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Natural Materials and Methods Used in Water Purification: A Review

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Review Article

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ABSTRACT

The review article presents the prevalent water problems; from needs, scarcity, management, pollution and the risk associated with waterborne disease. It also discusses the remediation methods using natural materials such as clay, activated carbon, zeolites, sand, rice husk, chitosan, hydroxyapatite, LECA, to combat the microbial, organic and inorganic pollutants. It includes insights from papers collected from original research work and reviews that covers the areas of study. The review serves as a guide to the authors who are working on the development of modified expanded clay aggregates for multiple contaminants removal.

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1. INTRODUCTION

One of the twenty first century's issues is water. Water is needed by all human, plants and animals for economic productivity and social well-being. Lack of water has enormous consequence and affects the general well-being of humans and limits economic development. Water and its importance has been a subject of discuss and a reoccurring decimal at United Nation's meetings. For instance, in her meeting at Rio de Jainero 1992 [1], several programme areas which included; integrated water resources development and management; water resources assessment; protection of water resources, water quality and aquatic ecosystems; drinking water supply and sanitation; water and sustainable urban development; water for sustainable food production and rural development and impacts of climate change on water resources were proposed for freshwater sector. Three decades after, water problems are still persistent.

Deeply concerned about the global lack to safe water and sanitation, the United Nations in its 2010 general assembly declared safe, clean and affordable drinking water and sanitation as basic human rights because they are essential to the sustainability of healthy living and fundamental in maintaining the dignity of all human beings [2]. This resolution was reaffirmed in 2019 and 2020 [3,4]. Previous declarations such as "International Year of Freshwater" (2003), "International Decade for Action 'Water for Life'" (2005-2015) and International Year of Sanitation (2008) culminated into the 2010 declaration. Despite the efforts of donor agencies, government and all relevant stakeholders on water and sanitation, billions of people globally still lack access to these basic needs although successes were recorded on improved services from 2000 to 2017 [5,6]. Goals and targets are set, monitored and reported from time to time. The Millennium Development Goal 7 worked towards halving the proportion of world population without sustainable access to safe drinking water and basic sanitation by the year 2015. Result indicated that, people without access to clean water reduced to 9% from baseline level of 24% while that of sanitation was missed and only reduced from 46% to 32% [7]. Currently, UN environment programme reported that global data availability increased to 59 per cent in 2022, from 34 per cent in 2018 and 42 per cent in 2020. And although only 38 per cent of the environment-related indicators indicate environmental improvement, this is a solid improvement compared to only 28 per cent in 2020 [8]. The Sustainable Development Goal 6 targets ensuring that clean, safe and affordable water and sanitation are accessible to all by the year 2030. This goal when actualized, will indirectly affect the attainment of other goals such as goal 1, 3, 5 and 15. The vulnerable, people living in poverty and least powerful are those without access to water and these could impede their potentials and visions [9].

1.1 Global Access to Drinking Water and Challenges

The challenge of access to clean water has been there since time immemorial. In the 1900s about 0.24 billion (14% of global population) are without access to clean water. The figure increased to 3.8 billion (58%) in the 2000s [10]. Despite the achievement of the MDG goal 7C, i. e increment on successful access from 71% in 1990 to 91% in 2015 [11], many people are still without access to clean water globally. Global coverage point at 96% success if current indicator trends are maintained [12]. Due to growing population, socio-economic development, climate change, industrial and domestic usage, water use has been growing to about 1% since 1980 and it is expected to last up to 2050 [10,13]. The United Nation's world water development report 2019 also mentioned that over 2 billion people live in countries with high water stressed areas whereas about 4 billion people experience severe water scarcity at least one month in a year.

The disappearing rivers, shrinking lakes and dams will continue to be a global problem if adequate measures are not put in place. Agriculture and in turn food security is being threatened by water scarcity. Climate change has been identified as one of the major nexus of water challenge which give rise to higher temperature of seas, melting of the glaciers and intensification of water cycles that results in more flood and droughts [14-18]. Population explosion and urbanization contribute to groundwater depletion, salinity and other contamination and water shortages especially in the arid and semi-arid regions [19,20].

Fig. 1. Disappearing Aral sea [21]

Aral Sea in Kazakhstan North Uzbekistan Central Asia (Fig. 1) that used to be the world's fourth largest lake is about 10% its original size [21]. In 1998, it was reported that water level was down by 20m and a volume of 210km^3 as compared to 1, 060 km^3 in 1960 and 68, 000km^3 original size causing the lake to split into four lakes. The southern and eastern lakes that made up the southern Aral Sea shrunk to strip around 2009. While the southern lake keeps disappearing and reappearing, the eastern lake dried up completely in 2014 making a history. It is now known as the Aralkum Desert [22]. Efforts are being made to salvage the drying north Aral Sea by dam construction around the area that supplies the salty lake with fresh water although some researcher believed that the lake will dry up completely by the year 2020. Drought and irrigational diversions are major causes of such shrinkage [23].

The Sea of Galilee (Fig. 2) has receded for over 30 years due to drop in annual rainfall. In 2018, water level dropped to the lowest causing the Sea to become more salty and less viable as drinking water [21]. Desalination and expensive purification methods become necessary. However, water level has gradually increased since the rainy season of 2019 and as at April 2020, it rose about 16cm below the upper red line [22].

Poyang Lake in China and Lake Chad have been in the media report for the past decades. Notably, Lake Chad which is the sixth largest lake in the world is fast diminishing [25,26]. Bordered by Nigeria, Chad, Niger and Cameroun, the lake became about one tenth of its 1960 original size in 2017 (Fig. 3). It was reported that the lake spanned at least 22,000 Km^2 in the 60s [27] and 25, 000 Km^2 [18]. In the 70s, water started disappearing and reappearing in the Northern region depending on the season. However, the northern and southern region never reconnected back again as a whole lake. Hydrological and VIC models which was used to study the water level and extension [28,26] revealed that shortage of rainfall and continues drought around the basin contributed to drying of the lake. However, a proper management of renewable water resources was recommended. Models and satellite data are being used by researchers to understudy the lake as insurgency, kidnappings, bombings and wars have made ground-based measurements difficult to achieve.

The means of livelihood of the rural dwellers within the lake which comprises; farming, fishing, livestock farming, suffer a lot of setbacks. The ripple effects of this also forced the herdsmen to migrate down south in search of greener pastures and causing more bloodshed when they are not in peaceful coexistence with their host communities. Lake drying affects the socio-economic activities, draw backs and livelihood opportunities of the dwellers [29]. The water resources renewable management, joint inter-governmental efforts, political wills, developmental assistance, agricultural practices, etc are some of the strategies that will revitalize the lake and give succor to the communities that depend on it for survival. Conferences and seminars are being held among international communities as in the case of Lake Chad to save the lake in order to revive the basin's ecosystem for sustainable livelihood security and development.

Fig. 2. Map showing the drying Sea of Galilee

(NASA Earth Observatory images by Joshua Stevens, using Landsat data from the U.S Geological Survey and topographic data from the Shuttle Radar Topography Mission (SRTM) 2020. [24]

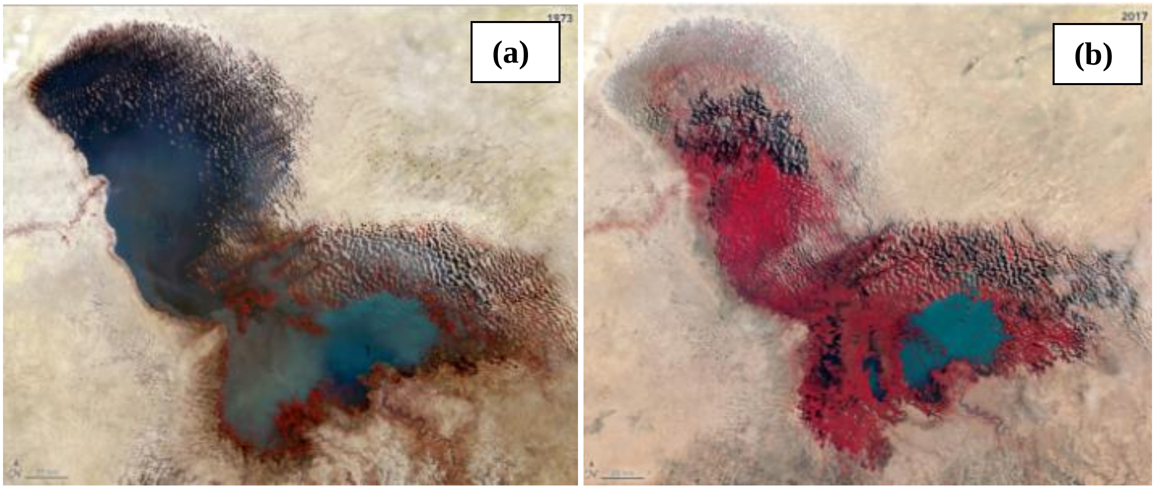

Fig. 3. Disappearing lake Chad (a) 1973 and (b) 2017 [30]

Consequently, this public outcry on the disappearing lakes, seas, rivers, dams and streams contribute to water scarcity and access lacked by one third of the world's population. Water productivity is low in most countries and the available ones are poorly managed. It is estimated that when enough water is produced, food production will double by the year 2050 thereby reducing the number of 925 million mal-nourished people on earth [14,31] since agriculture is the major consumer of fresh water. Research study on impacts on freshwater availability and further implications for global food production reported that 24% of the global population lives in area under chronic scarcity while 19% live under occasional water scarcity which consequently results in about 2.6 billion people living some degree of poor reference diet [32]. Organic and Inorganic pollutions as a result of human factors and natural disasters are also major problems with water which should necessitate remediation measures. Some of the trends and treatment technologies are reported in Warren-Vega's et al review [33].

1.2 Access to Safe Drinking Water in Africa

It was perceived that Africa has water scarcity which may lead to water crises. Global indicators and statistics are making it more real than myth [34]. The Joint Monitoring Program (JMP) report on Progress on household drinking water, sanitation and hygiene, quoted that "in 2017, nine out of ten of the 785 million people who still used limited services, unimproved sources or surface water live in three regions: Sub-Saharan Africa (400 million), Eastern and South-Eastern Asia (161 million), and Central and South Asia (145 million). More than half of the 144 million people who still collected water directly from rivers, lakes and ponds lived in Sub-Saharan Africa" [12].

General household survey using Probit regression in 2014 showed that about 29.68 % of the people living within a study area in South Africa pay for safe drinking water. Also, the survey reported that children under age five suffers diarrhea mobility due to fecal contamination resulting from lack of basic sanitation and exposure to pathogens via the food chain [35]. Similar result was reported for Limpopo province, South Africa [36]. Armah et al. [37] used a pooled regression analysis of the compositional and contextual factors that systematically vary with access to water and sanitation services over a 25-year time period in fifteen countries across sub-Saharan Africa (SSA) in their study. The study reported provision of access to improved water sources from 1990 to 2015 as against unimproved sanitation facilities over the same period which was attributed to environmental, cultural, economic and human behavior. Similar studies conducted about a poor peri-urban settlements of Abidjan, CoÃte d'Ivoire, using multivariate logistic regression model showed that about 25% of people do not have access to clean safe water while 57% lack basic sanitation practice [38]. In Eswatini (formerly known as Swaziland), Eswatini Multiple Indicator Cluster Surveys (EMCSs) data for access to clean water in 2010 and 2014 was analyzed using Bivariate and Multivariate complementary log-log regression, households' access to improved drinking water sources significantly improved from 73.1% in 2010 to 77.7% in 2014 (p < 0.0001) [39]. According to the study, in 2010, household heads between ages 35-54 years irrespective of sex had improved access while age 55 years and above had lower odds towards improved drinking water sources whereas in 2014, the lower odds were from households with female heads and more populated household. Successes in both years were attributed to wealth index of household.

1.3 Access to Safe Drinking Water in Nigeria

Nigeria is the largest country in Africa with a population of over 182 million people as at 2017 [40] and over 209 million in early 2021 [41]. Access to Water Sanitation and Hygiene (WASH) is markedly lower than counterpart countries. 57 million people continued to live with poor access to clean water while 130 million practice poor sanitation systems. The Nigeria water sector faces significant challenges [6,40]. Drinking water supply and distribution in Nigeria is still low despite being blessed with adequate water sources. Notably, there are variations between water sources availability in the North and the South. Mean number of rainy days' decrease from South to North. No part of Nigeria can claim good access to safe and affordable drinking water despite the natural water supply policy whose aim is to ensure adequate supply of quantity, quality and affordable access to safe drinking water for all citizens. National water programmes have been in existence since the 1960s. Lake Chad and the Niger River Basins Commission were set up within the Country and bordered countries while the Sokoto Rima and the Chad Basin Authorities were established in 1976 [42]. Other water issues related Agencies and Institutions including international organizations were set up to develop Nigeria's water resources and management to cushion the effect of anticipated population expansion and urbanization, yet most cities and citizens still lack access to clean water as result of poor performance of these agencies [40].

However, Nigeria recorded improved water supply from 47% in 1990 to 58% in 2008, she did not meet the benchmark of Millennium Development Goal (MDG) of 75% coverage by 2015 [43]. Research surveys using different models for analysis on access, quality, quantity, reliable and affordable in different parts of Nigeria showed poor access to quality water [44]. Some states like Lagos and Kwara have more access to pipe borne water than the Ebonyi and Taraba [45].

1.4 Factors Affecting Access to Drinking Water in Nigeria

The factors that affect access to drinking water in Nigeria are both man-made and natural phenomenon. In 2007, the Inter-Governmental Panel for Climate Change (IPCC), reported that global warming will be more intense in African than the rest of the world [46]. The climate change will be characterized by rising temperature which will amplify water loss with highest increase in the Western Sahara Region. Such proposition is now playing out especially in the non-coastal region of Africa; Nigeria inclusive.

The amount of time spent in collecting water (distance to the water source, queuing, filling of water containers and going back home) is high in countries where access to drinking water supplies located on premises is not common. Time factor associated with water scarcity is a man-made factor. WHO/UNICEF used threshold of 30 minute for water collection, above such time is described as limited access. Cassivi et al household survey in seventeen (17) countries with lowest rankings when it comes to on-premises water access, highlighted the burden of time factor which decreased access to water by 13% on the average when a 30 minute collection time was used as a monitor [47]. Similar result was reported for 23 countries where 50% of the population depends on the water sources outside their compounds where the main responsibility of fetching water lies more on women and children [48,49]. Rapid industrialization, population growth, climate change [50-53], and socio-economic status and slum settlement characteristics such as poor practices of water usage [54-56], contamination from sewage and latrines have been reported to be part of the factors that affect access to safe drinking water in some localities.

Abubakar utilized descriptive and inferential statistics to evaluate factors that influence household access to drinking water in Nigeria [57]. The reported regression analytical findings included but not limited to place of residence (χ^2=8328.2), geopolitical zone (χ^2=12042.8), education (χ^2=5346.2), wealth index (χ^2=16540.3), ethnicity (χ^2=8649.9), access to electricity (χ^2=8040.9), and gender (χ^2=537.3). Similar findings ($p < 0.01$) was reported by Akoteyon [58]. Other factors reported in literature are; corrupt government, failed central planning and implementation of water policies and standards [51], poor operation and maintenance practice of existing water treatment plants [59,40], drought due to human water consumption [60], insurgency, ethnic and tribal conflicts which often result in communal clashes and war [61,62].

1.5 Strategies for Improving Access to Drinking Water in Nigeria

Interdisciplinary research among scholars and research findings domestication by industries should be encouraged [37]. Socio-economic factors such as improved Gross national Income (GNI), policy interventions and implementation, control of corruption, political stability by the government can help improve access to clean and affordable water [63-66]. Physical aspect of water scarcity can be controlled by better management, establishing water supply infrastructure including mini water scheme, infiltration gallery and rural water collection pattern [67-70], increase sustainability to cushion evolving challenges [10,34], good water practices in terms of consumption /use and cost recovery [71,72] and recognizing local water vendors through public private partnership and hence control their charges which is higher than the average water board rate [73].

2. SOURCES OF WATER

The sources of water supply are broadly grouped into surface and ground water sources. Earth's water distribution constituents as shown in Fig. 4. Only about 2.5% is freshwater from which 30.1 % are underground, 1.2% are surface and 68.7% are trapped as glaciers and ice [74]. No wonder the global water crises, the compositions of river water are 0.49% while lake is 20.9%. The water characteristics, importance, resources, issues, challenges and management was discussed extensively in Olusumbo's lecture [42]. With increase in drying rivers and lakes due to climatic conditions and other prevailing issues, water recovery and treatment becomes necessary to mitigate such challenges. The sources of water affect the raw water quality which in turn determines the type of treatment and finished product expected. Treatment choice is largely determined by the quality of raw water, available processes, cost and the expected standard.

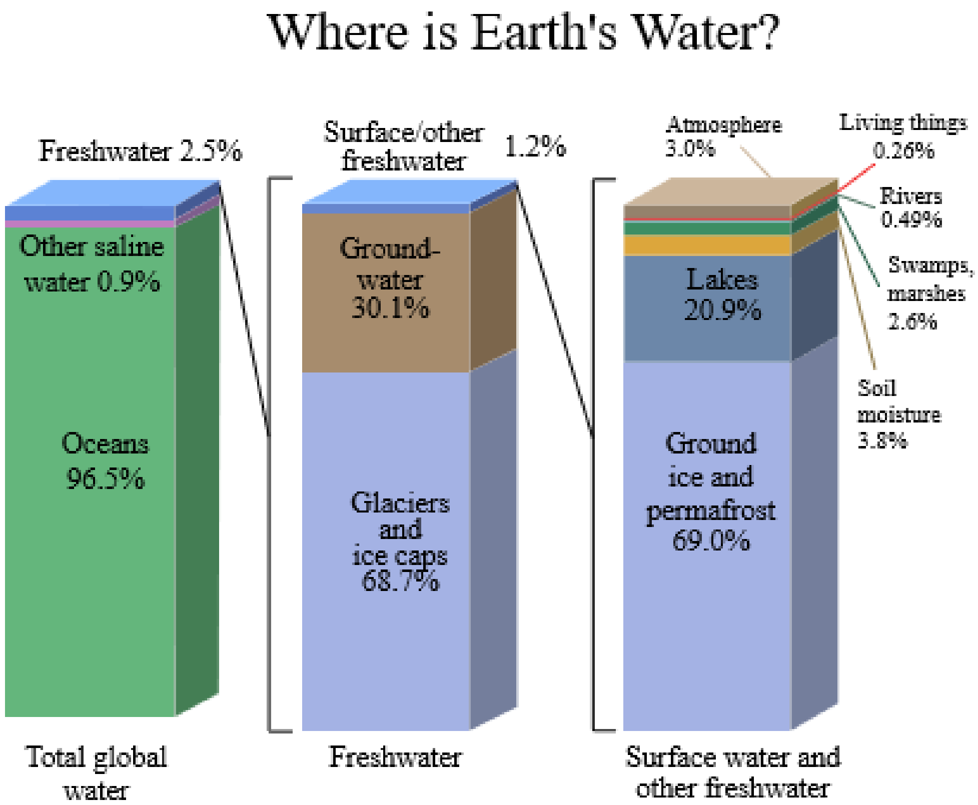

Fig. 4. The earth's water distribution [75]

2.1 Surface Water

Surface water includes; rivers, dams, lakes, canals and streams. They are easily contaminated by bacteria, protozoa and algae. These contaminants may arise as a result of runoff water after rainfall which carries a lot of particles from human habitation, agricultural fertilizers, pesticides, chemicals and industrial waste. Sewage, sludge and industrial effluents are usually discharged in surface water or in landfills in developing countries and quasi-developed countries. It is usually recommended that the water sources be cordoned off from human activities and should be surrounded by buffer zones covering a lot of area. The buffer zones help to filter out the large particles and prevent them from getting into the source. Rain and fog harvest may be considered sources of surface water [76].

2.2 Ground Water

This is mainly wells and boreholes dug underneath the earth surface into the water aquifers to extract water. These aquifers may have come to be as a result of rainfall over several years ago. Some aquifers are confined beneath rocks while some are found just some are found just below the water table. The quality of water here is determined by the depth of the well or borehole. Deep ground water is naturally filtered by materials such as soil, clay and rocks. These materials clean the water and present it with clarity and low in turbidity. It is usually free from pathogens and bacteria but contains a lot of dissolved carbonates, sulfates of calcium and magnesium and heavy metals especially cadmium and arsenic for shallow wells [77]. Nitrate, pesticides and other agrochemicals diffused from agricultural activities are widespread in groundwater which causes irreversible pollution. Once groundwater is polluted, aquifer zones tend to remain with polluted water [78].

3. SAFE DRINKING WATER: STANDARDS AND QUALITIES (WATER SAFETY)

Water has direct impart to human's health, whether used for domestic purposes, drinking, food/beverage production or recreational activities [79,80]. The quality of water is not to be compromised as the human body is more than 60%water [81]. Visualization of water such as odour, clarity and taste are not guaranteed ways of ascertaining water quality as clarity does not mean standard. Physical/chemical assessment and monitoring of water quality/standard are necessary and should be done periodically to ascertain the level of contamination at all times. Physical parameters such as pH, turbidity, colour, acidity, alkalinity and chemical contaminants such as levels of chlorides, nitrates, fluorides, nitrates, ammonium, phosphorous, chemical oxygen demand (COD), total dissolved oxygen (TDO), lead, arsenic, cadmium, etc are tested to measure standard. Biological assessments to determine the contaminants like bacteria (Escherichia coli (E.coli)), algae pathogens viruses and fungi are equally necessary as exceeding the acceptable limit may pose danger to health [82].

Water quality is not only achieved by purification; deficient minerals may be added to improve the properties. The water quality standards are predominately covered by World Health Organization Guidelines for Drinking Water and other international organizations [83]. However, every nation has its own standard which is usually extracted from international standard with little or no modifications. These standards are subject to change as soon as new water related discoveries are established through research. More so, quality standard depends on the given application of the water which in turn determines the maximum allowable level of pollution. Nigerian standard for drinking water quality was established in 2005 by National Council for Water Resources (NCWR) when it was discovered that the operational standards established by Standards Organization of Nigeria (SON) and Federal Ministry of Environment were not well accepted by all stakeholders [84]. It is sad to note that water quality and standards are not been enforced or checked in most developing countries including Nigeria especially around the urban areas.

4. WATER CONTAMINANTS

Common contaminants or pollutants found in drinking water may lead to chronic health effects like cancer, liver, bladder and kidney problems when they are above permissible threshold. These contaminants are grouped into microbial, chemical pollutants (organic and inorganic) and disinfection by-products contaminants. Others include biological pollutants such as turbidity, organic matter, natural and anthropogenic which occurs due to seasonal factors. Chemical pollutants include heavy metals and metalloids and other synthetic organic chemicals. They can be transmitted through food chain that are irrigated with contaminated water or poisonous chemicals that are absorbed by aquatic animals like fishes and sea foods. Swimming frequently in contaminate surface water can also lead to illnesses which affect human health. The global discuss on water pollution was captured in Schwarzenbach et al's [85] review even though it is inexhaustible.

4.1 Microbial Contaminants (Pathogens)

Microbes with minute infectious dose (e.g., *Giardia, Cryptosporidium*, and *Shigella* species; hepatitis A virus; enteric viruses; and enter hemorrhagic *Escherichia coli*) may cause illnesses no matter how little is swallowed. This is because total immunity does not develop for most enteric pathogens and hence may induce a re-infection [86]. *Cryptosporidium* is an emerging pollutant excreted from oocyst from infected animal with currently no specific cure. It is a protozoan, gastrointestinal parasite which gives rise to severe, self-limiting diarrhea when ingested. This has caused waterborne disease outbreaks in United Kingdom and United States of America killing immune-compromised patients [87]. Some pathogens like *Aeromonas* species are harmless [88]. *Pseudomonas aeruginosa* may multiply during distribution and known to cause infection in patients with weak immune system [89]. Traditionally, it is believed that freezing of water eliminates microorganism. This is not true as most enteric pathogens and organisms including *shigella* species and *salmonella typhosa*, hepatitis A virus, and *cryptosporidium* species can survive for a long period of time in both cold and frozen waters [90].

4.2 Inorganic Contaminants

These include heavy metals such as Lead (Pb), Zinc (Zn), Chromium (Cr), Nickel (Ni), Mercury (Hg), Copper (Cu), Cadmium (Cd), Pitmuim (Pu) and metalloids such as Arsenic (As) and Selenium (Se). They are highly toxic even when present in small quantities. Their transport mechanisms depend on reactions to varying conditions which include but not limited to oxidation/reduction, adsorption, complexation, and precipitation/dissolution reactions. X-ray spectroscropies have become veritable tool in the study of metal ions and their interaction on mineral surfaces and at such exposes the factors that affect the mobility of metal ions.

4.3 Organic Contaminants

Organic contaminants or pollutants are compounds that contain carbon, hydrogen and other elements. They include pesticides, herbicides, pharmaceuticals, hydrocarbons, phenols, plasticizers, tissues of plants and animals. Most organic contaminants originate from domestic sewage (septic tanks, latrines), urban run-off from rains, industrial effluents and agriculture wastewater, sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. Presence in traces or quantum of organic contaminants in food, water or environment may pose harmful to health due to their undesirable properties such as toxicity and flammability [91,92] especially the Persistent Organic Pollutants (POPs). Organic contaminants exhibit different transport mechanisms from inorganic ones. They exhibit partitioning behavior in environment and therefore require different methodological approach in analyzing them. More complex multi-functional polar chemicals such as biological active compounds (pesticides, biocides, herbicides and pharmaceuticals) are very difficult to analyze. Common materials used in disinfection are chemical based materials, biochars, activated carbon, clay and composite membranes, etc. There are so many reported research and reviews on the successful use of these materials in the removal of organic pollutants [93-96]. Mechanisms of destruction are commonly by oxidation, partition, adsorption or thermal decomposition [96,97].

5. WATER TREATMENT (PURIFICATION) METHODS

5.1 Straining through Cloths

Filtration through cloth is a physical process and an age long tradition used in the removal of larger particles and insects from water. It is regarded as an emergency water filtration technique which has been reported to reduce the infection of cholera by half [98,99] and 4.2% bacteria [100]. Cloth filtration method can serve as pre-filtration method for micro and ultra-filtrations. Old Sari cotton fiber cloths are usually preferred. Other fibers such as nylon, polyesters, vinylon, etc used as cloth filters have been reviewed pointing out their advantages and challenges [101,102]. The cloth is folded at least into four times before usage, washed, rinsed with filtered water and sun-dried after usage to prevent diseases.

5.2 Aeration

Aeration is usually the first treatment in municipal treatment plant systems and sometimes pilot plants. Oxygen saturation is maintained in water through aeration. Usually air is infused into the bottom of the water source say pond, lake or lagoon or surface agitation for oxygen exchange thereby releasing gases like carbondioxide, hydrogen sulphide and methane [103]. Ferrous iron is converted to filterable ferric iron via oxidation. In the same vein, hydrogen sulphide is oxidized to elemental sulphur which can easily be removed through filtration. Basic methods of aeration are aerobic and anaerobic while modified methods include; tapered aeration, diffused aeration, deep shaft aeration etc. Different methods are efficient in the removal of Chemical Oxygen Demand (COD), Total Dissolved Solid (TDS), Biological Oxygen Demand (BOD) and other biological contaminants in both freshwater and wastewater [104-108].

5.3 Coagulation, Flocculation and Sedimentation

Coagulation involves the use of coagulants such as aluminum sulphate ($Al_2(SO_4)_3.14H2O$) known as alum, iron salt, calcium and magnesium salts and alkaline liquids, to separate colloidal particles from water which are too small to settle by gravity. When alum is used, the polyelectrolytes converts the aluminum sulphate into polynuclear ($Al_{13}O_4(OH)_{24}{}^{7+}$) species forming aluminum complexes which help in the coagulation process [109]. Addition of these coagulants induces electrostatic and ionic forces which causes the particles to stick together prior to filtration / disinfection. Baking powder and white ash were used in the case of emergency. Recent research has explored the use of *MoringaOleifera* seeds as coagulants /flocculants which has produced up to 95% efficiency and acceptable results above established standards in reduction of total coliform and turbidity [110-116].

Flocculation uses stirring of the water to cause formation of larger particles. Flocculants are mostly added to promote the agglomeration of particles with continuous stirring for about 5 minutes. Then the water is allowed to sit for about 30 minutes for proper settling of colloids. Coagulation and flocculation have been proven to mitigate the fouling of membrane filters when coupled in the filtration process [117].

Sedimentation: When large particles such as sand and silt, settle rapidly at the bottom of the container through gravity, the process is referred to as sedimentation. It was used in the olden days to purify water for clarity before the evolution of modern technologies; however, it is still being practiced by the peri-urban people living in poverty. Sedimentation does not disinfect water rather allows clearer water to be collected through the top of the container while the large particles settle at the bottom of the container.

5.4 Filtration

Purifying water by filtration is also common. It involves the use of medium in the form of membrane or aggregates. Filtration utilizes both physical and chemical processes while adsorbing and absorbing contaminants on the medium. Filtration media includes ceramic (clay) membrane for point of use filtration, cloth or fiber membrane, compressed granular activated carbon (GAC), polymer membranes, sand, gravel or crushed rock and clay aggregates. Water quality after filtration depends on the filter media, raw water and flow rate and pore size of the filter [118]. Table 1 displays the microorganisms susceptible to filtration by size. Viruses are very smaller in size than bacteria and are susceptible to passage through filter media with larger pore size which can filter bacteria. More so, electrochemical attraction can cause them to attach themselves on the surface of the filter media. So engineering the filter media taking cognizant of pore size is very important.

Filters are easy to handle and operate. They require no special skill but can clog by suspended colloidal particles after repeated usage. Such particles may cause fouling and reduces water permeability of the filters. Careful surface cleaning such as back-flushing (reversal of pressure such as pure water applied to the permeate side of the membrane) and/or chemical cleaning (chlorinated water, acid or base solutions, disinfectant and detergents) in the case of natural organic material or bio-fouling is required for point of use filter while backwashing is employed when using aggregates as in the case of treatment plants. Filtration can eliminate bacteria, protozoa, cyst and viruses depending on the porosity of the media [119].

Reverse Osmosis (RO) i.e filtration using a semi permeable membrane was a major breakthrough in membrane filtration technology (Fig. 5). The earliest RO had salt rejections of approximately 96-97% and could only produce potable water from low concentration brackish water. Subsequent research was able to yield membranes that could reject salt up to 99.7% and could produce potable water from sea water [120]. RO membrane feeds under high pressure (100-800psi) has been used to filter viruses, ions, molecules, solids and achieve a 4-log reduction in viruses whereas mechanical filters can achieve up to 2-3 logs in virus reduction [86]. The results depend on permeation of different species. This is not efficient enough that is why mechanical filtration is used in conjunction with other treatment methods [121].

5.5 Disinfection

Disinfection involves the use of chemicals such as chlorine (chlorination), calcium and sodium hypochlorite which readily dissociates in water and is non-carcinogenic, but reacts with other pollutants to form harmful compounds. The technology is easy to use, has strong and wide-spectrum antimicrobial activity and low toxicity to humans when controlled dose is used. Limitations of chlorine disinfection method are the formation of disinfection by-products (DBPs) such as chloroamines, Tri Halo Methanes (THM’s), trichloroacetone (CCl3COCH3), chlorophenols, chloroforms, chlorinated hydrocarbons and other halogenated intermediate compounds which are very dangerous to health [91,92]. Iodine is also used in water disinfection of bacteria, cyst and viruses on lower concentration and fungi on higher concentration [122]. Iodine is known to increase the susceptibility of thyroid problems in certain individuals (e.g, pregnant women). Other chemical disinfectants are ozone (ozonation) and chlorine dioxide. They are highly effective in killing *Cryptosporidium* species [123,124]. The use of Ultraviolet (UV) radiation is also very effective in water disinfection. This is commonly used by food and beverage industries. The major challenge with UV disinfection is the power generation which is expected to be in sufficient dose to produce the require energy for disinfection. More so, the water must be free from dissolve solids or particles to avoid interference and shield of organisms [125].

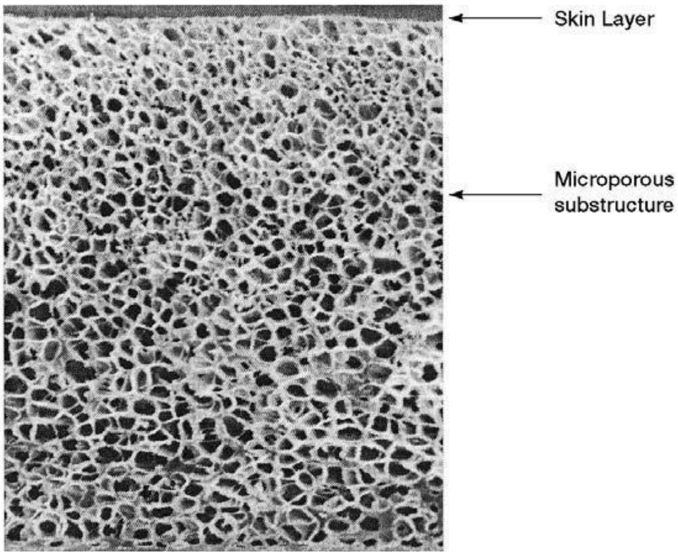

Fig. 5. Scanning electron micrograph of the cross-section of a Loeb-Sourirajan reverse osmosis membrane. The development of this type of anisotropic membrane was a critical breakthrough in the development of membrane technology

(Reprinted from R. W. Baker, Membrane Technology & Research Inc. (MTR), Menlo Park, CA, USA. Copyright @ 2000 Academic Press) [120]

Table 1. Susceptibility of micro-organisms to filtration by size. Retrieved from [86]

Organism	Approximate size (μm)	Maximum recommended filter rating (μm)
Virus	0.03	NA[a]
Escherichia coli	0.5 X 3-8	0.2- 0.4
Campylobacter species	0.2-0.4 X 1.5-3.5	0.2- 0.4
Vibrio chlolerae	0.5 X 1.5-3.0	0.2- 0.4
Cryptosporidium oocyst	2-6	1
Giardia cyst	6-10 X8-15	3-5
Entamoebahistolytica cyst	5-30	3-5
Nematode egg	30-40 X 50-80	20
Schistosomecercariae	50 X 100	Coffee filter or fine cloth
Dracunculus larvae	20 X 500	Coffee filter or fine cloth

[a] *Not applicable to most portable filters; only reverse-osmosis membranes exclude viruses by virtue of pore size*

5.6 Boiling and Distillation

Bringing water to a boil at 100^0C is the oldest and effective method of water purification for killing pathogenic bacteria, viruses and protozoa. This helps to eliminate pathogens and microbes-causing intestine diseases up to 100% if done correctly [86,126,127]. However; boiling water does not remove inorganic chemical contaminants such as heavy metals and metalloids. Treated water can get re-contaminated if stored or handled improperly [128,129]. Boiling is very effective in reduction of E.Coli up to 98.5% when stored in a covered container [130]. However, boiling water for purification has its challenges such as the cost of heat source, electricity, biomass, waiting for the water to cool before using and handling to avoid recontamination.

Distilled water is collected in the form of vapour after heating and condensing using distillation method. It is one of the oldest methods of water purification. It is capable of removing bacteria, inorganic and most organic contaminants from water. However organic contaminant such as pesticides and herbicides, benzene and toluene whose boiling points are below 100^0C cannot be efficiently removed as they vapourize with the distilled water and re-contaminate it. Also, pollutants with boiling points greater than 100^0C are difficult to remove. These organic compounds are removed prior to condensation [131]. Water purification by distillation is a very slow process, requires a lot of energy, carefulness and large quantity of water to produce and hence is a costly method. Moreover, distilled water lacks oxygen, has low pH (acidic) and also flat to taste which informed its application industrially rather than drinking and other household applications [131].

6. WATER FILTRATION AGGREGATES AND MEMBRANES

Sand is the most common aggregate used in water filtration especially for municipal treatment plants. Other aggregates and granules used in water filtration are charcoal, crushed rocks, blast furnace slags and clay [132]. These are also used in filtration of wine and other liquids. There are three main types of sand bed filtration namely, rapid gravity, upward flow and slow sand filter [133]. While rapid and upward flow sand filters use chemicals for flocculation, slow sand filters do not use chemicals, reduces turbidity, bacteria and organic matters producing high quality clean water [134]. Flocs and other impurities are trapped within the sand bed by means of absorption or encapsulation. Different grades of sand are used to filter water. Most bacteria and pathogens are removed through this process however; odour and taste may be problems which are effectively removed using activated carbon granules. The sand aggregate is backwashed after series of use and the effluent are dislodged through a septic tank. The frequency of backwashing depends on the shape of grains, packing, depth and the type of flocculants used while the overall performance of the filter is affected by the shape, strength, susceptibility to salts and chemical attacks, resistance to internal erosion of fines, resistance to abrasion and composition of the materials especially during compaction, placing and frothing [132].

Membrane filtration involves forcing a liquid through a semi-permeable (porous) membrane. It is utilized in water, beverage and bio-processing industries. The utility of membranes to purify water involves membranes classified by their pore size and separation capabilities (Fig. 6). The order of pore size increment starts with reverse osmosis membranes, nanofiltration, ultrafiltration and microfiltration membranes. Microfiltration is a size exclusion pressure or vacuum driven membrane filtration which operates at ambient temperature, velocity of about 1-3m/s and pressure ranging from 5psi to 54psi, 100-400kpa [135,136]. It is capable of removing bacteria, protozoan's cyst, and suspended particles of 0.1-10 micrometers [120]. Ultra filtration filters through a pore size range of 0.1-0.01 micrometers are capable of removing viruses, bacteria, colloids and particles. It shows higher removal of pathogens than microfiltration medium [137]. Also, the use of coagulants and sludge production are drastically reduced [138].

Reverse osmosis involves dense membranes where solution-diffusion governs the separation process [139]. It is preferable during desalination and filters up to 1 nanometer. It is efficient but an expensive technique. Nano filtration uses organic thin film composite membranes of typical pore size range of 1-10 nanometers. Its properties are found between reverse osmosis and ultra-filtration. Nanofiltration has gained popularity due to the emergency of nanotechnology and nanomaterial and their applications in efficient water and wastewater treatments [140-143]. It is efficient in separation of inorganic salts and small organic molecules [144]. It operates at low pressure with excellent properties such as high resistance to fouling, high degree of ions selectivity, capable of reducing hardness, Total Dissolved Solids (TDS), turbidity, sulfates, tannis, etc.

Ceramic membranes commonly called clay membranes have been in existence since time immemorial. They have special attributes of high resistance to heat, chemical attack, performance indices, mechanical strength, good cleaning ability and affordability, applicable over a wide range of pH and are very durable [145]. Studies have shown that clay ceramic membranes are very efficient in microbes and fluorides removal [77,146].

Polymeric membranes have also been used in water purification studies of water and wastewater r [143,147]. Researchers have conducted reviews on reported advances of polymer membrane in water desalination and purification revealing production processes, opportunities, challenges and way forward [140,144,148-151]. Polymers used in the production of membranes can be made from organic, inorganic and composite materials. Examples include polysulfone, poly (ether sulfone), polyacrylonitrile, poly(vinylidene fluoride), aromatic polyamides, sulfonated poly(ether sulfone), and cellulose acetate. Nano and ultrafiltration polymeric membranes are usually produced by phase inversion process [139].

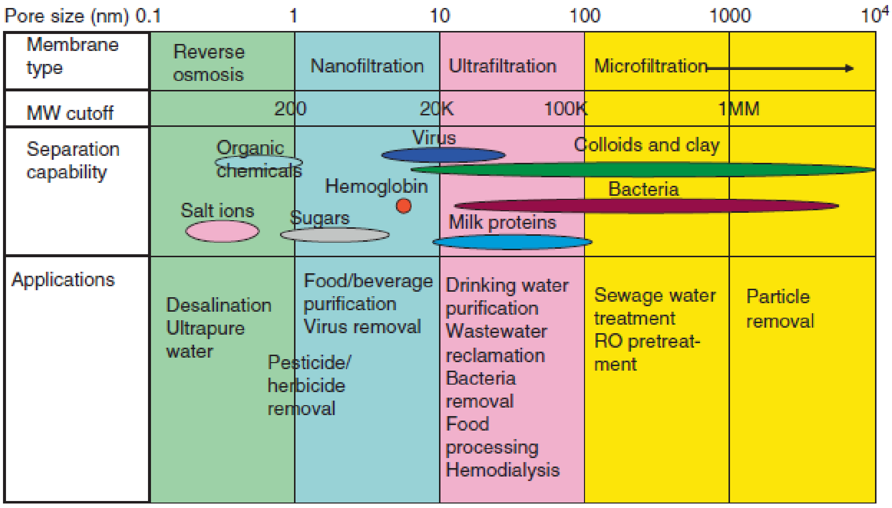

Fig. 6. Membranes used in water filtration (reprinted from polymer membranes LM Robeson, Lehigh University, Macungie, PA, USA © 2012 Elsevier B.V. All rights reserved) [139]

6.1 Adsorbent Materials Used in Water Filtration

6.1.1 Activated Carbon (AC)

The use of activated carbon in water filtration dated since time immemorial. Generally, activated carbon has large surface areas and large pore volume (porosity). These characteristics gave rise for its high adsorption and absorption capacities through the porous network of the particle. No wonder it is used in common home-based water filters. The major role of AC is to adsorbed contaminants which may affect the odour and taste of drinking water. Several studies have been done on the use of AC for adsorption in aqueous solutions and the removal of total suspended solid (TSS), biological oxygen demand (BOD) and other organic pollutants such as bacteria and viruses. Result indicated high efficiency (99.999%) with improvement in odour and turbidity of the drinking water [121,152-155].

6.1.2 Zeolites

These are three -dimensional structured crystalline aluminosilicates comprising mainly aluminium, silicon and oxygen. Each oxygen atom is shared by two tetrahedral. The presence of water and larger cavities differentiates it from Feldspar mineral [156]. Natural occurring zeolites have mono or di-valent cations like sodium, calcium, potassium, magnesium and barium interconnected cavities enclosed in their framework. The honeycomb-like structure consists of pores of order of few atoms in width (~2-10Å) which allows the movement of ions within the cavities, thus, necessitates reversible dehydration and exchange of cation. The widely accepted general formula of natural zeolites is written below:

$$(Li, Na, K)_p\ (Mg, Ca, Sr, Ba)_q\ [Al_{(p+2q)}\ Si_{n-(p+2q)}O_{2n}]\ .\ m_oH_2O$$

Where; p- no of monovalent metal ion, q- no of divalent metal ions, n- no of oxygen atom/ 2 and m_o- no of water molecules

Zeolites can be synthesized from Kaolin by calcining it to a high temperature, say above 600°C [157,158]. Natural zeolites such as Clinoptilolite (Clino zeolites), Mordenite, Chabazite, etc have been used extensively in water treatments due to their exceptional cation-exchange ability, sorption and molecular sieve properties [159-161]. They are divided into seven main groups and the division is based on their physical properties, crystal structure, exchangeable ions, pore volume /size, morphology, binding ways, etc. In the past decades, both natural and modified zeolites have been widely used as adsorbent to purify water. Zeolites and clay matrix (sometimes doped with silver nano-composite) are excellent in adsorption of heavy metal ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, As^{2+} and Zn^{2+} and have efficiently removed bacteria, heavy metals and other microbial growth from polluted water [159,162-165].

Thermal properties of zeolites (stability, resistance conductivity and heat capacity) depend on $SiO_2/Al2O_3$ ratio. Thermal stability increases with increase in crystallinity. Higher silica/aluminum ration affects the temperature resistance. Depending on type of zeolite, some have been found to be thermally and chemically stable up to 1000°C. Thermal conductivity depends on the particle size, temperature range, degree of packing and voids distribution [166].

6.1.3 Chitosan

Chitosans are strong adsorbents of heavy metals. They are synthesized from shells of fishery waste such as shrimp shells and crab shells, hence are cheap. Chitosans have molecular structure similar to that of cellulose. Modification of Chitin, a biological polymer from the exco skeletons of crustaceans, forms Chitosan excellent properties such as biocompatibility, biodegradability and non-toxicity. Researchers have reported its use in the efficient removal of pollutants such as COD, TDS, Turbidity, pathogens and heavy metals. Chitosan concentrations increment from 0 to 1 g 100 ml^{-1}, resulted in decrease in turbidity, TDS, electrical conductivity and from 1.98 to 0.98 NTU, 5.67 to 4.13 g L^{-1}, 10.18 to 5.27 mS cm^{-1}, 6.1 to 5.71 respectively. Coliform bacteria and Staphylococci at different concentrations were completely eliminated [167,168]. Experimental research has reported removal of phosphates reducing it from ~19 µg/ml by 6-30 fold and attenuating dissolved hydrosulfides from 1mM by 100-fold using metal ion modified chitosan [169].

Successes have been recorded for the use of Chitosan as a natural coagulant in remediation of microbes and turbid waters to over 90% efficiency and wastewaters [170-175]. Adsorption studies of heavy metals (arsenic, copper, zinc, mercury, uranium), dyes and pharmaceuticals from aqueous medium using chitosan including modified form have been reported and reviewed to be successful although results depended largely on the modification method adopted, materials used for the modification and adsorption experimental conditions [176-181]. The presence of amino and hydroxyl groups in chitosan molecules serve as attachment sites towards metal ion thereby contributing majorly to its adsorption capabilities. Other parameters of dependent are deacetylation degree, molecular weight, particle size and crystallinity [182].

6.1.4 Hydroxyapatite (HAp)

HAps are naturally synthesized from egg shells, bones of fish and mammals because of high content of calcium and carbonates. The common one is the calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. Adsorption studies have shown their high capabilities to adsorb heavy metals such as lead, Arsenic and Cadmium under varying conditions like initial metal concentration, pH, temperature and reaction time [23,183-186]. Ion exchange mechanism by substitution of calcium with the heavy metals is commonly proposed by researchers.

6.2 Clays: Characteristics and Composites in Water Filtration

Clays occur naturally and are abundant in earth's surface, hence are available and affordable. Generally, clay is formed as a result of weathering process greatly influenced by the parent rock, vegetation, topography, climate conditions and duration. Clay mineral structure may be destroyed or modified at high temperature beyond dehydroxylation. There is tendency for rapid fusion after dehydroxylation temperature when using fluxes such as potassium, iron and magnesium [156]. Clay and clay minerals are the most important industrial minerals whose application is dependent on their microstructural morphology, mineral compositions, phase constitution and chemical composition. Clay minerals are phyllosilicates minerals with layers of silica tetrahedral (Fig. 7a) and layers of Al, Fe, Mg octahedral, similar to gibbsite or brucite (Fig. 7b). The arrangements of these layers' accounts for major and minor differences in the properties of clay.

There are three main groups of clay mineral are kaolin (usually referred as kaolinite), Illite and Smectite of Montmorillonite, each with specific properties and formation as shown Table 2. Associated clay minerals like vermiculite, quartz, micas, chlorite, etc, do not impart plasticity to clay but interfere with its identification. Montmorillonite are known to adsorb more water than kaolinite, illite, and chlorite [187,188]. The chlorites and illites have similar water sorption properties. Clay has wide range of utilization and industrial application. Characterization and classifications of clay have been done successfully using technical equipment such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transmission Infra-Red (FTIR), Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM), Atomic Absorption Spectroscopy (AAS), Instron, Casagrande and others [189-193]. Documented and reported results are veritable tools and are handy for use and for industrial applications purposes.

With regards to water treatment, clay has been used extensively since time immemorial in water filtration and purification studies both in sole and modified forms. Clay ceramic water filters have shown capabilities in removing water contaminants such as microbes [195], chemicals [192,196-198], and heavy metals [199,200]. Ceramic water filters made from clay and clay minerals are very efficient for water filtration through adsorption/absorption, molecular sieving and ion exchange mechanisms [160,201,202]. More so, clay is inexpensive, abundant, widespread and readily available. Other considerations are user friendliness, cultural acceptability and a low maintenance cost.

Industrial waste, such as rice husk and saw dust are some of the materials that forms composite with clay in water purification studies. The kernel of rice typically known as rice husk is obtained after separation of rice from paddy in a rice mill and it is a rich source of silica. Other non-renewable sources are; wheat, oats, barley and maize. Silica is found at the epidermal layer of these crops. They are abrasive and brittle as well. Complete combustion of rice husk gives rise to white ash which contains 86-99% silica [203-205]. Rice husk has been found useful in so many applications like; polymer reinforcement, water purification, road construction, dye and acid removal, cosmetics and cosmetology, dentistry, building construction, food industry, adsorbents, etc. However, this discussion is limited to water purification using clay-rice husk composite. Pachauri [206] prepared column and ball rice husk ash-based filters for water/waste water purification. The treatment efficiency for total suspended solids (TSS) for the waste water were 63, 81 and 88% after 1,2 and 3 hours respectively with ball filter while that of column were 50, 66 and 76% after 1, 2 and 3 hours respectively. The result also showed reduction in chloride content from 283 mg/l to 189 mg/l after 6 hours of retention time.

The removal of Cadmium II and Zinc II ions from binary systems was effective using rice husk filter. Higher percentage of the duo ions were absorbed by the adsorbent during filtration [207]. The use of microwave for the incineration of rice husk used in water filtration has been studied for the adsorption of heavy metals, chromium and copper respectively. The results indicated efficient removal of these ions by means of adsorption [208,209]. Nitrites removal in water was studied using rice hull- derived zeolites. The husk was washed with distilled water and acids prior to calcinations. Results showed that both the untreated and treated were able to remove nitrite by 97.03% and 97.22% respectively [203]. Rice husk has great potentials as adsorbents due to the presence of functional groups, high porosity and surface area. Its major constituent is silica, carbon and other trace elements like alumina, potassium oxide, iron oxide,

Table 2. Three major clay minerals showing formation, characteristics and uses

Group	Examples	Formation	Characteristics	Uses
Kaolin	Kaolinite, nacrite and dickite	Decomposition of orthoclase feldspar	1:1 (Fig. 7c) phyllosilicates, non-swelling with fine texture	Ceramics production, fillers for papers and paints, water treatment
Illite similar to Muscovite	Gluaconite	Decomposition of micas and feldspar, predominant in marine clays and shales	2:1 phyllosilicates, commonest clay mineral, possession of exchangeable cations (K, Ca and Mg)	Cosmetics, binders, water treatment
Smectite or Montmorillonite	Bentonite and vermiculite	Alteration of mafic igneous rocks rich in Ca and Mg	2:1 (Fig. 7d) phyllosilicates, weak linkage by cations (e.g. Na+, Ca++) results in high swelling/shrinking potential and isomorphous substitution	Drilling mud for oil and water wells, binder in pharmaceuticals, feeds for blast furnace, water treatment

Table 3. Review of the usage of expanded clay aggregate in water purification

Authors	Adsorbent	Contaminant(s)of study	Outcome
[212]	LECA LECA+$CaCO_3$	Phosphorus from wastewater	Higher P-sorption was observed for LECA+$CaCO_3$ more than LECA
[213]	ECA	TOC, COD, colour and ozonated humid water	Removal rate between 57-75% for all experiment was achieved
[214]	Sintered LECA with addition of carbonates of calcium and or magnesium as flux materials	phosphorus	High phosphorus binding capacity with very good hydraulic conductivity
[215]	LECA Al or Fe oxide coated LECA	Removal of Arsenite (AS^{III}) and impact of Phosphorous on removal efficiency	Enhanced sorption of AS^{III} at pH 7, 68µg g^{-1} and 114µg g^{-1} for LECA and Al or Fe modified LECA respectively
[216]	Natural LECA, H_2O_2 and $MgCl_2$ modified LECA	Fluoride	At pH 6, fluoride was reduced from 10 g/l initial concentration to 0.39 mg/l, 1.0 mg/l and 0.075 mg/l for Natural LECA, H_2O_2 and $MgCl_2$ modified LECA respectively at sorption capacities; 8.53 mg/g, 17.83 mg/g and 23.86 mg/g.
[217]	LECA granules and powder	COD, BOD, TSS, nitrate and phosphate in dairy industry wastewater	Efficiency of COD removed after 20hrs is 65.9% TSS& BOD had great reduction Nitrate=63.87% Phosphate- reasonable reduction
[218]	ECA	Phosphorous and Nitrogen on river water	12-16% removal efficiency for phosphorus and 5-6% for Nitrogen
[219]	LECA MgO-modified LECA	metronidazole (MNZ)	Removal efficiency of MNZ increased by 8% with addition of carbonates for LECA and total removal of MNZ for MgO/LECA. Maximun adsorption capacity under optimum conditions are 56.31 to 84.55 mg/g for LECA and MgO/LECA respectively
[220]	Zeolite containing LECA	Ammonium from domestic wastewater	High ammonium removal at high ammonium loading rate by a combination of nitrification and ion exchange
[192]	ECA	E. Coli, Nitrate, Phosphate, Arsenic III and Lead II	Aluminosilicates and associated minerals with high surface areas between 456.143–566.998 m2/g and significant adsorption sites were revealed. Log four bacteria disinfection assay was achieved. Reduction efficiencies for phosphate and nitrate for all adsorbents varied from 27.33% to 76% and 10.67% to 46% respectively. High correlation coefficients made Langmuir isotherm model more favourable than Freundlich model.

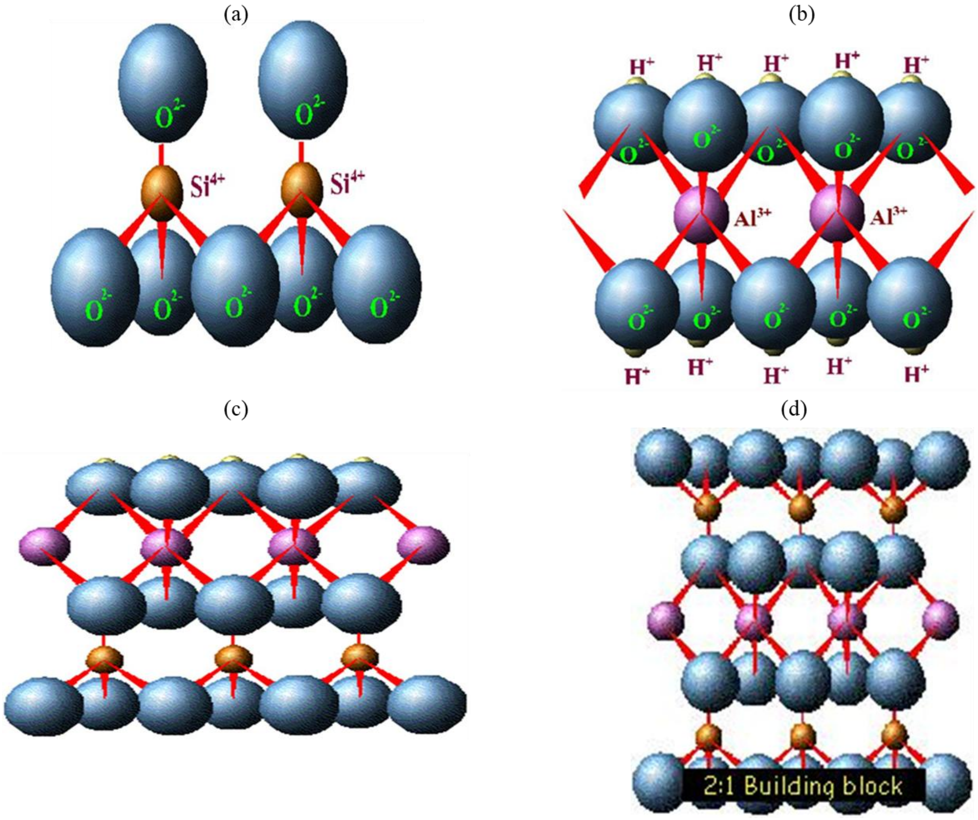

Fig. 7. Building blocks for clay minerals. (a) Silicon-Oxygen Tetrahedral ($Si_2O_5^{-2}$) ; (b) Al-Octahedral (Gibbsite sheet)$Al(OH)_6^{-3}$; (c) Kaolinite 1:1 Building block; (d) Smectite 2:1 Building block [194]

manganese, sulphur, calcium oxide and phosphorous pentaoxide, etc. Similarly, clay-sawdust composite as an adsorbent in water purification have been studied and documented by researchers. Results have shown that such composite is very effective in removing heavy metals, oils, dyes and chemicals [77,210,211].

6.3 Expanded Clay Aggregates (ECA) for Water Filtration

The uses of ECAs in water filtration are still evolving. Their major applications tilt more towards sustainable building material than in water filtration studies. New technologies on water treatment have been reported but not much can be found in literature on the use of Expanded Clay Aggregate application in surface water treatment especially biomass-modified ECAs. Some of the reviewed literature centers attention on the use of Light Expanded Clay Aggregate (LECA) and ECA in the adsorption of phosphorous in wastewater Table 3.

7. CONCLUSIONS

The importance of water to health, education, environment, economic productivity, peace and stability and agriculture cannot be overemphasized. Different water problems from scarcity to pollution and natural remedies have been discussed in this review. The deduction here is that natural cheap-based effective measures are preferred in water treatment. However, each measure disinfects one or two contaminants at a time. The gap here is the need to develop filter aggregates capable of removing multiple contaminants (organic and inorganic) at the same time which is expected to be integrated in large water filtration technologies such as municipal treatment plants, water boards, as well as portable water filtration systems. The authors are working on the possible development of nano-modified expanded clay aggregates to filter out multiple common contaminants in water for large filtration systems and also to produce filter inserts for water buckets and bottles for low income earners, Internally Displaced Persons

(IDPs), rural farmers, dissert travelers, school children and hospitals.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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