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MECHANICAL ENGINEERING | REVIEW ARTICLE

Application of clay ceramics and nanotechnology in water treatment: A review

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Abstract: The increasing demand to provide clean water for drinking has brought to the fore the importance of seeking other materials with the ability or combined effect with other materials to purify water. Clay ceramics are known to be natural and also easily engineered porous-structured materials. Review papers on water filtration over the last decade have been on specific mechanisms or technologies. This review paper presents a single platform which provides information encapsulating all these technologies. This paper highlights water contaminants, and their various treatment technologies. The effectiveness of these technologies are evaluated via scholarly documented peer-reviewed papers. Moreover, the discussions are interspersed with the World Health Organization's (WHO) standard for various contaminants along with the exploration of the efficiency of clay minerals as potent water filtration material. Finally, current trends in application of nanotechnology in water purification systems are also highlighted. These technologies include adsorption, microbial disinfection, and photocatalysis.

Subjects: Environmental Change & Pollution; Materials Processing; Nanoscience & Nanotechnology; Technology; Heavy Chemicals; Environmental



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Ebenezer Annan is a senior lecturer at the Department of Materials Science and Engineering, University of Ghana. He obtained his PhD in materials science and engineering with speciality in developing water purification systems. Some of his current research works involves examining the adsorption properties of micro- and nano-porous ceramic water filters. Emmanuel Nyankson is well versed in the synthesis and application of nanomaterials for environmental application (remediation). Abu Yaya has immense expertise in computational materials modelling of nano systems. Yaw Delali's background speciality and research is mainly focused on interfacial thermodynamics and has keen interest in water filtration systems. Benjamin Agyei-Tuffour research focusses on multifunctional materials development. David Sasu Konadu has research experience in corrosion and welding of metals. Professor Boateng Onwona-Agyeman has decades research experience in developing solar cells.

PUBLIC INTEREST STATEMENT

According to the World Health Organization (WHO), about 2.1 billion people do not have access to safe, readily available water at home. This current statistic is a far improvement since the adaption of the millennium development goals (MDGs). Policy makers, world leaders and researchers are hopeful for increase access for now adapted sustainable development goals (SDGs). The statistics brings to the fore the inherent significance of providing safer or improved drinking water source. Ceramics are very potent in conducting research in this area with technologies such as particle filtration, membrane filtration, photocatalysis, combined systems, and use of modern materials such as Carbon Nanotubes, etc. In providing safe drinking water, various researchers have published in relation to materials for water purification. This research review paper therefore looks at the various ways by which water can be made clean or safe for drinking. Authors have attempted to cover as wide areas across water filtration scholarly papers as possible.

Keywords: water treatment; water contaminants; clay ceramics; clay minerals; water filtration; nanotechnology; adsorption; photocatalysis

1. Introduction

According to Human Development report in 2006, global population quadrupled (from 1.6 billion in 1900 to 6 billion in 2000), while the world demand for clean water also increased sevenfold (about 500 cubic kilometres in 1900 to about 3800 cubic kilometres in 2000) (Watkins, 2006). This occurrence dubbed a “global water challenge” has become greater as the population and economies of developing countries also expand. It is estimated, for instance, in the next 40 years, the global population is to grow nearly 40%, and hence, domestic, agriculture, industry and energy demands on water resources will continue to grow (Water, 2007). The World Water Council estimates that by 2030, 3.9 billion people will live in regions characterized as “water scarce” (Lewin et al., 2007).

The growing population does not only affect water demand but more importantly also the health of the populace. For instance, as many as 2.2 million people die of diarrhoeal-related disease every year most often caused by waterborne infections, and the majority of these cases are children under the age of 5 years (World Health Organization 2015). More than ever, existing fresh water resources need protection and new water treatment technologies must be developed in order to meet the world's growing demand for improved drinking water. This brings to the fore need to adapt water recycling (or re-use after treatment for targeted future use). The World Health Organization (WHO) estimated that approximately 9.1% of the global burden of disease and 6.3% of all deaths worldwide could be prevented by improving water, sanitation and hygiene. People who lack access to improved drinking water are more likely to be affected by diarrhoea disease. The millennium development goals (MDGs) and the sustainable development goals (SDGs) both have themes on sanitation and water. Although the MDGs target for water in terms of supply and quality was largely met, that on sanitation was disappointing. There is concern about the possibility of even the improved water sources to be contaminated with faecal indicator bacteria which results in increasing infection rate of water-borne diseases mainly due to poor sanitation (Ramírez-Castillo et al., 2015).

Furthermore, the corrosive nature of most of the metallic pipelines that are often used in municipal water treatment distribution system may also result in possible leaching of chemical contaminants into the drinking water at source. Also, there could be cracks or faulty welded joints on the pipelines and these may serve as some infiltration from faecal pollutant sources, industrial water wastes and chemicals from soils. Therefore, water from any source, municipal, river, borehole, etc., may have some dissolved minerals, microbiological contaminants and suspended particles as well. The amount present in the final analysis and whether it is suitable for its intended purpose is primarily determined by the WHO health standard. Microbes such as bacteria, viruses, chemical contaminants such as fluoride, arsenic, iron, magnesium, nitrates, sulphates, PH of water, etc., are a number of issues found in drinking water that are underlying causes of most health risks. The WHO estimated that approximately 9.1% of the global burden of disease and 6.3% of all deaths worldwide could be prevented by improving water, sanitation and hygiene (Prüss-Üstün et al., 2008). Unsafe drinking water alone can cause many different illnesses, one of which is diarrhoea.

There are various methods that have been documented as point of use water treatment technologies or household water treatment methods (HWTS) (Sobsey, Stauber, Casanova, Brown, & Elliott, 2008). These methods are summarized in Table 1.

The treatment methods given in Table 1 can be used to provide chemical, microbiological and physical treatments depending on the type of contaminant in drinking water. In cases where there are multiple contaminants, combined or multi-barrier treatment approach is recommended. Suspected highly turbid waters are often given prior filtration to attempt to reduce the turbidity

Table 1. General properties of household water treatment system

Treatment	Availability & practicality	Technical difficulty	Cost ^a	Microbial efficacy ^b
Boiling at 100°C	Varies ^c	Low-moderate	Varies ^c	High
Chemical treatment	High to moderate	Low-moderate	Moderate	High
Solar disinfection	High	Low-moderate	Low	Moderate
UV lamp treatment	Varies ^d	Low-moderate	Moderate-High ^d	High
Coagulation sedimentation/ filtration	Varies ^e	Low-moderate	Varies ^e	Varies ^f

Source: (2006) ^aCategories for annual household cost estimates in US dollars are less than US\$10 for low, >US\$10-100 for moderate and > US\$100 for high. ^bCategories for microbial efficacy are based on estimated order-of-magnitude or log₁₀ reductions of waterborne microbes by the treatment technology. The categories are < 1 log₁₀ (< 90%) is low, 1 to 2 log₁₀ (90-99%) is moderate and > 2 log₁₀ (> 99% is high). ^cDepends on heating method at a certain location as well as availability and cost of fuels, which range from high to low. ^dDepends on availability and types of lamps at a certain location, housings, availability and cost of electricity, as well as operation and maintenance needs (pumps and system cleaning methods). ^eDifferent types of coagulation, flocculation and filtration are available. For filtration process, practicability, availability, and cost depend on the filter medium and its availability: granular, ceramic, fabric, etc. For faecal coliform (FC) processes, practicability, availability, and cost depend on the FC prices and availability (alum vs. natural plant extracts). ^fFor filtration: depends on pore size and other properties of the filter medium, which may vary widely. For FC: depends on types of FC effectiveness (alum vs. natural materials).

before further treatment is undertaken. In the case of high turbid water, the sustainability of the filter will be extremely compromised. Aside the use of chemicals in treating high turbid waters, clay ceramics, both traditional and modified types are proven to be effective as well. Although a number are yet to be commercialized due to economic and other factors, there are several HWTS that are available in the market using clay minerals as main filtering element.

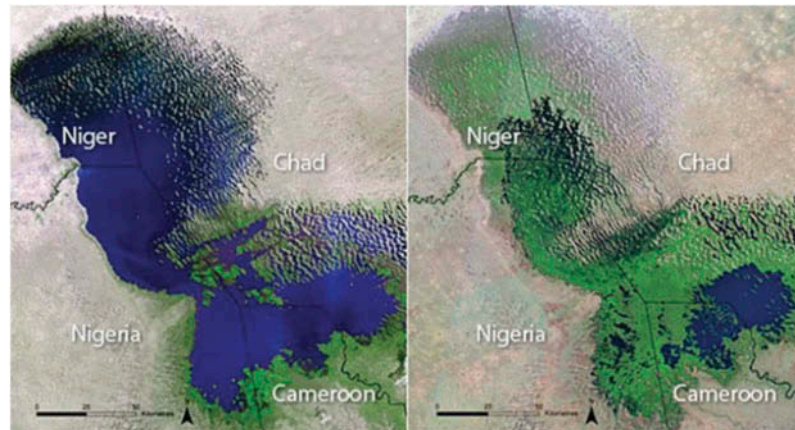
In addition to clay ceramics, nanomaterials with high surface-to-volume ratio and high aspect ratios have been examined for their potential application in water treatment technologies. The unique properties of nanomaterials have made them applicable as antimicrobial agents, adsorbents and photocatalyst. The inclusion of nanomaterials such as TiO₂, carbon nanotubes, halloysite nanoclays, Fe₂O₃, etc., into already existing water treatment technologies may enhance their efficiency in decontaminating of polluted water bodies. Recently, researchers are examining the potential role that halloysite nanotubes can play in water treatment technologies. Halloysite nanocalys are aluminosilicate clay minerals with tubular structure and unique surface charge characteristics which makes them potential adsorbent for water pollutants (Yuan, Tan, & Annabi-Bergaya, 2015).

Over the last decade, there has been increasing study in water filtration technologies. Most of these studies have been limited to specific technologies. However, to the best of our knowledge, there has not been a paper which discusses all these water treatment technologies. In this review paper, we present a platform where clay ceramics potency in all these is discussed. Moreover, it also discusses current trends in application of nanotechnology in water purification systems. These technologies include adsorption, microbial disinfection, and photocatalysis. Several scholarly papers are enumerated and discussed throughout this paper with emphasis on those based on clay ceramics relevant in developing countries. Furthermore, knowledge of technologies and mechanisms in water treatment (used in developed countries) for water treatment is highlighted and explored along resources endowed in developing countries.

2. Water: availability, supply and quality

Water is a basic human necessity and right, hence the need for safe or improved water source for drinking is very essential to the health and development of a community. There are two main water sources available: surface water and ground water sources. The earth's surface is known to have water covering over 70%. However, only 2.5% is fresh and only 1% is easily accessible. The

Figure 1. Disappearing Lake Chad: a high-profile case of diminishing surface water sources shrinking maximum surface area from (25,000 km²) 1972 (left) to (3,000 km²) 2007 (right). Source Gr et al. (2009).



available water continues to diminish due to harsh climatic conditions. Figure 1 gives an idea of the extent of depletion of Lake Chad surface waters from year 1972 to 2007. Climatic conditions continually affect the availability of surface water aside the human activities that equally affect the tributaries of water bodies. It is equally important to note that underground waters are often contaminated and required specialized filters to make them safe for drinking.

Rural communities in developing countries are known to depend on rivers and streams as their source of drinking water, whereas the urban communities do have services from centralized water treatment system managed by municipal authorities. Indeed, the municipal centralized systems also do depend mainly on rivers but undergo further multi-treatment techniques before distribution. Rural communities are more bedevilled with other competitors such as animals, washing and farm irrigation for the use of the waters available.

2.1. Drinking water contaminants

2.1.1. Biological contaminants: water-borne pathogens

These are also referred to as microbes or micro-biological organisms in water which include bacteria, viruses, and protozoa, etc. Pathogens in drinking water can cause diseases which can also be spread through contaminated food and swimming in contaminated water. Pathogenic bacteria can occur in surface water in large numbers, either being in excreted faeces or occurring naturally in the environment.

Bacteria is a single-celled or non-cellular spherical, spiral or rod-shaped organism lacking chlorophyll that reproduce by fission; they are important as pathogens and for biochemical properties. These bacteria may or may not be harmful depending on the bacteria type and the quantity present but the cumulative effect could be disastrous. Bacteria typically range in size between 0.5 and 2 μm . Common bacteria that can be transmitted through water include *Vibrio cholerae*, *Salmonella sp*, *Campylobacter sp*, *Shigella sp*, and *Staphylococcus aureus*.

Arnone and Walling between 1986 and 2000 research compiled outbreaks in the USA and reported almost 6000 cases and 100 outbreaks associated with recreational water, of which about 29.53% was attributed to gastrointestinal illness (GI) (Arnone & Walling, 2007). GI is caused by variety of different microbes and germs, which causes symptoms, such as diarrhoea, nausea, vomiting, fever, abdominal pain, etc. In addition, 10.99%, 10.08% and 6.59% of the cases were caused by *Cryptosporidium parvum*, Adenovirus 3, and *Leptospira*, respectively. Nearly 23% and 21% of the outbreaks were caused by GI and *Shigella spp*, respectively. Also, 16.84%, 12.63% and 7.37% of the outbreaks were caused by *Naegleria fowleri*, *Escherichia coli* 0157:H7, and *Schistosoma spp.*, respectively. It should be noted that aside acute gastroenteritis, major

etiological agents such as *Giardia*, *Cryptosporidium*, *E. coli* O157:H7, *V. cholera*, and *Salmonella* were the agents responsible for many outbreaks (Arnone & Walling, 2007; Pandey et al., 2014).

Viruses do vary widely in size and shape. They are also known to be the smallest of all pathogens, ranging in size from 0.03 to 0.1 μm . There are more than 100 known types of human and animal enteric viruses that may be transmissible through water. Viral diseases that can be transmitted by water include rotavirus, enterovirus, norovirus and hepatitis A. Researchers success with deactivating or removal of viruses from drinking water has been minimal.

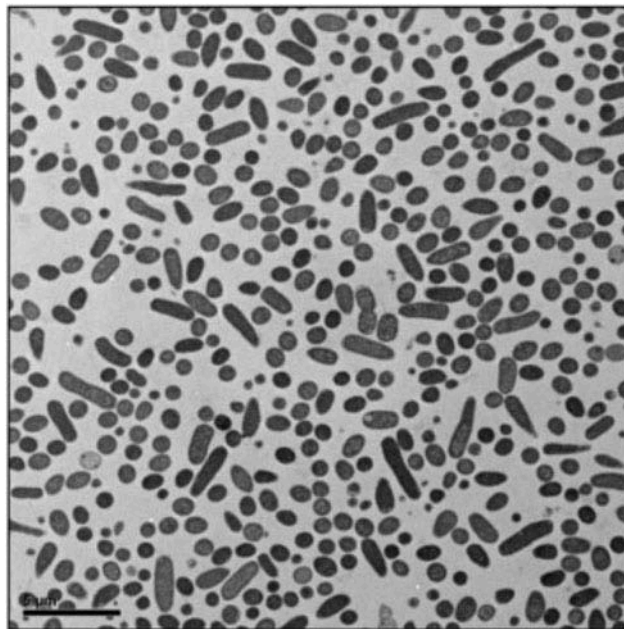
Protozoa are single-celled eukaryotes and part of a group of protozoans referred to us waterborne pathogens. This group comprises of amoebae, *Naegleria fowleri* and *Entamoeba histolytica*, and *Giardia* and *Cryptosporidium*. It is worth knowing that the “Enteric protozoa” such as *C. parvum* and *Giardia lamblia* are considered the most important protozoa pathogens in water quality testing. This is mainly because they form thick walled oocysts and cysts that survive for long periods in the environment and are resistant to many disinfectants (Craun, Craun, Calderon, & Beach, 2006). Most often than not, indicator organisms are used to assess the levels of pathogens in water resources. Monitoring the levels of indicator organisms (such as faecal coliforms, *E. coli*) is a common approach for quantifying the potential pathogen loads in ambient water bodies. For decades, public health officials/scientists have evaluated water quality by enumerating FCs and *E. coli* levels in rivers, lakes, estuaries, and coastal waters (Pandey & Soupir, 2013). Figure 2 is transmission electron micrograph of *E. coli* (O157:H7; ATCC: 35,150) (Pandey et al., 2014).

Safe drinking water is a necessity for every individual. Both international and non-governmental organizations continue to fund activities relating to water quality and resources preservation. Researchers are also undertaking investigations in various aspects to de-activate pathogens and also to further understand the mechanisms that lead to their de-activation. There are several reported incidences of waterborne infectious diseases affecting numerous communities especially in developing countries.

2.1.2. Chemical contaminants

Chemicals exceeding permissible limits in drinking water may be harmful to human health. This could be caused by human activities or from natural occurrences. It is undisputable that the use of

Figure 2. Transmission electron micrograph of *Escherichia coli* (O157:H7; ATCC: 35,150) (Pandey et al., 2014).



pesticides, bleach, etc., are few man-made actions that could introduce harmful chemicals into drinking water bodies. Also, chemical contaminants in drinking water have been associated with broad array of adverse health effects, such as cancer, cardiovascular disease, neurological disease, and sometime miscarriages of pregnancies. Indeed, some of the chemicals enter water through leaching, spills, runoff, and atmospheric deposition. The presence of a contaminant may not necessarily translate to adverse health impact but the levels of the contaminants are of greater importance. There are currently about 120 chemical contaminants catalogued by the USA Environmental Protection Agency (EPA) (World Health Organization 2004). The most common ones are fluoride, mercury, arsenic, cadmium and some organic pollutants.

Fluoride is a naturally occurring element in minerals, geochemical deposits, and natural water systems and enters food chains through either drinking water or eating plants and cereals (Pandey & Soupir, 2013). Also found to occur naturally as sellaite (MgF_2), fluor spar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2Ca(F,Cl_2)$]. According to the WHO, the tolerance limit of fluoride content in drinking water is 1.5 mg/L (World Health Organization, 2004). Fluoride concentrations in the range of (1.5–4) mg/L result in dental fluorosis, whereas with prolonged exposure to (4–10 mg/L) progresses to skeletal fluorosis. Fluoride which is nearly insoluble in water has been found in many groundwater bodies at levels around 30 mg/L, notably in Africa, USA, and Asia (Mohapatra, Anand, Mishra, Giles, & Singh, 2009) (Maheshwari, 2006). The main methods used in defluoridation from aqueous solutions are membrane techniques and adsorption techniques (alumina-based adsorbents, clays and soils, carbon, zeolites and layered double hydroxides (Mohapatra et al., 2009). The adsorption techniques have been found to be most effective and widely used because of its low maintenance cost and even appreciable fluoride removal at low concentrations.

Arsenic may occur naturally, and excess exposure to arsenic in drinking-water may result in a significant risk of cancer and skin lesions. The presence of nitrate and nitrite in water has been associated with methaemoglobinaemia, especially in bottle-fed infants, of which an obvious symptom is a bluish skin. Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater or other organic wastes into surface water and groundwater. Particularly in areas with acidic waters, the use of lead pipes and fittings or solder can result in elevated lead levels in drinking water, which cause adverse neurological effects.

Arsenic leaching into water bodies has been recorded in several places including Cambodia, Nepal, Vietnam, Bangladesh, etc. HWTS are mentioned in literature to have admirable capacity to remove arsenic from drinking water. These include iron-coated sand, activated seawater-neutralized red mud (Genç-Fuhrman, Tjell, & McConchie, 2004), mixture of powdered iron, sulphur and hydrogen peroxide, sunlight or ultraviolet rays, and zero-valent iron appended with limestone (Kanel, Greneche, & Choi, 2006). Others also are iron oxide-coated sand and manganese oxide-coated sand (Ngai, Shrestha, Dangol, Maharjan, & Murcott, 2007), ENPHO and MIT Filter (Ngai et al., 2007). In summary, arsenic content in drinking water could be removed using ceramics made of clay with high iron content. Iron oxide with magnetic properties has been applied in the removal of arsenic in water. Clay minerals impregnated with iron oxide nanoparticles will demonstrate greater potency in achieving higher adsorption capacity. Van Halem (2006) demonstrated the reduction in chemicals such as Barium, copper, manganese, etc., in drinking water using clay filters fabricated from three different countries.

2.1.3. Heavy metals

Heavy metals are any metallic element that has a relatively high density and is toxic at even low concentrations (Lenntech, 2004). It is a general collective term which applies to group of metals and metalloids with atomic density greater than 4 g/cm^3 , or five times or more, greater than water (Duruibe, Ogwuegbu, & Ekwurugwu, 2007). Examples of “heavy metals” include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements.

Table 2. WHO standards for heavy metal contaminants in drinking water (World Health Organization, 2004)

Heavy metal	Max. acceptable concentration (WHO) Mg/L
Zinc	5
Arsenic	0.01
Magnesium	50
Calcium	50
Cadmium	0.003
Lead	0.01
Silver	0.0
Mercury	0.001

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time (Duruibe et al., 2007; Lenntech, 2004). In rocks, they exist as their ores in different chemical forms, from which they are recovered as minerals. The ores for heavy metal ores include: sulphides, such as iron, arsenic, lead, lead-zinc, cobalt, gold, silver and nickel sulphides; oxides such as aluminium, manganese, gold, selenium and antimony. Some of them co-exist and can be recovered as both sulphide and oxide ores such as iron, copper and cobalt. Table 2 gives the maximum acceptable limits of heavy metals in drinking water according to the WHO, whereas Table 3 gives the uses, sources and health effects of having some of these chemicals in the body (if they exceed the maximum acceptable limit).

3. Water treatment methods and filtration mechanisms

A water treatment method could comprise of a number of mechanisms to achieve its objective. Thus, a filtration mechanism is part of a whole system or method by which the ultimate objective

Table 3. Sources and health effects of some toxic metals (Uddin, 2017)

Metal	Uses	Health effects	Sources (industry)	Sources (natural)
Nickel	Catalyst and battery manufacture, nickel coating, nickel stainless steel, catalyst and pigment.	Causes chronic bronchitis, reduced lung function, cancer of the lungs, intestinal cancer.	Electroplating, Ferrous and non-ferrous metal production, smelting operations, thermal power plants, nickel-cadmium battery industries.	Wind-blown dust, soil and dust volcanoes, sea salt, forest fires and vegetation.
Lead	Car batteries, pigments, lead crystal glass, radiation protection, and architecture.	Carcinogenic, anaemia, abdominal, muscle and joints pains, kidney problems, and high blood pressure.	Lead acid batteries, paints, e-waste, smelting operations, coal-based thermal power plants, ceramics, bangle industry.	Sea and salt late aerosols, forest fires and volcanic eruptions.
Zinc	Batteries, coating, compound, crops, die casting alloys.	Stomach cramps, skin irritations, vomiting, nausea, respiratory disorders, anaemia and mental fever.	Smelting, electroplating, pig and poultry manures.	Surface water, soil and ruck.
Copper	Electrical wiring, sieves, portable CD players, transmission wires, copper alloys and coins.	Stomach ache, irritation of nose, mouth, and eyes, headaches.	Mining, electroplating, smelting operations.	Wind-blown dust, decaying vegetation, forest fires and sea spray.

(Continued)

Table3. (Continued)

Metal	Uses	Health effects	Sources (industry)	Sources (natural)
Cadmium	Electroplating of steel, nickel-cadmium batteries, cellular telephones, laptop computers and camcorders.	Carcinogenic, causes lung fibrosis, dyspnoea.	Zinc smelting, waste batteries, e-waste, paint sludge, incineration & fuel combustion.	Coal combustion, iron and steel production, phosphorus fertilizer manufacture and use, and zinc production, volcanic activities and from anthropogenic sources.
Mercury	Batteries, fluorescent lights, felt production, thermometers and barometers.	Headache, abdominal pain and diarrhoea, paralysis, and gum inflammation. loosening of teeth, loss of appetite.	Chlor-alkali plants, thermal power plants.	Volcanoes, geologic deposits or mercury and volatilization from ocean.
Arsenic	Rat poisons, bronzing, in forming special glasses and preserve wood.	Carcinogenic, producing liver tumours, and gastrointestinal effects, diabetes.	Geogenic/natural processes, thermal power plants, fuel burning.	Earth's crust, ground water geothermal processes, volcanic action, mineral ore.
Chromium	Electroplating, stainless steel production, leather tanning, textile manufacturing and wood preservation.	Nasal and sinus cancers, kidney and liver damage, nasal and skin irritation, ulceration, eye irritation and damage.	Mining, industrial coolants, chromium salts manufacturing, leather tanning.	Rocks, animals, plants, soil and in volcanic dust and gases.
Metal	Uses	Health effects	Sources (industry)	Sources (natural)
Manganese	Decolorize glass, oxidizing agent, depolarizer in dry cells, to form alloys.	Toxic and causes growth retardation, fever, sexual impotence, muscles fatigue, eye blindness.	Coal mining, production of dry battery cells, matches, fireworks, porcelain and glass-bonding materials.	Ocean spray, forest fires, vegetation, and volcanic activity.
Cobalt	Electroplating, magnet steels and stainless steels, paint pigments.	Lung effects, such as asthma and pneumonia, vomiting and nausea, vision problems, heart problems, Thyroid damage, hair loss, weight loss.	Sewage sludge, phosphate fertilizers, processing of cobalt alloys.	Erosion (wind-blown continental dusts), weathering of rocks and soil, seawater spray, volcanoes. Forest fires, extraction by plants, continental and marine biogenic emissions.

is achieved. Undisputably, a single mechanism may also be water treatment method depending on the contaminants of the available water. Increasing the temperature above the boiling point of water (approximately 110°C at 1 atmosphere) is an effective mechanism (to deactivate certain bacteria) while the corresponding SODIS is the corresponding water treatment method. In this section we describe and critique the various water treatment methods and mechanisms.

3.1. Water treatment methods

The need for water treatment is well established in the challenges in attaining targets in MDG's with regard to sanitation. The relationship between water, sanitation and health is undisputable. It must also be noted that the economic and also industrial development are dependent on the significance of having synergy in these key parameters. Several water treatment systems can be used to provide microbiological, chemical, or physical water treatment. They include (1) disinfection [chlorination, solar disinfection (SODIS), solar pasteurization, ultraviolet irradiation with lamps, and boiling], (2) particle filtration (cloth fibre, ceramic filter, bio-sand, and other slow sand filter technologies), (3) adsorption media (granular activated carbon and activated alumina or clay), (4) combined system (combined flocculation and disinfection or filtration), and (5) other approaches

(plain sedimentation settling, safe storage, flocculation with iron or alum salts, and membrane processes) (Sobsey et al., 2008). These methods are discussed along the various treatment technologies enumerated and other sections interspersed in this paper. For instance, the use of solar energy in disinfection has been observed to be effective at approximately 110°C. However, the users of this strategy have to wait for hours for reduction in temperature. The use of clay pots as water storage facilities could be effective in temperature reduction. Membrane filtration has been very effective and instrumental in many treatment methods. It is very critical to know the characteristics of the water to treat. The membrane filtration is then composed of components with needed chemicals to ensure the removal of the contaminants. The following sub-sections enumerate and discuss water filtration methods and mechanisms.

3.2. Water filtration mechanisms

3.2.1. Fundamentals of adsorption

This is defined as a process used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. It is a fundamental property having origin in attractive forces between molecules. The force field creates a region of low potential energy near solid surface and, as a result, the molecular density close to the surface is generally greater than in the bulk gas. In the case of multi-component system, composition of the surface layer generally differs from that of the bulk gas and as such the surface adsorbs the various components with different affinities. Adsorption is known to mainly involve various chemical species that may migrate via inter-facial surface into another (possibly) solid phase. The material on which adsorption occurs is termed adsorbent, whereas adsorbed species is termed adsorbate. Adsorption can be termed chemisorption or physical adsorption, depending on nature of surface forces. In physical adsorption, relatively weak inter-molecular forces are in play whereas in chemisorptions, there is significant electron transfer (resulting in a chemical bond between the adsorbate and the solid surface). The term bio-sorption is also often used to describe the adsorption process that has microbes and viruses as adsorbate. Generally if adsorption occurs in the liquid phase, there exists a little difference in molecular density between the adsorbed and fluid phases. It is relevant to also know that there are hydro-philic and hydro-phobic adsorbents.

The factors affecting adsorption process include the following:

(i) surface area, (ii) nature and initial concentration of adsorbate, (iii) PH of solution, (iv) temperature, (v) interfering substances, and (vi) nature (and dose of adsorbent)

The fundamental equation governing adsorption is given as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at a time, t , C_0 (mg/L) and C_t (mg/L) are the initial and at a time t concentration of adsorbate, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent. In a solid-liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm and found to be in conformity with Equation (1). Isotherms that express the relation between concentration of adsorbate and extent of accumulation on the adsorbent surface at constant temperature are used mostly in modelling of most adsorption processes (Meenakshi, Sundaram, & Sukumar, 2008).

The most widely used models to describe the adsorption process in water and wastewater applications were developed by (i) Langmuir, (ii) Brunauer, Emmet, and Teller (BET), and (iii)

Freundlich. The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms reflecting apparent multilayer adsorption. This means that when the limit of adsorption is a monolayer, BET isotherms reduce to Langmuir expression. It is important to know that the two equations are limited by assumption of the uniform energies of adsorption on the surface. The two, Langmuir and Freundlich, equations are given, respectively, as follows:

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (2)$$

where q_e (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium, C_e is the liquid-phase concentration of the adsorbate at equilibrium (mg/L), q_m is the maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg):

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F (mg/g) (L/mg)^{1/n} is the Freundlich capacity factor and $1/n$ is the Freundlich intensity parameter. The constants in the Freundlich isotherm are determined by plotting $\log(q_e)$ versus $\log(C_e)$.

According to Meenakshi et al. (2008), there are three main stages, theoretically, for mass transport of adsorbates. These are as follows:

- (I) Mass transfer from the bulk of the adsorbent to the surface of it (often called bulk diffusion or external mass transfer)
- (II) Intra-particle diffusion of species through liquid filled pores
- (III) Systematic accumulation of adsorbate at the adsorbent sites

Adsorption diffusion models are used for modelling rate determining step which is either intra-particle diffusion or liquid film diffusion. In physical adsorption process the mass action or transfer process is very rapid and can be neglected for kinetic studies. Adsorption diffusion models are used to describe the process of film deposition and intra-particle diffusion. Two main models used in the liquid film deposition model are (i) linear driving force rate law and (ii) film diffusion mass transfer rate equation whereas intra-particle diffusion has (i) homogeneous solid diffusion model (HSDM) (Cooney, 1999), (ii) Weber–Morris Model, (Alkan, Demirbaş, & Doğan, 2007) and (iii) Dumwald–Wagner model (Wang, Chen, & Zhai, 2004).

In linear driving force rate law for a liquid/solid adsorption system, the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law. The rate of accumulation is given by

$$V_p \left(\frac{\partial \bar{q}}{\partial t} \right) \quad (4)$$

where \bar{q} represents average solute concentration in the solid, and V_p is the volume of the particle. It is known that the rate of solute transfer across the liquid film is proportional to the surface area of the particle A_s and the concentration driving force $(C - C_i)$. Therefore, it equals to $k_f A_s (C - C_i)$, where k_f represents the film mass transfer coefficient (Cooney, 1999). From the above discussion it is obvious that

$$V_p \left(\frac{\partial \bar{q}}{\partial t} \right) = K_f A_s (C - C_i) \quad (5)$$

where C_i and C denote the concentration of solute at the particle/liquid interface and in the bulk of the liquid far from the surface, and A_s/V_p defined as the particle-surface area per unit volume, S_o . The equation resulting from the S_o substitution is termed the “linear driving force” rate law.

The film diffusion mass transfer rate equation presented by Boyd, Adamson, and Myers (1947) is given as

$$\ln\left\{1 - \frac{q_t}{q_e}\right\} = -R^l t \quad (6)$$

where R^l is also expressed as

$$R^l = \frac{3D}{r_o \Delta r_o k'} \quad (7)$$

where R^l (min^{-1}) is liquid film diffusion constant, D (cm^2/min) is effective liquid film diffusion coefficient, r_o (cm) is radius of adsorbent beads, Δr_o (cm) is the thickness of liquid film, and k' is equilibrium constant of adsorption.

Under intra-particle diffusion model, HSDM can describe mass transfer in an amorphous and homogeneous sphere and the mathematical expression given as

$$\frac{\partial q}{\partial t} = \frac{D_s \partial}{r^2 \partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (8)$$

where D_s is intra-particle diffusion coefficient, r is the radial position, and q is the adsorption quantity of solute in the solid varying with radial position at time t .

Weber and Morris (1964) and Alkan et al. (2007) found out that for many adsorption processes the uptake of solute varies almost proportional to $t^{1/2}$ rather to the contact time, t :

$$q_t = K_{int} t^{1/2} \quad (9)$$

where K_{int} is the intra-particle diffusion rate constant. If intra-particle diffusion is the sole rate limiting step, then the plot of q_t against $t^{1/2}$ must pass through the origin. However, the adsorption kinetics may be controlled by both film diffusion and intra-particle diffusion simultaneously.

Another intra-particle diffusion model proposed by Dumwald-Wagner (Wang et al., 2004) is given as

$$\log(1 - F^2) = -\frac{K}{2.303} t \quad (10)$$

A plot of $\log(1 - F^2)$ versus t should be linear and the rate constant K can be obtained from the slope. Dumwald-Wagner model proved to be reasonable to model different kinds of adsorption systems such as p-toluidine adsorption from aqueous solutions onto hyper-cross-linked polymeric adsorbents (Alkan et al., 2007). Adsorption is undisputably a surface phenomenon and since adsorption is a surface phenomenon, the extent of adsorption is directly proportional to the specific surface area, so for nanoparticles with high surface to volume ratio and porous solids offer greater percentage of adsorbate per unit weight.

3.2.2. Size exclusion

This mechanism is sometimes referred to as size exclusion. In this mechanism, the filtration element has pores with dimensions smaller than the contaminants thereby restricting the contaminants from passing through the filter element. Most HWTS are known to adopt this mechanism as in membrane filtration. Clay water filters are an example of HWTS and have pores in their filtration elements created via burnt out combustible materials in the clay mixture after firing. Clay ceramics fired at about 200°C to 300°C have most combustible materials burnt out leaving out pores in the fired clay composite. Therefore, the size of the combustible materials is mainly responsible for the size of the pores created. Contaminants with sizes greater than the pore dimensions created are mechanically prevented from going through the pores during a filtration process. A good example is the exclusion of *E. coli* in membrane filtration. The pores, sizes of pores,

are usually between 0.3 and 2.5 μm , thus making it capable of restricting bacteria (*E. coli* is usually 3 μm) bigger than this size range. The flow studies for the frustum-shaped ceramic water filters have been critically examined by Annan, Mustapha, Odusanya, Malatesta, and Soboyejo (2014) and Yakub et al. (2012). Annan et al. (2016) also considered the mechanical robustness of the frustum-shaped clay filters which affects the overall flow through the filtration element and the strength characteristics at different temperatures. In their studies, they employed woodchips (or sawdust) as combustible material and were in the 1:1 ratio in volume per cent. Rice husks, wheat husks, coconut fibres, starch and other cellulose materials could also be used as combustible materials. Indeed, cellulose and starch has been used in other polymer-ceramic membrane filtration studies at low temperatures.

3.2.3. Sedimentation

Sedimentation is defined as a process whereby particles are allowed to settle usually due to their greater density mainly through agglomeration. This mechanism enables treatment methods to remove particulate suspended matter of finer sizes than the pore openings by precipitation upon the surface of the clay material. This is not an effective mechanism to trap pathogens since suitable conditions may make the pathogens active. However, solid suspensions that attribute to turbidity in water can greatly be reduced using this mechanism. In most cases HWTS, allowable distance is ensured prior to the downpour or release of filtrated water.

3.2.4. Coagulation

Coagulation sometimes referred to as flocculation, is where chemicals are added to aqueous medium in bringing of small de-stabilize colloidal suspensions together to larger aggregates to allow easy removal from water. The level of strength of the Van dar waals forces plays an important role in the flocculation process. Figure 3 gives a representation of the mechanisms that can remove contaminants and thus affects flow. **Two particles can agglomerate in the same aqueous phase to remove different contaminants. The agglomeration of the two particles can be enhanced with the aid of a "binder"**. Indeed the varying factors need to be experimented to ensure the good mix and also attain most agglomeration of the bi-particles. In cases where single medium is being used, a bio-compatible and anhydrous powder with high Van der waals force to attain effective coagulation could be employed. Most villagers in developing countries are prone to the use of alum and chlorination of their river dependent water to ensure some level of coagulation. In most cases the quantities are not accurate and may be the cause of other long-term health effects.

4. Clay ceramics and removal of contaminants

Brief description of main categories of contaminants in water is given in Section 2.1. There are known clay minerals that are employed for specific as removing targeted contaminants through various mechanisms. Indeed, the combination or modified forms of any of the clay minerals have also been shown to be effective in adsorption of certain contaminants from drinking water and wastewaters. Clays are ubiquitous and largely culturally acceptable, and therefore the modification with either inorganic or modern functional materials is not envisage to be an issue in acceptance, although their processes may require certain level of diversion from the normal steps. The following sub-sections give details on classification of clays, removal or adsorption of heavy metals with kaolinite, and other minerals capacities are discussed. It is important to know the chemical compositions of the clays mineral to understand the underlying mechanism.

Figure 3. Schematic representation of some mechanism in water treatment (Metcalf & Eddy, 2003)

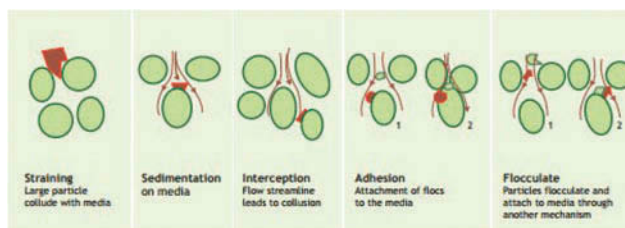
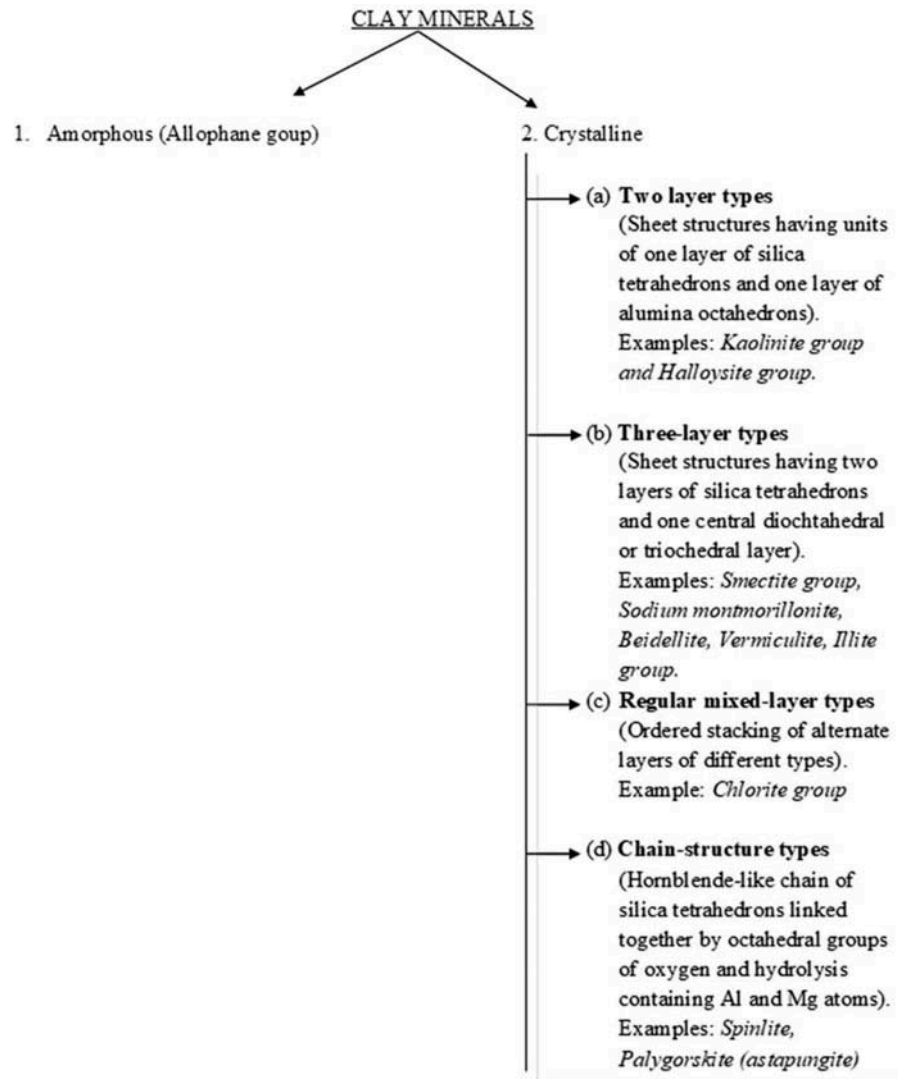


Figure 4. Classification of Clay Minerals (Uddin, 2017).

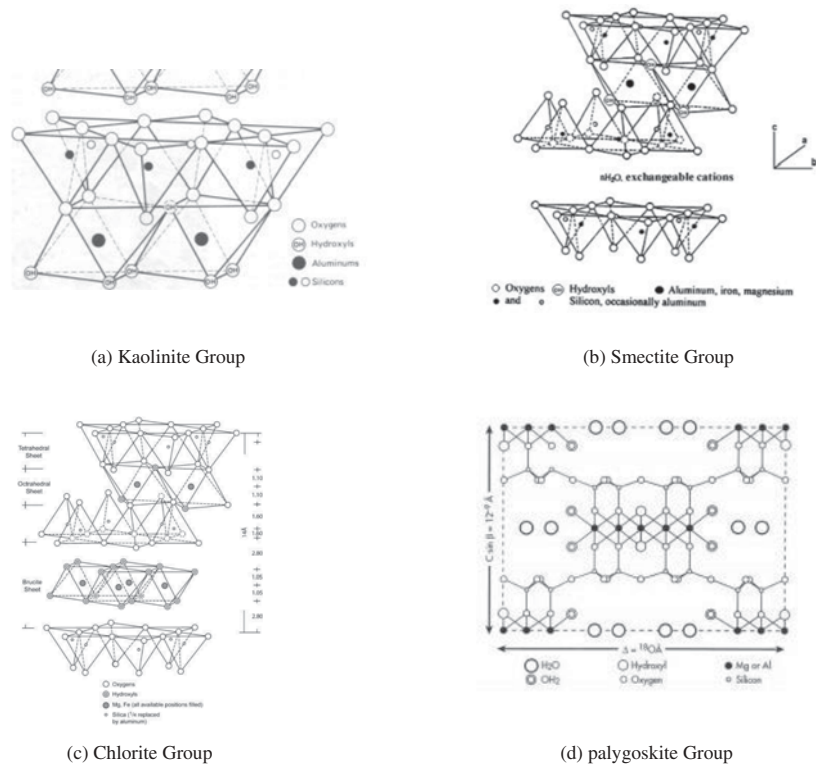


4.1. Clay minerals

Uddin et al. (2017) define the term clay as materials having particle size of less than 2 μm with chemical analysis that reveals similar compositions and common crystal structures. **Figures 4 and 5 give structural classifications of clay minerals with brief expositions.** Clays could also be classified as phyllosilicates that belongs to three principle groups: montmorillonite, illite and kaolinite. Phyllosilicates are two-dimensional arrays of silicon–oxygen tetrahedral and two-dimensional arrays of aluminium or magnesium–oxygen–hydroxyl octahedral. Montmorillonite-layered silicates (MLS) has 2:1 layered structure, Illite also has 2:1 layered structure and kaolinite 1:1 layered structure. Their physico-chemical properties varies but are essentially noted for their hydrous alumina-silicates components. Clay ceramics are also noted for their hydro-plasticity (Annan et al., 2012; Bergaya & Lagaly, 2006; Uddin, 2017).

The ancient clay has kaolinite and other varying proportions of quartz, mica, feldspar, illite and montmorillonite. It is important to note that the structure and crystal chemistry and the surface chemistry are responsible for the properties they exhibit and thereby their environmental benign applications. The majority of clays have silica and alumina sheets, which belong to a class of layered silicates referred to as the phyllosilicates group. These groups can be subdivided according to the type of layer structure.

Figure 5. Structural types of clay minerals (a) 1:1 mineral group, (b) 2:1 mineral group (exchangeable cations and water in the interlayer), (c) 2:1 mineral group (chlorite and hydroxides in the interlayer), and (d) 2:1 nonplanar (modulated) silicate (palygorskite). [kaolinite and smectite structures adopted from (Grim, 1962); Palygorskite adopted from (Murray, 2006).



Clays consist of interconnected silicates sheet combined with a second sheet-like grouping of metallic atoms, oxygen, and hydroxyl ions (Bergaya & Lagaly, 2006; Weaver & Pollard, 1973). The basic structure units are divided into silica sheets and brucite or gibbsite sheets (Miranda-Trevino & Coles, 2003). The 1:1 clay mineral type consists of one tetrahedral sheet and one octahedral sheet (Miranda-Trevino & Coles, 2003; Yaya et al., 2012).

Octahedrons consist of two planes of hydroxyl ions between which lies a plane of magnesium or aluminium ions, which is typically coordinated by hydroxyl sheets octahedrally. These octahedrons are also arranged in a hexagonal pattern which is called octahedral sheet. The 2:1 (three layer) layer lattice silicates consist of two silica tetrahedral sheets between which is an octahedral sheet. The 2:1 clay minerals include the mica and smectite groups, which are the most abundant among the clay minerals. The serpentine and mica group is subdivided on the basis of dioctahedral and trioctahedral type (Weaver & Pollard, 1973).

4.2. Kaolinite and heavy metals

The kaolin structure has advantage in many processes, and this is due to its high chemical stability, cation exchange capacity and low expansion coefficient (Miranda-Trevino & Coles, 2003). Their structure has one tetrahedral sheet linked to an octahedral sheet, making them classified as 1:1. An investigation by Omar et al 2007, on adsorption capability of kaolinite for removal of lead ions from aqueous solutions showed interesting results (Omar & Al-Itawi, 2007). For instance, as the temperature increases, the adsorption potential was found to be proportional. The measured adsorption kinetic data at different temperature proved that surface adsorption together with intra-particle diffusion controlled are responsible for the rate of adsorption.

The adsorptive behaviour of arsenic As (V) ions with kaolinite, montmorillonite, and illite minerals in aqueous medium has been investigated as temperature increases. Increasing adsorption temperature was found to decrease with As (V) adsorbed (Mohapatra, Mishra, Chaudhury, & Das,

2007). The results showed that kaolinite was active clay constituent for both As (V) adsorption and mobility. Matlok *et al.* (2015), Dina and Mbadcam (2015) and Kul *et al.* (2007) have demonstrated the adsorption capacity of natural kaolinite (and also activated kaolinite) for removal of Zinc (II) from aqueous solution (Joh & Mbadcam, 2015; Kul & Koyuncu, 2010; Matlok, Petrus, & Warchot, 2015). Vecitis *et al.* (2017) have demonstrated that the sorbent dosage could be optimized at four (4 g) and that obtained zeolite could be modified to serve as great ion exchanger in removing heavy metals from wastewaters (Das *et al.*, 2017).

Modified kaolinite has also been demonstrated to adsorb some heavy metals. For instance, a two-batch adsorption approach adopted by Unuabonah, Adebowale, and Ofomaja (2009), for sodium polyphosphate modified kaolinite had increased adsorption sites. Using sodium polyphosphate-modified kaolinite clay, increase in adsorption capacity is also shown for removal of lead, zinc and cadmium from aqueous solutions (Amer, Khalili, & Awwad, 2010). In total, 25% aluminium sulphate and unmodified kaolinite clay used as adsorbent to remove lead (II) had greater adsorption capacities under optimized conditions (Qiu *et al.*, 2009). Lasheen *et al.* (2005) synthesized nano magnetite (Fe_3O_4) and composited with kaolinite and tested for heavy metal removal. The adsorption capacity of the magnetite-kaolinite composite increased as compared with the unmodified kaolinite as the pH increases (Lasheen, El-Sherif, Tawfik, El-Wakeel, & El-Shahat, 2016). In most documented cases, the raw and unmodified kaolinite has achieved appreciable adsorption capacities increasing with pH. The optimum pH for many metals was found between 5 and 6, and is demonstrated in the removal of fluoride via ion exchanges with iron oxide in adsorption studies (Lasheen *et al.*, 2016). The adsorption in most cases was found to be faster at the initial stages and equilibrium assumed after few hours with increasing temperature. Arsenic adsorption, however, has been found to decrease with increasing temperature. It is therefore imperative for researchers to adopt a broad range of pH during adsorption studies, except for techniques where literature has proven beyond doubt. The kinetics of the adsorption cannot also be ignored. Kinetic adsorption studies of kaolin have been described using the Langmuir and Freundlich models. Unuabonah *et al.* (2009) have demonstrated adsorption of Pb^{2+} and Ca^{2+} onto phosphate-modified kaolinite clay. They demonstrated that the adsorption reaction is chemically activated and endothermic with energy of activation at 500mg/L for Pb^{2+} and 10.68 KJmol^{-1} for modified and unmodified kaoline adsorbents respectively.

4.3. Smectite group and contaminants removal

All clays with structures that show expansive lattices are referred to us smectite according to the clay minerals group. Examples of clay minerals in this group include: montmorillonite (MMT), bentonite, nontronite, beidellite, etc (Bergaya & Lagaly, 2006). Usually the ion exchange capacity, specific surface area, and adsorption capacities of these clays are larger compared with others.

Montmorillonite (MMT) has become synonymous to smectite clay. This has been confirmed by some materials analyses techniques and widely accepted. Though organo-MMT clays have been demonstrated to remove copper (II) as a function of pH, organo-clays in general have received little interest as adsorbents for heavy metals because of their competing sites between organic cations and metals for adsorption sites (Cruz-Guzmán *et al.*, 2006). Such clay minerals are more hydro-plastic but do compromise the mechanical robustness of membrane filtration system if such compositions are employed. And so clay water filters it is important to restrict the quantity that is used in the ceramic mix. We recommend the quantity be measured in percentage per volume and not more than 50%.

Kaolinite and bentonite are also clay minerals that have been applied in the removal of fluoride from water. Coating of these minerals have shown better potency in removal at a pH range of 6. Kaolinite coated with aluminium oxide and iron oxide shows 72.3% and 61.3% fluoride adsorption respectively better than no coating of 45.1% (Puka, 2008). Bentonite (no coating) adsorption studies for fluoride resulted in 49.6%, greater than kaolinite (no coating) adsorption. When

bentonite is coated with aluminium oxide and iron oxide had 95.3% and 80.4% fluoride adsorption (Puka, 2008).

Organo-Modified MMT have been used to show good removal rate for copper (II) at a pH of 3.0–8.0 with a stirring time of 10 min (Abou-El-Sherbini & Hassanien, 2010). The maximum removal efficiency of (99.2 ± 0.9) was at pH 6.0 with interest on stirring time, ion effects, concentration and volume. It will be important to vary the variables to ensure maximum important removal through adsorption for comparative study: raw MMT and modified MMT. Interestingly, modified MMT, Zwitterionic surfactant has shown comparable removal of Cu (II) with that of raw MMT. Removal of lead (II) and Cadmium (II) from spiked water samples through adsorption onto MMT has been studied by (Gupta & Bhattacharyya, 2009; Karamanis & Assimakopoulos, 2007). The mechanisms for these appreciable removal rates are well explained in the referenced papers. It is worth mentioning that activated MMT–Illite clay from India has been examined for removing Cu (II) and Zn (II) ions from industrial wastewater containing meagre amounts of Pb (II) (Oubagaranadin, Murthy, & Mallapur, 2010).

4.4. Biological contaminants removal

Researchers have modified systems that use sunlight (and applied irradiation) on water samples as a means to deactivate Bacteria. The first application of this was done in 1910 in Marseille, after the establishment of mercury vapour lamps and the establishment of germicidal effect of UV irradiation. The UV irradiation initially was more expensive than the other methods like chlorination, boiling and other methods but it was found to be much effective compared to those mentioned above (Malato, Fernández-Ibáñez, Maldonado, Blanco, & Gernjak, 2009). This approach is often termed the solar disinfection or UV disinfection. It tends to disrupt the sequence of the normal cellular functions and also, the activities of the ATP synthesis. Finally, efflux pump both stops shortly after exposure followed by a gradual loss of membrane potential and a reduction in the glucose uptake. The cytoplasm membrane of the bacterial cells then become permeable which results in the loss of cultivability (Pigeot-Rémy et al., 2011).

The effectiveness of the clay water filter in microbe removal is mainly due to two mechanisms; mechanical screening and colloidal silver impregnation. The removal efficiency is done using indicator organisms. And this is often in literature done by using *E. coli*. Logarithm (10) return values (LRVs) ranging from 2 to 5 has been recorded for various researchers, with some mimicking the waters in the field (Van Halem, 2006). Some also could not find the corresponding log return value since the *E. coli* count in most filtered samples were zero. Using *C. parvum* oocysts and *G. Lamblia* cysts, Lantagna, 2010 found LRV of 4.3 and 5, respectively. Similar results were obtained for the removal of sulphite reducing Clostridium oocysts for a clay water filter produced in Nicaragua (Lantagne et al., 2010). This continued research using MS2 bacteriophages as virus indicators found unsatisfactory logarithm return values (< 1) and therefore not suitable as sustainable treatment system (Lantagne et al., 2010). However, it was observed to decrease diarrhoeal cases in 80 Cambodian households (Ngai et al., 2007). It is important to mention that silver nanoparticles aside Silver nitrate has been effective in the “killing” of bacteria. The coating is usually done via dipping of the filter or membrane in a colloidal solution of the particle or chemical. Spraying coating technique is envisage not to be effective as coating, mainly due to the colloidal not getting to the intrinsic sections of the filter membrane.

Solar disinfection method has been applied on viruses and was found not to be as effective as on bacteria (Fisher, Iriarte, & Nelson, 2012). And so virus removal remains a challenge with ceramic water filters due to the small sizes of viruses. Furthermore, silver/silver nanoparticles which is effective against bacteria has not been of same efficacy level against viruses. It has also been found that the LRV of MS2 bacteriophages is slightly reduced in filters with colloidal silver and therefore it has been suggested that colloidal silver application does not have a positive effect on virus removal (Kallman, Oyanedel-Craver, & Smith, 2010). However, ceramic water filters have not been found to be effective in removing MS2 bacteriophages in filters with or without colloidal silver.

An example is the encephalomyocarditis virus which disintegrated after close to 6 h of natural sunlight while others also did not disintegrate at all proving that the SODIS method is not effective in deactivating viruses compared to other methods like boiling (Wegelin et al., 1994).

5. Nanotechnology and water filtration

Materials with smallest dimensions ranging from a few nanometers to less than 100 nanometers are known as nanomaterials. On the nanometre scale, the properties of materials are size dependent and materials with higher surface to volume ratios possess high catalytic activities. The unique properties of materials on the nanoscale can be utilized to address some of the most pressing environmental problems such as water pollution, air pollution and oil spill remediation. The potential application of nanomaterials in water purification systems as reported in literature over the years are reviewed below under the headings; adsorption, photocatalysis and microbial disinfection.

5.1. Adsorption

Adsorption is used to remove organic and inorganic pollutants from contaminated water. Nanomaterials such as TiO_2 (Xu, Cai, & O'Shea, 2007), Fe_3O_4 (Liu, Zhao, & Jiang, 2008), carbon nanotubes (Tan, Fang, Chen, Yu, & Wang, 2008) and ZnO (Wang et al., 2012) have been investigated for their potential application in adsorbing pollutants from water. Commercial TiO_2 has been studied for their potential application in the removal of arsenic (III), arsenic (V), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Xu et al., 2007). A adsorption efficiency of 100% was observed for As (III) and As (V) while about 85–95% of MMA and DMA was adsorbed on the TiO_2 . The adsorption behaviour of MMA and DMA was attributed to their chemical structure and the pH of the adsorption medium. The high adsorption efficiency of TiO_2 nanoparticles towards these pollutants can be attributed to the high surface to volume ratio of nanomaterials implying that nano- TiO_2 has a lot of active sites for adsorbing the pollutants. The adsorption efficiency of anatase TiO_2 synthesized by solvothermal treatment is dependent on the pH of the adsorption medium and the TiO_2 crystal size (Gao et al., 2004). The synthesized TiO_2 could adsorb $142.241 \mu\text{mol/g Cd}^{2+}$. To enhance the adsorption efficiency, TiO_2 can be combined with other materials to form a composite. Most researchers have therefore examined different materials that can form good composite with TiO_2 and a result enhance adsorption efficiency. Some of the TiO_2 composites investigated are TiO_2 /activated carbon (Lim, Yap, Srinivasan, & Fane, 2011), TiO_2 /zeolite (Fukahori, Ichiura, Kitaoka, & Tanaka, 2003), TiO_2 -chitosan (Zhang, Zhao, & Su, 2011) and $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ (Zhou et al., 2008). As already mentioned, addition of secondary material to the TiO_2 enhances its adsorption efficiency. For instance the addition of zeolite and activated carbon to TiO_2 helped in the capturing of toxic intermediate by products released during TiO_2 photocatalysis and hence helped in the purification of the contaminated water (Fukahori et al., 2003; Lim et al., 2011). Zeolite and activated carbon are materials that are mesoporous with high pore volume and as a result provided a lot of active sites for adsorption. $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ bifunctional composite has the ability to photo-oxidize As (III) to As (V) and further remove As (V) by adsorbing onto the surface of $\alpha\text{-Fe}_2\text{O}_3$. The photo-oxidation results from the fact that TiO_2 as a semiconducting materials creates hydroxyl radicals when it absorbs photons with energy greater than or equal to its band gap. The combination of adsorption and photo-oxidation enhances the removal efficiency of pollutants by this composite system. Other modifications of TiO_2 such as titanate nanofibres have also been investigated for their potential removal of heavy metals (Yang et al., 2008). Nanofibres are known to possess high aspect ratios and high surface to volume ratio. Generation of titania nanofibres are expected to enhance its potential in removing water pollutants.

Magnetite (Hu, Lo, & Chen, 2004; Yantasee et al., 2007) and maghemite (Yavuz et al., 2006) nanoparticles have been investigated for the removal of Cr (IV). Flower like magnetic nanoparticles have been explored for the potential removal of toxic, As(V) from water bodies (Zhong et al., 2006). Their study revealed the role that nanoparticles play in enhancing the removal efficiency of adsorbents. The removal efficiency of these particles are dependent on their structural morphology and particle size. Despite the excellent removal of heavy metals by iron oxide nanoparticles, they

easily aggregate in aqueous solution and are easily oxidized. Different strategies have been adopted by researchers to address this problem. Fe_3O_4 nanoparticles are therefore functionalized or coated with humic acid (Liu et al., 2008), chitosan and dimercaptosuccinic acid (Yantasee et al., 2007). Fe_3O_4 nanoparticles coated with humic acid has also been investigated for their potential application in removing toxic metals such as Hg(II), Pb(II), Cd(II) and Cu(II) (Liu et al., 2008), while Fe_3O_4 nanoparticles functionalized with dimercaptosuccinic acid has been examined for the removal of Hg, Ag, Pb and Cd (Yantasee et al., 2007). Fe_3O_4 -C has recently been investigated for the removal of organic dyes such as methylene blue and cresol red (Zhang & Kong, 2011; Zhang, Zhang, Zhao, & Zhou, 2016). Fe_3O_4 @polydopamine-Ag core-shell microsphere with high adsorption capacity, high regeneration ability, cyclic and acid stability has been studied as adsorbent in water purification systems. The excellent adsorption performance for this composite was attributed to the high monodispersity of the Ag nanoparticles coupled with the mussel-inspired polydopamine layer coated on the magnetic microspheres (Xie et al., 2014).

ZnO semiconductor is a photocatalysts with a wide band gap of 3.37 eV (Yang, Ren, Zhang, Huang, & Liu, 2011). The photocatalytic performance of ZnO has been enhanced by forming a composite with graphene sheets (Yang et al., 2011) and reduced graphene oxide (Chen, Chang, Yang, Chiu, & Lee, 2013; Li, Liu, Wang, & Wang, 2012; Luo et al., 2012; Wang et al., 2012). In addition to enhancing the photocatalytic efficiency, reduced graphene oxide and ZnO composite (RGO@ZnO) synthesized by self-assembly and in-situ photoreduction method has been reported to exhibit high adsorption towards rhodamine B dye. The high adsorption efficiency was attributed to the hydrophilic surface of ZnO which helped in the aqueous dispersion of RGO@ZnO and hence improved the adsorption of rhodamine B dye (Wang et al., 2012).

Since carbon nanotube was discovered by Iijima (1991), its adsorption properties have been intensely and widely investigated by researchers. Carbon nanotubes can be single or multi-walled as presented in Figure 6(a) and 6(b), respectively.

Some of these properties are as follows: chemically inert surface, high porosity and hollow structure, high surface to volume ratio, light mass density and strong interaction between carbon nanotubes and water pollutants (Chen, Hu, Shao, Li, & Wang, 2009). Due to these unique properties carbon nanotubes have been investigated for the removal of pollutants from gas streams and water bodies. The structure of single-walled carbon nanotubes (SWNTs) also needs to be considered to gain insights into the various pollutants adsorption sites (Figure 7). The pollutants can be adsorbed through its interior site, exterior site, groove site and the interstitial site (Kondratyuk & Yates, 2007) as can be seen in Figure 7. Carbon nanotubes have been investigated for their potential application in removing organic pollutants such as dyes (Ai & Jiang, 2012; Ghaedi, Hassanzadeh, & Kokhdan, 2011; Gong et al., 2009; Machado et al., 2011; Wang et al., 2014), dichlorobenzene (Peng et al., 2003), dichlorodiphenyltrichloroethane (Zhou, Xiao, & Wang, 2006),

Figure 6. (a) Single-walled carbon nanotube and (b) multi-walled carbon nanotube. Carbon nanotubes possess unique properties that make them suitable as an adsorbent for water pollutants.

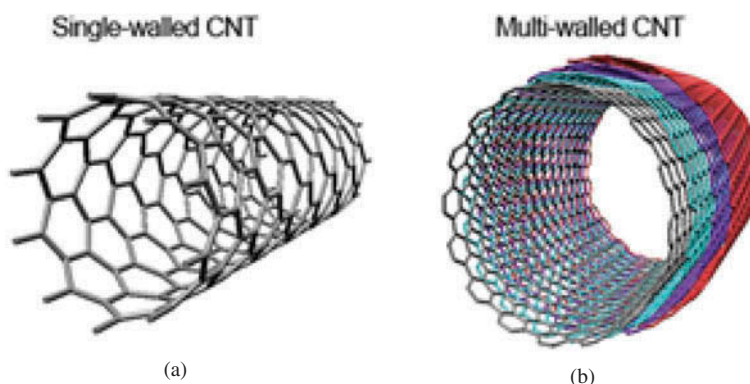
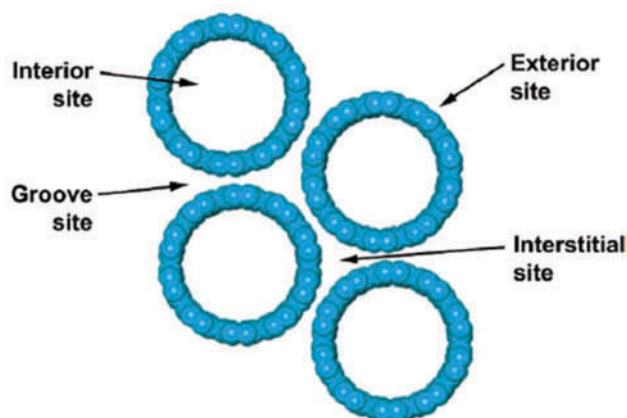


Figure 7. Schematic of hexagonally packed single-walled carbon nanotubes bundle showing the various adsorption sites (Adopted from reference (Kondratyuk & Yates, 2007))



atrazine and simazine (Zhou et al., 2006) and, naphthalene and anthracene (Ma et al., 2010). Another promising area where carbon nanotubes have been utilized is in the removal of pharmaceutical wastes. Some of the pharmaceutical wastes removed with carbon nanotubes are bisphenol A, 17 α -ethinyl estradiol (Joseph, Heo, Park, Flora, & Yoon, 2011), and tetracycline (Zhang et al., 2011).

The unique properties of carbon nanotubes have been utilized for the removal of heavy metal contaminants. Carbon nanotubes sheets were utilized in the removal of divalent metal ions such as Cu²⁺, Cd²⁺, Pb²⁺, Zn²⁺ and Co²⁺. The removal efficiency was reported to be dependent on the initial metal ion concentration and the pH of the adsorption medium since the surface charge characteristic of carbon nanotube is dependent on pH (Li et al., 2003; Lu & Chiu, 2006; Tofighy & Mohammadi, 2011). In addition to these metals, the efficiency of carbon nanotubes in adsorbing Ni²⁺ has also been investigated (Kandah & Meunier, 2007). The adsorption and removal efficiency of heavy metals by carbon nanotubes can be enhanced by forming carbon nanotube composite with other materials. Carbon nanotubes coated with alumina recorded an increased Pb²⁺ removal than the uncoated carbon nanotubes. The removal efficiency was dependent on pH and the electrostatic attraction between the negatively charged carbon nanotube surface and the positively charged lead ions (Gupta, Agarwal, & Saleh, 2011b). Carbon nanotube coated with magnesium oxide has also been examined for their potential application in water purification (Saleh & Gupta, 2012). During application, one major problem encountered is the removal of the carbon nanotubes after adsorbing the heavy metal pollutants. One way to overcome this is to form magnetic responsive carbon nanotube composite. Hu et al. synthesized a magnetic composite made up of β -cyclodextrin grafted onto multi-walled carbon nanotube/iron oxide. The improved adsorption of Pb(II) and 1-naphthol was ascribed to the presence of multiple hydroxyl groups and the hydrophobic cavity of the β -cyclodextrin which aided in the formation of metal ion and organic pollutant complexes (Hu et al., 2010). Carbon nanotube-iron oxide magnetic composite for the removal of metal ions such as Cr (III) (Gupta, Agarwal, & Saleh, 2011a; Hu et al., 2009), Cu(II) (Peng et al., 2005) and As(V) (Peng et al., 2005) have also been investigated. The main objective of creating a magnetic-carbon nanotube composite is to aid in their removal after application and also to enhance their adsorption efficiency towards heavy metals.

5.2. Antimicrobial disinfection

Many nanoparticles has been reported to possess antimicrobial properties and as a result are envisaged to find their applications in three critical areas namely; disinfection, membrane biofouling control and biofilm control (Qu, Alvarez, & Li, 2013). Different antimicrobial mechanisms of nanoparticles have been reported in literature. The nanoparticles can directly attack the microbial cell and as a result disrupt the cell envelope or produce reactive oxygen species (ROS) which can

oxidise the cell components (Li et al., 2008). Some of the nanomaterials which have been reported to possess antimicrobial activity include TiO₂, ZnO, Ag-based materials and carbon nanotubes.

A mesoporous TiO₂ has been investigated for their potential in deactivating *E. coli*. The high deactivation rate was attributed to the high surface area, small crystal size and more active site for deactivation (Liu, Wang, Yang, & Yang, 2008). The antimicrobial activity was enhanced after incorporating Ag into the TiO₂ mesoporous structure. The improved antimicrobial activity was attributed to the improved photocatalysis and the fact that Ag has an antimicrobial property (Liu et al., 2008). The photocatalytic properties of TiO₂ has been reported to be responsible for its antimicrobial activity (Kubacka et al., 2014). Irradiation of TiO₂ with UV will result in the production of ROS or radicals which can attack bacteria, algae and fungi and result in their deactivation (Blake et al., 1999). By incorporating Fe³⁺ compounds such as Fe₃(SO₄)₂, the antimicrobial efficiency is improved through the Fenton reaction (Cho, Chung, Choi, & Yoon, 2005). To aid in the easy separation of antimicrobial nanoparticles after application, a magnetic responsive nanocomposite nanoparticles made up of titania shell and nickel ferrite magnetic core has been synthesized using a combination of reverse micelle and hydrolysis processing techniques. The nickel ferrite-titania core-shell nanocomposite recorded an improved antibacterial efficiency (Rawat, Rana, Srivastava, & Misra, 2007). TiO₂, CuO and TiO₂/CuO antibacterial activity on *E. coli* and bacteriophage T4 has also been investigated (Ditta et al., 2008). The TiO₂ recorded a lower microbial killing than CuO and TiO₂/CuO. This trend was attributed to the generation of toxic Cu²⁺/Cu⁺ in the solution. The antimicrobial activity of TiO₂ has been enhanced by combining it with biocidal polymer to form TiO₂-biocidal polymer nanocomposite. A biocidal polymer is able to inhibit or kill microorganism. During UV irradiation, the TiO₂/biocidal polymer showed improved inhibition of bacterial growth against gram-negative *E. coli* and gram-positive *S. aureus* in comparison to the pristine TiO₂ nanoparticles (Kong, Song, & Jang, 2010).

It is well known that silver nanoparticles has strong biocidal effect on microorganisms (Slawson et al., 1992). Different processing techniques such as precipitation (Halaciuga, LaPlante, & Goia, 2011; Lu & Goia, 2013; Sondi, Goia, & Matijević, 2003), chemical reduction method (Zielińska et al., 2009), green synthesis (Bar et al., 2009; Sathishkumar et al., 2009; Sathishkumar, Sneha, & Yun, 2010; Sharma, Yngard, & Lin, 2009), photoreduction method (Cui et al., 2008; Tian, Chen, & Cao, 2006; Xiong, 2011) and the polyol method (Coskun, Aksoy, & Unalan, 2011; Lim et al., 2014; Wang, Zheng, Huang, & Xia, 2013) have been reported in literature. Aside silver nanoparticles, silver ions and silver-based compounds have been reported to be toxic to microorganisms (Zhao & Stevens, 1998). However, the application of silver salts as antimicrobial agent is limited due to the interfering effect of salts. This problem is solved by using silver nanoparticles but the antimicrobial efficiency of Ag nanoparticle is reported to be dependent on the characteristics of certain bacterial species (Kim et al., 2007). It has been reported that, the antimicrobial property of silver nanoparticles is dependent on their particle size, the shape of the nanoparticle (Pal, Tak, & Song, 2007) and also on the capping agent. For silver to have any antimicrobial property, it must be in its ionized form. In its ionized form, silver is inert but it releases silver ions when in contact with moisture (Ahmed, Ahmad, Swami, & Ikram, 2016; Klueh, Wagner, Kelly, Johnson, & Bryers, 2000). The silver ions form complexes with the nucleic acid of the bacterial cell resulting in their inactivation. In addition, the positively charged silver ions electrostatically interacts with the negatively charged bacterial cells (Cao, Jin, & Mirkin, 2001). These nanoparticles can accumulate inside the cell membrane and penetrates in the cell resulting in their damage. The Ag atoms can bind to the thiol group of enzymes resulting in their deactivation (Ahmed et al., 2016). Free radical generation by Ag nanoparticle also contributes to the inactivation of microorganisms (Kim et al., 2007). Silver nanoparticles has therefore being studied for their potential application in deactivating water bodies polluted with *E. coli* (Aymonier et al., 2002; Cao et al., 2010; Sondi & Salopek-Sondi, 2004; Yoon et al., 2007), *Bacillus subtilis* (Yoon et al., 2007), *S. aureus* (Cao et al., 2010; Raheman, Deshmukh, Ingle, Gade, & Rai, 2011), streptococcus pyogenes, *S. typhi*, *Klebsiella pneumoniae*, and *V. cholera* (Nanda & Saravanan, 2009), and *M. tuberculosis* (Song et al., 2006).

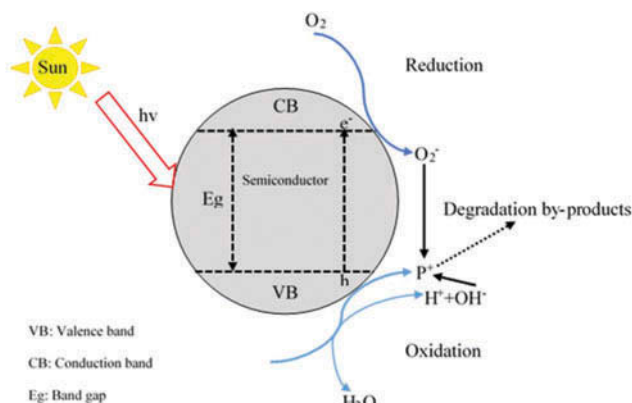
Aside its photocatalytic activity, ZnO has been reported to exhibit excellent antimicrobial activity as a function of ZnO concentration and particle size (Padmavathy & Vijayaraghavan, 2008). The excellent antimicrobial activity of ZnO nanoparticles has been examined using *Listeria monocytogenes*, *Streptococcus mutans*, *S. enteritidis*, and *E. coli* (Hernández-Sierra et al., 2008; Jin et al., 2009). The antibacterial effect of ZnO nanoparticles has been attributed to membrane damage caused by the interaction between ZnO nanoparticles and cell surface, and the production of ROS (Fu, Vary, & Lin, 2005; Stoimenov, Klinger, Marchin, & Klabunde, 2002). In view of this, ZnO and ZnO composites have been investigated for their potential application in water purification. The antimicrobial efficiency of ZnO and ZnO composites have been investigated on *C. jejuni* (Xie, He, Irwin, Jin, & Shi, 2011), gram-negative *E. coli* and gram-positive *S. aureus* (Hwang et al., 2011; Mujeeb Rahman, Muraleedaran, & Mujeeb, 2015), *Lactobacillus plantarum* (Emamifar, Kadivar, Shahedi, & Soleimanian-Zad, 2011), *S. aureus*, *S. marcescens*, *P. mirabilis* and *C. freundii* (Gunalan, Sivaraj, & Rajendran, 2012), *B. subtilis* NRRL B-543, *B. megaterium* ATCC 25848, *Sarcina lutea*, *Pseudomonas aeruginosa*, *K. pneumoniae*, *Proteus vulgaris*, *Candida albicans* and *Aspergillus niger* (Yousef & Danial, 2012) and *C. albicans* (Wang, Zhang, Zhang, & Li, 2012). ZnO showed strong deactivation rate towards these pathogens.

SWNTs have also been identified to possess antimicrobial activity. However, it should be stated that the antimicrobial mechanism of SWNTs is poorly understood (Li et al., 2008). It has been reported by Kang et al. that deactivation of *E. coli* by SWNTs results from favourable attachments and complete coverage of *E. coli* by SWNTs. Through fluorescence dye test and SEM imaging, it was confirmed that cells in contact with SWNTs suffered severe membrane damage (Kang, Pinault, Pfefferle, & Elimelech, 2007). SWNT has also been reported to be more toxic to bacteria than multi-walled carbon nanotubes (MWNTs) implying that the antimicrobial property of carbon nanotubes is dependent on the diameter of the carbon nanotube (Kang, Herzberg, Rodrigues, & Elimelech, 2008) and hence their aspect ratio. In view of this finding, Yang et al investigated the effect of carbon nanotube length on the antibacterial properties of carbon nanotubes (Yang, Mamouni, Tang, & Yang, 2010). SWNTs with longer length were more effective in deactivating bacterial than those with shorter length, implying that indeed length of nanotubes really matters. The antibacterial effect of carbon nanotubes on *E. coli* (Aslan et al., 2012; Vecitis, Zodrow, Kang, & Elimelech, 2010), *S. typhimurium* and *S. aureus* (Zardini, Amiri, Shanbedi, Maghrebi, & Baniadam, 2012), *S. typhimurium* and *B. subtilis* (Arias & Yang, 2009), and *K. pneumoniae*, *P. aeruginosa*, and *B. cereus* (Zardini et al., 2014) has also been investigated and the results were promising.

5.3. Photocatalysis

Most of the water treatment technologies discussed so far are not able to completely remove contaminants present in water. Water-soluble contaminants are very difficult to remove hence other water purification strategies need to be developed. Advanced oxidation processes as an alternative water purification technology has been proposed by several researchers. Advanced oxidation processes result in the formation of highly oxidising radical species that are able to disinfect different kinds of pollutants present in water (Andreozzi et al., 1999). Heterogeneous photocatalysis is one of the most widely investigated advanced oxidation processes. In heterogeneous photocatalysis, a semiconductor is irradiated with either a UV or visible light source in the presence of water or dissolved oxygen and this results in the generation of ROS that can degrade organic pollutants or deactivate microbes. TiO_2 is the most widely investigated photocatalyst since Fujishima and Honda (1972) reported that TiO_2 can be used in water photolysis. The fundamental concepts associated with photocatalysis have been widely reported in literature by many researchers (Fujishima & Honda, 1971; Nakata & Fujishima, 2012). When a semiconductor is irradiated with photo energy greater than or equal to the band-gap of the semiconductor, electrons are excited from the valence band to the conduction band creating an electron-hole pair. The conduction band is strongly reducing while the valence band is strongly oxidizing. The electrons and holes trapped on the surface of the semiconductor react with dissolved oxygen and water molecules resulting in the formation of ROS that can be used in degrading organic pollutants and deactivating pathogens (Fujishima, Rao, & Tryk, 2000; Gaya & Abdullah, 2008). This is illustrated in Figure 8.

Figure 8. Photo-degradation of water pollutant (P) by a semiconductor photocatalyst. Adopted from reference 166 (Chong, Jin, Chow, & Saint, 2010).



Potential application of photocatalyses in removing pathogens, organic pollutants, and heavy metals have been investigated. A brief review for each of these categories of pollutants is provided below.

5.3.1. Pathogens

The application of different semiconductors such as TiO_2 (Sichel et al., 2007), ZnO (Seven et al., 2004), and $\text{g-C}_3\text{N}_4$ (Zhao et al., 2014) in photocatalytic disinfection of water has been investigated. As already stated irradiation of a semiconductor with photon energy greater than or equal to the band-gap of that semiconductor results in the generation of ROS. These ROS attacks the cell wall of the microorganism reducing cell viability and hence rendering the microorganism inactive (deactivation) (Maness et al., 1999). Cho et al. recently reported that the OH radical is the primarily oxidation reactive species responsible for the deactivation of *E. coli* (Cho, Chung, Choi, & Yoon, 2004). In addition to the OH radical other factors also influence the disinfection efficiency. Photocatalytic disinfection of *acanthamoeba polyphaga*, *C. albicans*, *fusarium solani*, *P. aeruginosa*, *E. coli* and *B. subtilis* by ZnO and TiO_2 photocatalyst was investigated by Lonnen et al. (2005). The disinfection efficiency was reported to be dependent on reactor type, solar irradiation time, type of microbe, photocatalyst concentration and photocatalyst time. To increase the efficiency of photocatalytic disinfection of pathogens, different photocatalysts have been synthesized by coupling two or more different Semiconductors such as $\text{TiO}_2\text{-ZnO}$ (Karunakaran et al., 2011a). The efficiency of such a composite system is dependent on the valence and conduction band alignments of the employed semiconductors and their Fermi levels. The photocatalyst reported so far are effective in the UV section of the electromagnetic spectrum due to their large band-gap. Various UV-active photocatalysts have been modified to be active in the visible light while new visible light photocatalyst capable of disinfecting microbes have been synthesized and investigated. The efficiency of copper doped TiO_2 in disinfecting *E. coli* using visible light has been reported (Karunakaran et al., 2010). Other visible light active systems investigated include: Cd-TiO_2 for disinfecting *E. coli* (Karunakaran et al., 2011b), Ag-TiO_2 nanofibres for disinfecting bacteria (Liu et al., 2012), dye-sensitized TiO_2 for disinfecting *enterobacter cloacae* SM1, *erwinia carotovora* subsp. *carotovora* 3 and *e. carotovora* subsp (Yao et al., 2007) and copper doped $\text{TiO}_2/\text{glass}$ fibres for disinfecting *E. coli* (Pham & Lee, 2014).

5.3.2. Organic pollutants

Most water bodies all over the world have been polluted by organic pollutants such as dyes used in the textile industries and water-soluble petroleum components such as benzene, toluene and xylene (BTX). Reactive oxidation species through photocatalysis can be used to degrade these components into innocuous compounds that are biodegradable and less toxic. The organic pollutants are essentially mineralized into CO_2 . The photocatalytic degradation efficiency has been reported to be dependent on pH, catalyst loading, catalyst type, catalyst processing technique used, structural morphology of the photocatalyst, initial pollutant concentration, irradiation

intensity and time, and type of pollutant (Akpan & Hameed, 2009). Similar to the discussion on photocatalytic disinfection of microbes, degradation of organic pollutants through photocatalysis has been achieved through both visible and UV-active photocatalysts.

Photocatalytic degradation of organic dyes such as methylene blue, rhodamine B, AZO dyes Congo red, indigo, indigo carmine and methyl red has been widely investigated (Konstantinou & Albanis, 2004; Lachheb et al., 2002; Vautier, Guillard, & Herrmann, 2001; Xiong, Zhang, Ma, & Zhao, 2010). The degradation of water-soluble dyes by different photocatalyst such as reduced graphene oxide pillared with carbon nanotubes (Zhang, Xiong, & Zhao, 2010), TiO_2 (Neppolian, Choi, Sakthivel, Arabindoo, & Murugesan, 2002), SnO/TiO_2 (Vinodgopal & Kamat, 1995), Au-ZnO (Pawinrat, Mekasuwandumrong, & Panpranot, 2009), Ag_3PO_4 (Ge, Zhu, Zhao, Li, & Liu, 2012), and Ag_2CO_3 (Dai, Yu, & Liu, 2012) has been investigated. Aside dyes, current studies have shown that most water bodies are polluted through agro chemicals such as pesticides (Geissen et al., 2015). Photocatalytic degradation of cyproconazole (Lhomme, Brosillon, & Wolbert, 2008), azoxyxtrobin, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil, primicarb (Navarro, Fenoll, Vela, Ruiz, & Navarro, 2009), chlorpyrifos, cypermethrin, chlorothalonil (Affam and Chaudhuri, 2013), and tetrachlorvinphos, fenitrothion, pirimiphos-methyl, and fenamiphos (Herrmann & Guillard, 2000) has been reported with the final degradation product being CO_2 . In areas where oil is drilled and transported, the major water pollutants are BTX which are all water soluble. Since photocatalysis works better in an environment with enough water and dissolved oxygen, these pollutants can easily be oxidized through photocatalysis into innocuous compounds that are biodegradable and less toxic and finally mineralized into CO_2 . The concept of removing BTX from contaminated water bodies through photocatalysis has been proven using W-doped TiO_2 (Laokiat et al., 2012; Sangkhun et al., 2012), TiO_2 (Cho et al., 2006; Martinez, Bertron, Escadeillas, Ringot, & Simon, 2014), $\text{TiO}_2/\text{SiO}_2$ immobilized on aluminium sheets (Tasbihi, Kete, Raichur, Tušar, & Stangar, 2012), Ag/TiO_2 thin films on PVC (Peerakiathkajorn et al., 2012) and reduced graphene/ TiO_2 nanocomposite (Singh et al., 2015).

5.3.3. Heavy metals

The potential application of photocatalysis in removing heavy metals such as cyanide and arsenic in water bodies has received a lot of attention from researchers. Photocatalytic removal of heavy metals is achieved by either reducing or oxidizing the metal to a less toxic and harmful form (Barakat, 2011). As an example, chromium (VI) which is more toxic can be reduced to a less harmful form chromium (III) through photocatalysis (Chen & Ray, 2001; Yoon, Shim, Bae, & Joo, 2009). The Cr(III) is easily coprecipitated through the addition of $\text{Fe}(\text{OH})_3$ (Wang, Pehkonen, & Ray, 2004). Arsenic is one of the major water pollutants in mining communities. A similar concept can be used to oxidized a more toxic As(III) to a less toxic and less water-soluble form As(V) (Guan et al., 2012; Lee & Choi, 2002). TiO_2 is the most widely used photocatalyst applied in the removal of arsenic from contaminated water bodies (Fostier, Pereira, Rath, & Guimarães, 2008). The rate of oxidation of As(III) to As(V) has been reported to be dependent on pH, catalyst amount, and irradiation time and intensity (Dutta, Pehkonen, Sharma, & Ray, 2005). The removal efficiency has been enhanced through the addition of adsorbent. That is arsenic ions [As(III) and As(V)] is easily removed from aqueous media by activated alumina as an adsorbent (Nakajima et al., 2005). In addition to arsenic, cyanides can be removed from contaminated water bodies through photocatalysis (Frank & Bard, 1977a). The photocatalytic removal of cyanides involves (a) reaction between the CN^- and the hydroxyl radicals to form cyanide radicals which dimerize to form cyanogen, (b) cyanate is then formed by the dismutation of the cyanogen, and (c) oxidation of the cyanate leading to the formation of CO_2 and NO_3^- (Chiang, Amal, & Tran, 2002; Doménech & Peral, 1988). The removal of cyanides has been investigated using TiO_2 (Frank & Bard, 1977b; Siboni, Samarghandi, Yang, & Lee, 2011), $\text{TiO}_2\text{-SiO}_2$ (Ismail, Ibrahim, Ahmed, Mohamed, & El-Shall, 2004), Ce-doped ZnO (Karunakaran, Gomathisankar, & Manikandan, 2010), carbon naotubes/ZnO nanocomposites (Saleh, Gondal, & Drmosh, 2010) and copper phthalocyanine-zeolite X composite (Mohamed & Mohamed, 2008). A summary of some nanomaterials and their application in water purification are presented in Table 4.

Table 4. Different nanomaterials and their application in water purification

Material	Contaminants	Removal efficiency	Reference
Adsorption and a combination of adsorption and photocatalysis			
TiO ₂	As(III), As(IV) Monomethylarsonic and dimethylarsonic Cd ²⁺	100% 85–95% 142.24 μmol/g	Xu et al. (2007) Gao et al. (2004)
TiO ₂ /activated carbon	Bisphenol-A	204 mg/g	Lim et al. (2011)
TiO ₂ /zeolite	Bisphenol-A and intermediate compounds	Not stated	Fukahori et al. (2003)
TiO ₂ /chitosan	Rhodamine B	94.3%	Zhang et al. (2011)
TiO ₂ /Fe ₂ O ₃	As(III) As(IV)	79–80% 95–99%	Zhou et al. (2008)
Titanate nanofibers	Sr ²⁺ Ba ²⁺ Pb ²⁺	0.57–0.68 mmol/g 0.95–1.17 mmol/g 1.18–1.35 mmol/g	Yang et al. (2008)
Fe ₃ O ₄	Cr(IV) As(V)	84.6–99.8%	Hu et al. (2004)
Fe ₃ O ₄ /humid acid	Ag(II), Pb(II) Cu(II), Cd(II)	>99% >95%	Liu et al. (2008)
Fe ₂ O ₃	Cr(IV) As(V)	3.86–4.47 mg/g 4.75–5.31 mg/g	Zhong et al. (2006)
Carbon nanotubes	Atrazine and simazine Anthracene and naphthalene Cu ²⁺ Cd ²⁺ Pb ²⁺ Zn ²⁺ Co ²⁺ Ni ²⁺	>80% ~100% 50.37 mg/g 75.84 mg/g 101.05 mg/g 58 mg/g 69.63 mg/g 12.3–37 mg/g	Zhou et al. (2006) Ma et al. (2010) Tofiqhy and Mohammadi (2011) Kandah and Meunier (2007)
Carbon nanotubes-Fe ₃ O ₄ magnetic nanoparticles	Cr(III) Pb(II) Cu(II)	~90% 0.51 mmol/g 0.71 mmol/g	Gupta et al. (2011a) Peng et al. (2005)
Carbon naotube-ceria nanoparticles	As(V)	78.8–81.9 mg/g	Peng et al. (2005)
Antimicrobial agents			
TiO ₂	<i>Escherichia coli</i>	7.6% survival ratio	Liu et al. (2008)
TiO ₂ shell and nickle ferrite magnetic core	<i>E. coli</i>	Decrease in E.Coli concentration to <10 ⁶ CFU/ml	Rawat et al. (2007)
TiO ₂ /CuO composite	<i>E. coli</i> and bacteriophage T4	>9 log reduction	Ditta et al. (2008)
Ag nanoparticles	<i>B. subtilis</i> <i>S. pyogenes</i> <i>S. typhi</i> <i>K. pneumoniae</i> <i>V. cholerae</i> Methicillin resistant staphylococcus epidermidis Methicillin resistant <i>Staphylococcus aureus</i>	Susceptibility value of 0.0622 ml/μg Survival diameter 16 mm 11 mm 0.8 mm Nill 18 mm 17.5 mm	Yoon et al. (2007) Nanda and Saravanan (2009)
ZnO	<i>L. monocytogenes</i> <i>Streptococcus mutans</i>	1.4 log CFU/ml Minimum bacterial concentration of 500 μg/ml	Jin et al. (2009) Hernández-Sierra et al. (2008)

(Continued)

Material	Contaminants	Removal efficiency	Reference
Photocatalysis			
TiO ₂	Acanthamoeba polyphaga Candida albicans E. coli B. subtilis	>4 log unit reduction 1.7 log unit reduction	Lonnen et al. (2005)
g-C ₃ N ₄	E. coli	2 × 10 ⁷ CFU/mL	Zhao et al. (2014)
TiO ₂ -ZnO	E. coli	2.2 × 10 ¹⁴ CFU/mL bacterial survival	Karunakaran et al. (2011a)
TiO ₂ -Cd	E. coli	~0 CFU/mL survival	Karunakaran et al. (2011b)
Au-ZnO	Methylene blue	71% degradation	Pawinrat et al. (2009)
Ag ₃ PO ₄	Rhodamine blue	~100% degradation	Ge et al. (2012)
Ag ₂ CO ₃	Rhodamine blue	~100% degradation	Dai et al. (2012)
TiO ₂	Reactive yellow 17 Reactive red 2 Reactive blue 4	94% degradation 95% degradation 88% degradation	Neppolian et al. (2002)
TiO ₂	Cr(VI) Pb(II) Fe(III) Cr(VI) As(III)	79% removal 27.2% removal 100% removal 100% removal 500 µm As(V) formed from As(III)	Chen and Ray (2001) Yoon et al. (2009) Guan et al. (2012)
Carbon nanotubed/ZnO nanocomposite	Cyanide	~90% degradation	Saleh et al. (2010)

From the review above, the application of nanotechnology in water purification systems has been widely investigated. However, practical application of these technologies has not been realized. One major challenge facing nanotechnology is scale up. Macro-assembly of nanomaterials results in a dramatic change in the chemical and physical properties of nanomaterials which affect negatively on their performance. More research should therefore be channelled towards investigating into the different processes that can be used to assemble these nanomaterials without having any negative effect on their performance. In addition, most of the processing techniques used in synthesizing these nanomaterials are costly making their scale up expensive. New and simple processing techniques should therefore be developed. The photocatalytic application in water purification systems has a lot of challenges. These include synthesizing photocatalysts that are active and also stable in the visible light. Mixing of the photocatalyst and the contaminated water to form slurry is the best way of increasing purification efficiency since mass transfer limitation is reduced. However, separation of the photocatalysts in such a system is difficult hence immobilization of the photocatalysts onto supports has been employed. The immobilization however reduces the active surface area available for photocatalysis and hence reduces the purification efficiency. More research should therefore be conducted to make the practical and large scale application of nanomaterials in water purification systems a reality.

6. Recommendations and conclusion

Many countries in the world are endowed with enormous quantities of clays deposits. The mineral compositions of local deposits might differ depending on the formation process of the geographical location. The weathering and other factors such as human factors may have affected the chemical compositions over the years, however researchers must ensure key chemical oxides are present in relevant quantities for various applications. The fundamental explanations of some key issues in water filtration are tackled along the main categories of contaminants in drinking water initiates this paper. In this paper, we have elaborated on the types of clays that are common and their associated benefits with reference to water filtration and nanotechnology. Various

techniques or mechanisms that can be employed in the water filtration systems have also been systematically highlighted. It is imperative however to undertake research in regional communities to underscore possible differences in major oxides. This could be done via X-ray diffraction studies and X-ray fluorescence analysis. There are other deposits that could be rich in other oxides that may be explored for other environmental benign applications.

The efficiency of water purification systems can be enhanced through the application of nanotechnology. These nanomaterials possess high surface to volume ratios and high aspect ratios and hence have a lot of active sites to enhance the removal of pollutants through adsorption, microbial disinfection and photocatalysis. Nanomaterials can therefore be used in developing water purification systems or combined with other macromaterials. However, the pollutant removal efficiency of these nanomaterials can be greatly reduced during macro assembly. Research should therefore be conducted to develop techniques that can be used to assemble nanomaterials without reducing their efficiency.

List of Abbreviation

WHO-	World Health Organization
MDG's-	millennium development goals
SDG's -	sustainable development goals
HWTS-	Household Treatment Water Treatment System
FC-	faecal coliform
XRD -	X-ray diffraction
XRF -	X-ray fluorescence
GI-	gastrointestinal illness
MIT -	Massachusetts Institute of Technology
EPA-	environmental protection agency
BET-	Brunuar, Emmet, and Teller
HSDM-	homogeneous solid diffusion model
MMT -	montmorillonite
<i>E. Coli</i> -	<i>Escherichia coli</i>
LRV-	logarithm return value
MMA-	monomethylarsonic acid
DMA-	dimethylarsinic acid
ROS-	reactive oxygen species
SWCNTs-	single-walled carbon nanotubes
MWNTs-	multi-walled carbon nanotubes
UV-	ultraviolet
BTX-	xylene
PVC-	polyvinyl chloride

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