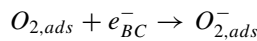
The hole/electron pairs duration (H^+/e^-) is very short and their recombination is through heat. When the electron donor and acceptor are not present, the recombination process is very fast.



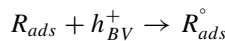
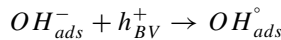
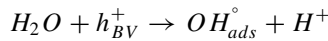
C. Oxidation and Reduction

This reaction takes place at the semiconductor's surface when there is a reaction between the positive holes and the water molecule which produces a radical of hydroxyl. These reactions of oxidation or reduction are what brought about treatment of wastewater.

Reduction Reaction



Oxidation reaction



Band Gap Photo-excitation

This is referred to as the energy changes which result from the difference between conduction band (Bottom) and valence band (top) of a semiconductor or photocatalyst. Photocatalysis process is referred to as photocatalyst excitation which occurs

through the illumination of light energy which may be equal to or greater than their band gap. Semiconductors with their band gaps are listed as follows: TiO₂ (3.43 eV) [89], ZnO (3.37 eV) [114], WO₃ (2.8 eV) [144], CdS (2.42 eV) [73], SnO₂ (3.6 eV) [57] and GaN (3.39 eV) [96] among others. It has been observed that the gap of the band is always depending on shape and the size of particles of the nanoparticles. From several studies, when the energy of the band gap increases, the semiconductor particle size also decreases. Among several reported semiconductors, TiO₂ has been treated promising and proven as the most suitable semiconductor for its application in ecosystem due to its non-toxicity, chemical stability, physical and convenience for use at ambient temperature and pressure [38]. Anatase TiO₂ with 3.2 eV has been activated under ultraviolet irradiation which takes about 5% of solar energy. Researchers have made some efforts to develop photocatalyst which required low energy with visible light via engineering of band doping [30]. Doping of transition metal such as cations namely; V, Fe, Cr and Ni on the site of Ti [141] and anions namely; S, N and C on the site of O [66] which are usually synthesized to improve the activity of photocatalytic reaction. [30] reported that synthesized of N + Zr co-doped TiO₂ exhibited excellent photocatalytic efficiency than Zr or N-doped. Non-metal ions N, C on the site of TiO₂ have been used to reduce the gap of band of the TiO₂.

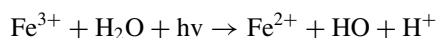
However, there are different challenges attached with mono-doping of TiO₂ induced into the system such as; instability, reducing the current of the photo-excited or carrier mobility, recombination of photo-excited electron-hole pairs [54] which is unfavourable to improve the efficiency of photocatalytic reaction.

4.2.2 Photo-Fenton

Photo-Fenton reaction is one of the commonly studied advanced oxidation processes used for the removal of emerging pollutants in wastewater [80]. Photo-Fenton reaction leads to generation of hydroxyl radical from hydrogen peroxide. Several studies have found this technique effective for the removal of many classes of pollutants, such as pesticides [28], dyes [110], insecticides [29], pharmaceuticals [34], chlorophenol [112], Nitrobenzene [64] and polychlorinated biphenyls [42]. Furthermore, economic and environmental sustainability have been improved through the employment of solar energy in this process. However, this application has some setbacks which include a strict pH control to ensure that the catalyst (Fe(II) and Fe(III) species) plays their roles, by preventing formation of inactive iron oxyhydroxide precipitation so as to have optimum concentration of photoactive species. Therefore, there is a need to operate in a narrow pH range of 2.8–3.5.

Photo-Fenton reaction mechanism

Photo-Fenton reaction can be identified by reactions 1 and 2 below;





This reaction involves several stages based on the role in the reactions of these free radicals: (I) generation of active oxygen with the presence of oxidation species (that is, species that initiate oxidation reaction); (II) species transformation are present in active oxygen; (III) transformation reaction of species of oxygen with organic compound; (IV) intermediate reaction termination. The ferrous ions generated through photolysis entered Fenton reaction and generated supplemental radicals called hydroxyl. Consequently, the rate of oxidation of photo-Fenton is accelerated compared to Fenton process [41]. In addition, when there is high rate of oxidation, the total iron utilization and the generation of sludge are always reduced in photo-Fenton when compared with Fenton process [133]. Furthermore, it has been established that photo-Fenton via UV or solar light, has greater effects on inactivation of microorganisms in wastewater. However, the important of the technique is determined by microorganism present [87] and the nature of water under treatment [121]. In a study, it was found that the spores of *F. solani* is more resistant to the treatment by solar than the *E. coli* vegetative cells [39]. High oxidation like Hydroxyl radicals with a potential of 2.80 V, was said to degrade compounds of recalcitrant like chlorinated and phenolic compounds [47].

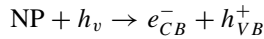
4.2.3 Photoelectrocatalysis

Generally, photoelectrocatalysis systems consist of photocatalysis as an anode material and exposed to light source (UV light or sun light) for effective breaking down of organic pollutants in the aqueous medium. Photoelectrocatalysis is more advantageous than photocatalysis due to easy separation of holes and electrons in the presence of electrical charges [83]. Graphene oxide based nanocomposites have been employed in Photoelectrocatalysis as working electrode and its performance has improved significantly [139] synthesized ternary polyaniline—graphene oxide—titanium oxide hybrid films and applied as photoanode in the photoelectrocatalytic degradation for reduction of water. When compare with pristine titanium oxide electrodes, the hybrid films with alternative graphene oxide, titanium oxide and polyaniline layers exhibited better photoelectrocatalysis activity with higher rate of hydrogen compared to most reported titanium oxide based nanophotocatalyst. The mechanism of Photoelectrocatalysis suggested that the efficient charged transfer occurred at the interface of polyaniline and graphene oxide—titanium oxide due to the potential of the matched band [139]. Polyaniline served as both electron transporter and collector and the transfer of the collected electrons to counter electrode was to form H_2 through the reduction of water under a bias voltage [139].

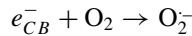
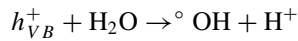
Photoelectrocatalysis mechanism

This technique involves combination of both photocatalytic and electrolytic processes for recombination of electron-hole (e_{CB}^-/h_{VB}^+) pairs and increasing the lifespan of the holes [99]. The fundamental procedures of photoelectrocatalysis are

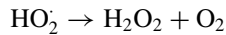
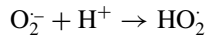
ejection of an electron (e_{CB}^-) through the valence band of a semiconductor which completely occupied conduction band and formed a positively charged vacancy (h_{VB}^+). When the semiconductor is being exposed to illumination energy which is greater than its band gap, it gives rise to the photo-excitation of the e_{CB}^- to conductive band from valence band. Then, the light allows formation of (e_{CB}^-/h_{VB}^+) pairs through Reaction (1) [78],



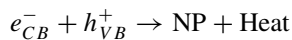
Considering reaction 1, in the product, photogenerated h_{VB}^+ is a strong oxidizing species and e_{CB}^- is the potential reductor. The photogenerated h_{VB}^+ then oxidized the organic pollutants till their mineralization completed. In reaction 2, h_{VB}^+ adsorbed water to generate strong oxidant $^{\circ}\text{OH}$ during mineralizes of the organic pollutants. Then in reaction 3, e_{CB}^- react with the adsorbed O_2 to produce the superoxide radical O_2^- .



Other reactive oxygen species are formed through reactions 4 and 5. The following reactive oxygen species are; H_2O_2 , OH^- and HO_2^- .



In reaction 6, e_{CB}^- is an unstable species at the excited state which tends to return to the ground state either with adsorbed $^{\circ}\text{OH}$ or via recombination with the unreacted h_{VB}^+



4.2.4 Catalytic Ozonation

Ozonation is considered one of the most commonly used wastewater treatment processes. This process was been employed to oxidized pollutants with a large spectrum of emerging concerns and to dissolved organic matters. Ozone is the main agent applied in ozonation. It is selective whereby react with electron rich moieties.

Ozonation partly oxidize chemical compounds and emits toxic by-products, such as bromate from bromine containing wastewater, which is carcinogenic [48]. Due to the need to control the release of toxic emission and reactive by-products, post treatment is required whereby activated carbon or sand filtration are applied after ozonation [113]. But [52] noted that some ozonation by-products are incompletely removed even during biological post-treatment steps.

Recently, researchers found that catalytic ozonation (combination of ozonation and catalysis) have overcome several disadvantages of ozonation process such as energy requirement and higher operational cost. Heidarizad [50] reported catalytic ozonation has a promising advanced oxidation process for degradation of pollutants in wastewater. Heidari [49] found the modified Graphene oxide with magnesium oxide also give high adsorption capacity of Methylene blue. The data reviewed that there was significant mineralization compare to that of ozonation which is without catalyst.

Heterogeneous and homogeneous catalytic ozonation

The fundamental aspect of the mechanism for homogenous catalytic ozonation is on decomposition reaction of ozone which produced radicals called hydroxyl. The metal ions speed up the decomposition process to generate $\cdot\text{O}^{2-}$ which further transfer to O_3 to gain $\cdot\text{O}_3$. Several researchers have proposed schemes for the mechanism of homogenous catalytic ozonation. One of them is [86] which proposed that a system of cobalt (II) oxalate/ozone at acidic pH (6) [130]. He proposed the first stage in the reaction pathway to form cobalt (II) oxalate and the centre of the metal was established to be site of attack. The electron density is partially donated to Cobalt (II) from oxalate which further caused the cobalt (II) oxalate reactivity to increase when compared with the free cobalt (II). This process can effectively improve the organic pollutants removal efficiency but its shortcoming is the introduction of ions which leads to secondary pollution and further increase the water treatment costs.

While for heterogeneous catalytic ozonation; there are three different phases in consideration such as; liquid, gaseous and solid which involves aqueous catalytic ozonation due to it heterogeneous nature of the process. Catalytic ozonation techniques are also affected by some shortcomings such as; target pollutants, nature of catalysts and the range of pH of the solution. Hence, it is not easy to develop efficient techniques to determine the reactive intermediate process. There are two typical mechanisms are as following.

i. Interfacial reaction mechanism

The catalysts first adsorb by its surface to mitigate organic pollutants. Then generate active site to react with the target pollutants to produced active complexes which make the pollutants oxidized via ozone or HO° present in the solution and the catalyst surface oxidize the intermediate or desorbed in order to oxidized via ozone or HO° [13].

Legube and Leitner [62] reported the use of Me-OH catalyst as an adsorbent only; where ozone and hydroxyl radical are oxidant species. The adsorption process of organic acid first takes place on the catalyst. Then, strong anions appear and

formed five or six membered chelate rings on the surface. While the hydroxyl or ozone radical oxidized complex surface and produce a by-product of oxidation. In this mechanism, the catalysts act as an adsorptive material that combines with the organic pollutants to generate chelate which can break down through HO° or ozone radical. However, there are some heterogeneous catalytic processes that have poor adsorptive ability and are difficult to explain via this mechanism.

ii. HO° Mechanism

This mechanism proposed that the solubility of ozone and initiates its decomposition can be increased through metal oxide catalyst. The hydroxyl functional group presents on the surface of the metal oxide play a crucial role in the formation of HO° . The surface of the catalyst adsorbed the soluble ozone in aqueous solution, transfer of series of radical chains to produce additional HO° which give high potential oxidation and can oxidize the pollutants in the wastewater. Poor adsorptive ability of catalytic ozonation system can be explained via this mechanism. Legube and Leitner [62], reported that in this mechanism, the catalyst reacts with the adsorbed organic pollutants and ozone together. Hence, the catalyst is being reduced as the ozone oxidized the metal. The reaction of ozone on the reduced metal leads to HO radicals. The organic acid was adsorbed on the oxidized catalyst and then oxidized by an electron—transfer reaction to gain again reduced catalyst.

5 Conclusion

In this review, physico-chemical parameters for wastewater and classification of pollutants in wastewater were first examined, certain aspects such as physical, chemical characteristics, organic and inorganic pollutants were discussed. The potentials of conventional water treatment methods to purify wastewater successfully along with their shortcoming were discussed. When comparing conventional water treatment with advanced water treatment methods, it was established that the advanced water treatment method performed better and successfully more than conventional water treatment especially when there are multi-pollutants in wastewater. Research trends and knowledge gaps are in the area of hybrid advanced water treatment where multi-advanced will be applied.

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