



Clay minerals and their role on wastewater decontamination: Past applications and future prospective

¹Hoda Kabary, ¹Mohamed Saber and ²Alaa Zaghoul

¹Researcher at Agricultural Microbiology Department, Agricultural and Biological Research Institute

²Soils and Water Use Department, Agricultural and Biological Research Institute

National Research Centre, Dokki, Cairo, Egypt

Corresponding author: hoda_kabary@yahoo.com

ABSTRACT

Water is highly essential element for every living being, and indispensable resource for everyday agricultural and industrial practices. Generally, most of the water resources are subjected to pollution through the discharging of varied types of contaminants into nature water bodies. Moreover, the insufficient water supply due to population expansion and the ultimate increase in social and economic activities, lead people, especially farms and domestic consumers, to use untraditional, hazardous water resources as wastewater effluents, for different domestic and agricultural practices. Consequently, the overall water quality characteristics are in decrease to be used for crop irrigation or for further consumption of the yield harvest.

The adverse agro-environmental consequences of using low quality water for irrigation should be constantly monitored. The follow up of these hazards would enable the scientific community to find a proper treatment to avoid such effects. The suggested treatments would be evaluated through both biologically on pathogens existence as well as chemically on organic and inorganic pollutants prevalence.

This review article outlines the super absorbent modified clay minerals economically available in Egypt associated with microorganisms applying to remediate different kinds of pollutants which found in low quality water. Different mechanisms of pollutants reaction take place with clay minerals were further discussed.

KEYWORDS: Pollutants- Wastewater treatment- Clay minerals- Environmental applications

INTRODUCTION

Global water pollution

Presently, the problem of water pollution has magnified specially in developing countries, with its further effect on restricting the environmental sustainability R&D goals, economic growth, and adverse effects on human health. According to Biswas et al. (2012), the reasons for the global water scarcity is not only because of the inadequate water resources accompanied by increasing in the consumption, but also due to the lack of comprehensive management of the developed wastewater with the subsequent health problems raised as global consequences.

The global agricultural demands for high quality water raised from multi purposes needed as livestock, fishery, agroforestry, and aquacultures which has been extensively expanded to meet the global food consumption needs in parallel with population expansion, mobility, and modern human dietary pattern (FAO, 2014a).

WWAP (2017) reported that, about 80% of low quality water is disposed without treatments in natural water bodies and the industrial process responsible for charging of millions of tons of pollutants includes heavy metals, organic and inorganic wastes, toxic sludge, annually. WHO (2012) had classified two new types of pollutants emerged from human and livestock activities, including emerging pollutants as antibiotics, hormones and vaccines, and biological pollutants as zoonotic waterborne pathogens, that flowed over farms and water coasts lines to the water ecosystems. UNEP (2016) described common farms route in releasing agrochemicals, sediments, organic matters, and nutrients into aquatic bodies, and explained the detrimental health effects posed due to such activities.

The intensive farming of crops and livestock production often inserts intensive amounts of chemical fertilizers and pesticides in varied terrestrial and aquatic ecosystems.

Worldwide, 80 percent of the municipal wastewater generated in the human settlement is discharged untreated into aquatic water ecosystems. Human settlements are one of the major factors in the degradation of soil and aquatic coastal ecosystems through eutrophication. Furthermore, the industry is responsible for releasing millions of tons of liquid wastes impregnated with potentially toxic elements, solvents, sludges, and other wastes into water bodies each year (WWAP, 2017). The resultant water pollution associated with these activities represents serious threats to aquatic and human life and the overall ecological ecosystem (UNEP, 2016). Several previous studies investigated the reclamation potentials of drainage water and the beneficial effect of the reclaimed drainage effluent on soil health and crop productivity (Hassan et al., 2018; Al-Afify et al., 2019). These studies explained the presence of plant growth promoting microbes (PGPR) together with nitrogen fixing bacteria that present in the drainage water in enhancing soil fertility and general healthy soil characteristics. The outcome from these studies demonstrated the probable beneficial effect of drainage water.

Agricultural drainage water in Egypt

Egypt suffers from the incompetent water and wastewater treatment systems. Moreover, the Nile River, which is the main source of water in Egypt, is being heavily polluted by discharges of untreated and/or partially treated domestic and industrial wastewater effluents and agricultural drainage water as well.

Agricultural drainage formed by the natural or artificial process that removes the excess surface and/or subsurface water from poorly drained agricultural lands. This process prevents the soil waterlogging and developing of anaerobic conditions what harmful for the plant root system. Agricultural drainage is necessary to create a well-aerated root ecosystem that enhancing plant growth and productivity.

Agriculture drains in Egypt aims mainly on increasing productivity and safeguarding the irrigation farming sustainability. The developments of new drainage system in Egypt allowed the establishing of intensive diverse irrigation water resources for agriculture (Abdel-Dayem et al., 2007).

Egypt has many agriculture drains particularly at Absoug, Abu-Wanass, Abu-keer, Ahnasia, Badaryl, Bahr-el-Bakr, Bahr-Hados, Bahr-Nashart, Ballas, Bany-shaker, Battas, Berba, Borg-Rashed, KomOmbo, Danfik, Edfu, Edko, Essawia, Etsa, Faraskour, Fetera, Ganayen, Gaba, Ghemeza El Kobra, Ghemeza El Soghra, Garbia El Main, Habil El Sharky, Hamed, Hegr El Sebaia, Hond El Sebaia, Khour El Sail Aswan, Khour El Sail Badrashin, Magrour Hoe, Main Draw, Main Ekleet, Massandra, Mataana, Mazata, Nag Hammadi, Qeft, Radisia, Raghama, Rayamoun, Saba and Saff (figure 1).

With all efforts taken by the governments to fill the gap between water consumption and supply, the gap is still expanded as results of growing population and modern, improved life standards. The National Water Resources Plan recently published (MWRI, 2005) stated that, to fill this gap, optimizing water use efficiency strategies must be taken.

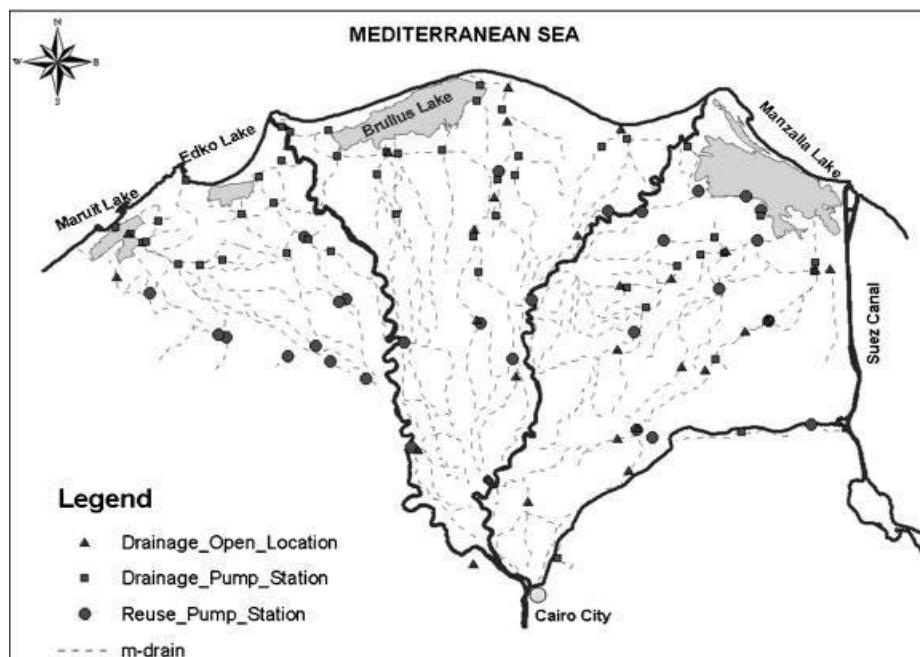


Figure (1) Drainage water network in the Nile Delta. Abdel-Dayem, (2007)

In Egypt low-quality water is a byproduct composed mainly of domestic wastewater from households, municipal sewage effluent, industrial wastewater and agricultural drainage water, the characteristics of such water vary depending on their source. Negm (2019) and Shukla et al.(2010) stated that low-quality water might contain physical, chemical, and biological pollutants that pose adverse environmental and health hazards to both human and biodiversity besides restricting water reuse.

Pollutants in agricultural drainage water

In the near past, adverse impacts associated with long-term reuse of drainage water received limited consideration. However, available estimates on the effect of prolonged use of drainage water in irrigation are already noteworthy. Symptoms of pollution with enteric pathogens, PTEs, and organic toxins in drainage water sources, nowadays, are customary events. If no drastic actions are taken, the existing trends illustrate that it is likely to become even senior during the third millennium as far as pollutants threaten the ecosystem quality, health, and agricultural revenues. World Health Organization (WHO) exhibited that 40 percent of the global population is still suffering from insufficient sanitation and agricultural drainage water systems that interrupt water supply quality (WHO, 2012). Therefore, there is an urgent need to provide basic, affordable agricultural drainage water treatment, especially in developing countries. Data collected in Egypt during the last decades validate the

rising anxiety with the deterioration of water quality in the Nile system, irrigation canals, and drainage ditches.

The numerous types of drainage water pollutants are mainly classified into three main categories, inorganic pollutants, organic pollutants, and biological pollutants.

Inorganic pollutants: There are varied types of inorganic pollutants that reach drainage waterways. The most important are PTEs, mineral fertilizer residues, nutrients, nitrate, phosphorus, and salts.

Potential toxic elements (PTEs): are the most serious inorganic pollutants in agricultural drainage water and are the main cause for several ecosystem and agricultural hazardous and risk issues including human health. In most cases, the concentrations of PTEs in polluted agricultural drainage water are often magnified in hundreds higher than those limits needed to cause a hazardous effect in an environment. A quality criterion gives numerical level only for some PTEs such As, Cr, Mn, Zn, Pb, Cd, Hg, Se, Ni, and Cu that usually have concentrations above the guideline levels in agricultural drainage water. PTEs as pollutants are considered of great interest due to their tendency to accumulate in the soil, and water ecosystems and taken up by higher plants. They are not biologically degradable and persist in the ecosystem indefinitely. Once accumulated in agricultural drainage water, PTEs inversely affect the metabolism of biotas. Despite no single classification encompasses all nutrients and PTEs, yet those of major concern is the group which includes the transition elements Co, Cd, Ni, Cr, Cu, Mn, Hg, V, Mo, S, and Zn. PTEs of concern to agricultural drainage water include mainly Ni, Zn, Cu, Cd, Pb, Hg, Cr, Se, Mo, As, V, and B, yet, As, B, Pb, and Se exerted special attention (Bolong et al., 2009).

The impacts of heavy metals exposure on living beings cause serious health issues for either human or animals. For example, cadmium in low concentrations can lead to “Itai-Itai” disease, as well as lung, kidney, and liver cancers. Ingestion or inhalation of chromium or nickel resulted in ulcers, inflammation, diarrhea, nausea, and chest pain. Exposure to excess lead, leads to mental retardation in babies as well as kidney and liver cancer in adults. Excess of zinc can lead to anemia, vomiting and fever. Cobalt excess consumption can lead to heart diseases and asthma (Akpomie&Dawodu, 2016).

Mineral fertilizers residues: All chemical fertilizers residues have major adverse impacts on soil, canals, drains and water supply sources. The breakdown and cycling of fertilizers, results in release of small nutrients and inorganic residues such as phosphates, nitrates and phosphorus which discharge into the water bodies excreteshazardous effect to the whole aquatic systems (US EPA, 2017). Salts, also considered as inorganic pollutant, formed as byproduct from fertilizers disintegration in the soil. Salts concentration increase in water bodies cause different of human disease such as hypertension, diarrhea, and skin irritation (World Bank, 2013; Khan et al., 2014). Salination of water bodies also resulted in decline in the microbial diversity and algal, animal existing species extinction (Lorenz, 2014).

Organic pollutants: Pesticides mainly include insecticides, herbicides, fungicides, which are nowadays applied so intensively within farming in many countries reported by Schreinemachers&Tipraqsa, (2012). The improper managements of pesticides usage in the agricultural process, resulted in the release of the excess pesticide into natural water bodies, that pose significant hazard effect on human, animals, and aquatic ecosystems (FAO, 2013). Pesticides detrimental effects on human health include various human diseases such as skin and eye irritation, abdominal disorder, nausea and eventually liver and kidney cancer (Aktar et al., 2009). Zhang et al. (2011) reported that, 67 thousand deaths poisoning incidents happens per year in United States, where it is magnified in China with 500 thousand poisoning cases with 100 thousand cases deaths a year due to such poisoning incidents.

Persistent organic pollutants (POPs): are classified as PBTs (Persistent Bio-accumulative and Toxic) or TOMPs (Toxic Organic Micro Pollutants). Most of POPs created from industrial processes, while very few of them compounds created as byproduct from natural processes. They are the most difficult of the pollutants to assess because of their relatively recent appearance, consequent lack of surveys, and ever-increasing numbers. The POPs can resistant ecosystem degradation by photo catalytical, biological and inorganic processes. Because of this, they had been observed to persist in water ecosystems. The existence of organic toxins in drainage water collected from different sites in Egypt was monitored in voluminous literature. Their results indicated that all drainage water samples contained both natural and industrial pollutants (man-made). While industrial pollution was rather low,

considerable natural pollution was present. Analyses of the aromatic fraction of water samples suggested that most of the organic toxins are still from natural processes.

Biological pollutants: In definition, water-borne diseases include enteric diseases that are transmitted by various microorganisms and parasites. Water-hygiene diseases are the consequence of inadequate personal cleanliness and include various enterics such as typhoid, typhus, and dysentery.

The discharge of pathogens from wastewater to agricultural drainage water and further to natural water bodies represents a major threat on livestock, aquatic animals, and human health in general (Hassanain et al., 2021). Drainage water had been implicated as a significant source of health risk for chronic, low-grade gastrointestinal disease as well as outbreaks of more acute diseases. Pathogenic microorganisms responsible for the spread of different zoonotic disease as gastrointestinal diseases including, *Salmonella spp.*, *Campylobacter spp.*, *Clostridium botulinum* and *Escherichia coli* O157:H7 (FAO, 2006; WHO, 2012). Those microorganisms were detected in reasonable intensities in two agricultural drains such as Al-Rahaway and Belbeis in Egypt, that known to be used for agricultural irrigation, reported by Kabary et al. (2021). Parasitic protozoa such as *Cryptosporidium parvum* was also detected in wastewater that causes thousands of infection incidences, annually (Christou, 2011).

Agricultural drainage water contamination by biological pollutants, usually measured by the estimating the intensities of fecal coliform bacteria count, either through direct plat count or MPN on specific medium, or more advanced using qPCR technique for each pathogen type (Hassanain et al., 2021). Fecal coliform bacteria are a group of pathogenic bacteria colonize the intestine of warm blood animals. The presence of these pathogenic bacteria in water ecosystem usually happened due to the discharge of domestic or livestock wastewater into the water bodies, and its existence usually accompanied by other pathogen existence as protozoa. Fecal coliforms such as *E. coli*, *Enterobacter sp.*, *Klebsiella sp.* and *Pseudomonas aeruginosa* (Kabary et al., 2021).

Emerging pollutants: Another category of pollutants in agricultural drainage water is emerging pollutants which represents a group of hard degrading, organic compounds which incidence are rare in nature environments. Emerging pollutants such as pharmaceuticals, drugs, hormones, vaccines, and healthcare byproducts are

characterized by reasonably long shelf lifetime to be degraded in comparison to other organic compounds in the same environment (UNESCO,2011; UNESCO, 2017). The disposal of these pollutants into water bodies and the subsequent use of these polluted water sources, pose a detrimental threat to human health altogether with any living being exposed to it (UNESCO, 2015). Diamanti-Kandarakeset al. (2009) reported that, many of these compounds interrupt hormones pathways synthesis and metabolism in human body. WHO (2011) reported the presence of pharmaceuticals and therapeutics in traces in contaminated ground and surface water in some areas.

Using of raw clay and modified clay minerals in decontamination of low-quality water
Clay minerals in nature

The use of clay minerals is traditional old practice for human health care which extend till the modern days with what is known as “healing clay”, that is applications outreach nutritional, therapeutically, and skin cares purposes(Gomes & Rautureau, 2021a). Clay minerals can be modified in the form of mud which applied oriental on the body in spa facilities and healing purposes (Carretero 2020a, 2020b), other common applications are the use of clays as bacteriostatic or bactericidal ointments (Gomes et al., 2020). Clay minerals are a heterogenous group of hydrous layers of aluminosilicate which particle size $<2 \mu\text{m}$ or even $4 \mu\text{m}$ in one dimension. Clay minerals’ particles can be amorphous or crystalline, fibrous, or platy with variations in colloidal dimensions. In composition, clay minerals composed of the same elements as the earth crust including O₂, Si, Al, Ca, Na, K, Mg, Fe (Table 1).They are considered as a major component of sediments, soil, rocks, lake and estuarine. Weathering condition and climate change effects as temperature and pressure, facilitates formation and assembly of different types of clay minerals from soil, sediments, and rocks. The unique characteristics of clay minerals due to the small particle size and large size to surface area, are enhancing cation exchange, catalytic activity, and elasticity behavior under moisture condition. Due to these vital criteria, clay mineral considered on or the highly potent adsorbents material for charged particles in any environment. Clay minerals interspace layer structure can be electrically neutral or negatively or, less common, positively charged. Clay minerals edges and faces can scavenge anions, cations, polar and nonionic contaminants from natural water bodies leading to their immobilization. Van Olphen (1977) had reported several active sites in clay minerals sides.

Table 1: Earth Crust elements (Barton and Karathanasis, 2002)

Element	Crystal average (gkg ⁻¹)	Ionic radius (nm)	Volume (%)
O ²⁻	466.0	0.140	89.84
Si ⁴⁺	277.2	0.039	2.37
Na ²⁺	28.3	0.097	1.84
K ⁺	25.9	0.133	1.84
Ca ²⁺	36.3	0.099	1.39
Al ³⁺	81.3	0.051	1.24
Fe ²⁺	50.0	0.074	0.79
Mg ²⁺	20.9	0.066	0.60

Clay minerals composition and classification

Clay minerals compositional properties are determined by ionic constitution, geometric distribution of ions and the electrical bonds that bind the ions together. Most of clay minerals visualized as successive sheets of tetrahedral and octahedral structures. Tetrahedral sheet is the bases of silicate structure that composed of four O²⁻ ions and one Si⁴⁺ atom at the center. When other ion binds to the structure, the atoms rearranged in one hydroxyl and two oxygen atoms. Octahedrons composed by interference of cations as aluminum, iron or magnesium ions which surrounded by six oxygen or OH⁻ groups that coordinate the structure into eight-sided building blocks called octahedral sheet. These cations may be divalent as Mg²⁺ and Fe²⁺ or trivalent such as Al³⁺ and Fe³⁺. When divalent cation binds to octahedron structure, the ratio of divalent cation to oxygen 1:2, meanwhile when trivalent cation exists, the ratio becomes 1:3. Sheets arrangements and composition within the aluminum silicate layers is the mean reason of chemical and physical variation specific for each clay mineral type (figure 2). Clay minerals can be grouped according to the ratio of tetrahedron to octahedron sheets in its structure such as Kaolinite (1:1) and Bentonite (1:2) (table 2).

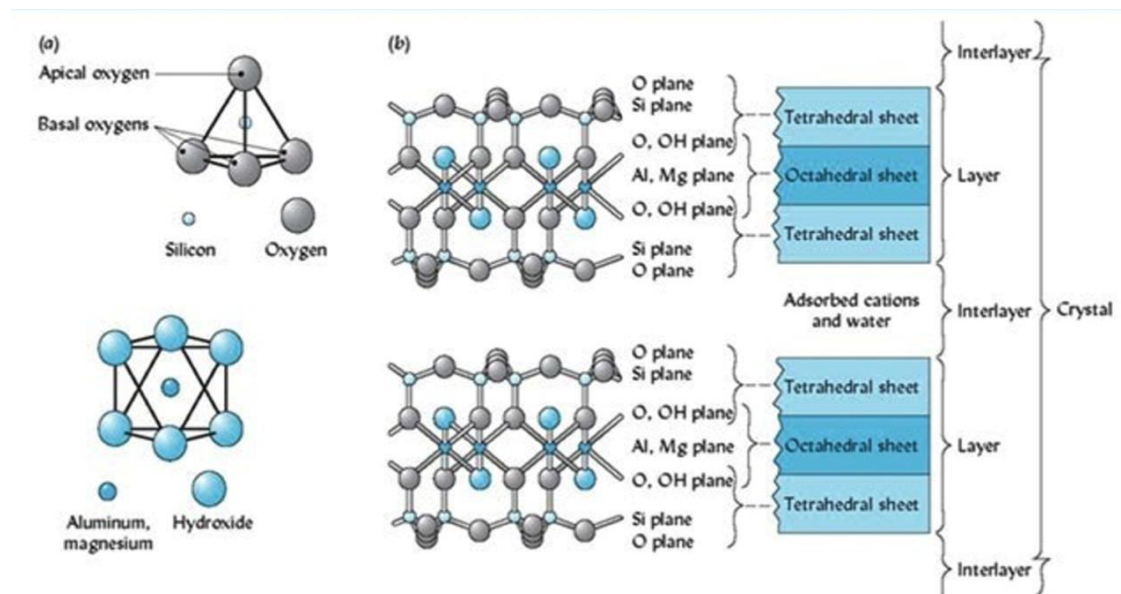


Figure (2): Tetrahedron (above) and octahedron (below) structural composition Adapted from “The Nature and Properties of Soils” Brady & Weil, 2008

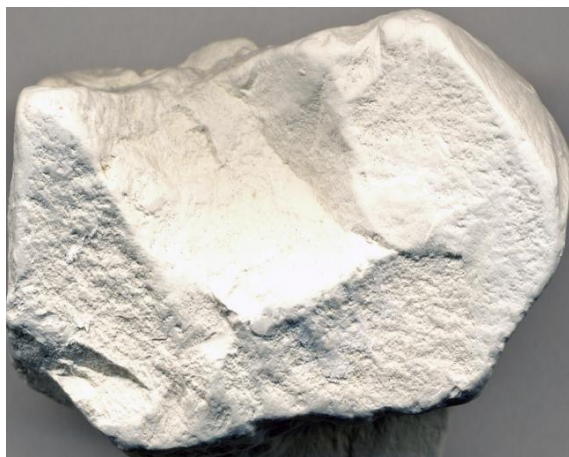
Clay mineral	Octahedral: tetrahedral layers ratio	Net negative charge (cmolk ⁻¹) ¹⁾	Surface area (m ²)	Basal spacing(nm)
Kaolinite	1:1	2-5	10-30	0.7
Fine- grained mica	2:1	15-40	70-100	1.0
Smectite	2:1	80-120	600-800	1.0-1.2
Vermiculite	2:1	100-180	550-700	1.0-1.5
Chloride	2:1:1	15-40	70-100	1.4

Table (2) illustrates, Kaolinite group have a small negative charge 10-30 mV, while Smectite group have a net charge of 600-800mV. The net electrical charge of the clay minerals particle is responsible for reactivity, hydrating and expansion capacity in aqueous environment.

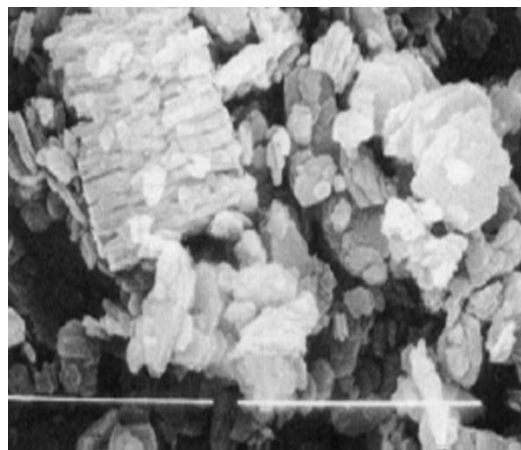
Kaolinite

Kaolinite structured feature composed of 1:1 tetrahedral to octahedral sheets described by Pauling (1930), tetrahedral sheet basic unit is SiO₄ while, octahedral sheet occupied by Al³⁺ as the main octahedral cation. The tetrahedral sheet is inverted on the octahedral sheet with apical oxygen atom between the two structures. In chemical structure, Kaolinite formula Si₄Al₄O₁₀(OH)₈ with composition percentage of 46.54%, 39.50% and 13.96% for SiO₂ and Al₂O₃ and H₂O, respectively. Kaolinite characterized by less reactivity and less expanded or changed by the presence of water

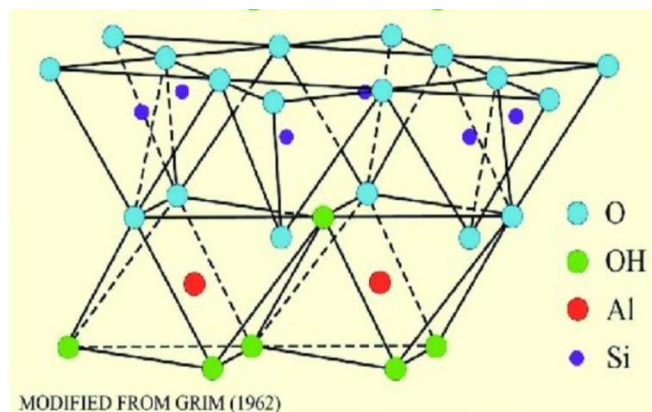
in the surroundings, therefore it is harder and most used for construction purposes. However, Kaolinite restricted reactivity is commonly overcoming by the change in the pH of the surrounding environment. The binding of metal ions as Pb, Zn or Cd on its surface edges usually accompanied by the release of proton (H^+) followed by the adsorption of the metal ion between its space, which in turn, affect Kaolinite structure and mode of action (figure 3).



Kaolinite clay mineral in nature



SEM image for Kaolinite clay mineral shows tetrahedral structured layers Imported from Ural, 2020



Dimensional structure of Kaolinite layer

Figure (3) Kaolinite structure

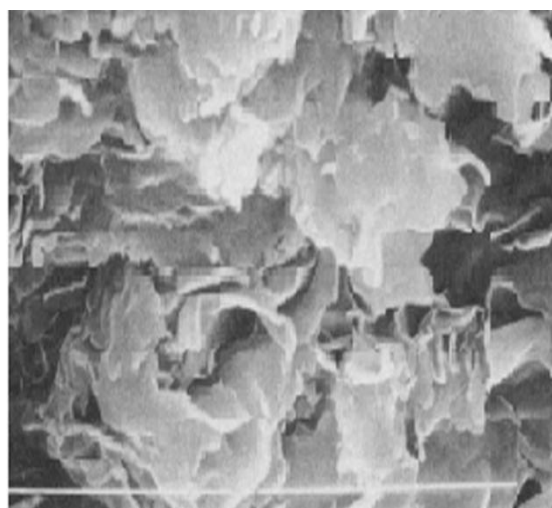
Bentonite

Bentonite is clay rock which formed by chemical alteration of glassy material such as tuff or volcanic ash. The basic unite of bentonite is Smectite group with group of dioctahedral minerals as Montmorillonite and trioctahedral minerals such as saponite. Montmorillonite is a hydrated Na, Ca, Al, Mg, Si hydroxide (Brana et al., 1986). The chemical formula of isMontmorillonite $(Si_{7.8}Al_{0.2})^{IV}(Al_{3.4}Mg_{0.6})^{VI}O_{20}(OH)_4$ and the

constituents percentages are 66.7, 28.3 and 5% for SiO_2 , Al_2O_3 and H_2O , respectively. Montmorillonite composed of two tetrahedral sheets centered by silica atom, and one octahedral sheet with aluminum center atom. The stack overlapping between Al- Si- Al layers cause the oxygen atoms of each layer to be adjacent to the neighboring layer, which make a very weak bond between those layers. This excellent feature of bentonite as a clay mineral that it makes the introduction of polar material and water molecules between the layers is so easy and resulted in the expansion of the layers in “c” direction (figure 4). This expansion and contracting properties of bentonite increase the adsorption ability of the metal ions to the hydrated, interspaced layer which make it an excellent candidate for pollutant removal from contaminated environments. Generally, the degree of expansion of the clay minerals layers depends on the hydrating capacity of the intercalating cations, which also responsible for disintegration of the molecule in dry environment (Gomes et al., 2021).



Bentonite in nature



SEM image of Bentonite with 2:1 octahedral to tetrahedral structured layers (imported from Ural, 2020)

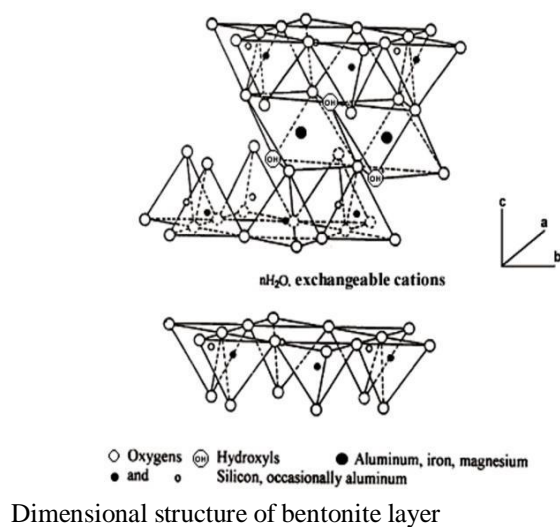


Figure (4) Bentonite structure

Natural clay minerals and Heavy metalsremoval mechanism

Sorption is the process of surface retention due to adsorption or precipitation mechanisms(Baioumy& Ismael, 2014). In any ecosystem, Sorption process plays a critical supporting role in contaminants control throughrestricting or removing of its toxicity. The benefits of using sorption technology in decontamination of any ecosystems especially wastewater treatments, lies in the fact that sorption process is highly reliable, efficient energy savers as well as its simply operated and costly inexpensive, depends on the type of the adsorbent used.

Sorption works throughreduction of soluble PTEs in aquatic environment in definite concentration to be below the limited range.It can also remove organic/inorganic PTE’s complexes as Cu, Cd, Pb, Zn together with anionic and oxyanionicforms as F⁻, SeO₃²⁻, SeO₄²⁻, CrO₄²⁻, AsO₃³⁻, AsO₄³⁻, etc. from wastewater in condition where precipitation process can be inefficient. Table (3) represents different types of low-cost and efficient sorbent materials with their role in heavy metal ions and organic pollutants removal.

Table (3) low-cost sorption materials and their efficiency in heavy metals removal				
Adsorbent category	Adsorbent type	Surface area (m ² /g)	pH condition	Adsorbate type
Activated charcoal and derivatives	GAC, PAC and ACF	500-1500	7.5-9.0	Organic pollutants as different aromatic hydrocarbons, dyes, and pesticides
Metal oxides and hydroxides	Activated alumina	150-260	6.2-9.6	Fluoride, arsenic and selenium

	Iron oxides and hydroxides	4-700	6.5-8.8	Arsenic, selenium and phosphates
	Fe-Mn binary oxides and hydroxides	265	5.9	arsenic
Natural and synthetic clay, ores and minerals	Montmorillonite and kaolinite	18.6 9.1	8.16 8.42	Various heavy metals such as Cd, Ar, Cu, Pd, Zn
	Sea nodule	-	7.4	arsenic
	Synthetic clay	50-250	8-12	Anionic species as fluorides, As, selenium, chromium, azo dyes, surfactants, and pesticides
Non-conventional low-cost adsorbents	Rice husk, coco nut coir, shell, bagaase	-	-	Various Heavy metals
Biopolymeric adsorbents	Chitosan	4-40	6.8-7.3	Heavy metallic ions
	Alginate	-	6.5	arsenic
	Untreated cellulose fibers	0.2-1	3,6-7.1	Heavy metals
	Microfibrillated cellulose	-	3.9	Ni, Cu and Cd divalent ions

Previous studies have exhibited the use of clay minerals such as Montmorillonite in sorption of different heavy metals, and several review articles published on the sorption removal of fluoride, arsenic, nitrate, PTEs, natural and synthetic organics and dyes signifies the importance of sorption in water purification (Mandal & Kulkarni 2011).

Generally, in an environment, when metallic ions contact with minerals, the ions sorbet on the minerals solid surface, consequently, the concentration of the ions decreases in the aqueous solution without the solubility of the solid minerals. Although the actual mechanisms of heavy metals sorption to clay minerals is not completely understood, it can involve other mechanisms including adsorption, ion exchange, specific adsorption, co-precipitation and organic complexes compounds, encapsulation, and fixation, depending on the clay mineral type (Ugwu & Igbokwe, 2019).

Determining the fate of heavy metals and their sorption to the solid phase minerals and consequently, restricting their mobility and availability in an environment, requires the complete knowledge of the main processes involved in the sorption reaction. In a study, cobalt ions are sorbet by goethite by complexation, precipitation, and elemental incorporation (Alvarez-Ayuso & García-Sánchez,

2003), however, adsorption and ion exchange are the widest mechanisms that take place in the decontamination of PTEs by clay minerals from wastewater.

In natural environment, surface functional groups or hydroxide groups (OH), originated from surface substances as oxides or solutes, dominate the environment as different metal oxides (Si, Al and Fe). When the surface group of the metal oxyhydroxide or carbonate ionized, the surface charge of the metallic ions developed and the pH of changed due to the sorption of ions or protons from the aqueous surroundings. The developed surface charge creates a potential difference between the sorbent and sorbate which in turn responsible for the attachment of ions towards the charged surface. Consequently, the type of functional surface group determines the sequence of the sorption reaction and the electrical properties of the interface (figure 5). In clay minerals case, the metal ions interact with the oxygen ions which instead of dissolved in the solution, it is attached to the surface and incorporated in the clay mineral structure (Alvarez-Ayuso & García-Sánchez, 2003).

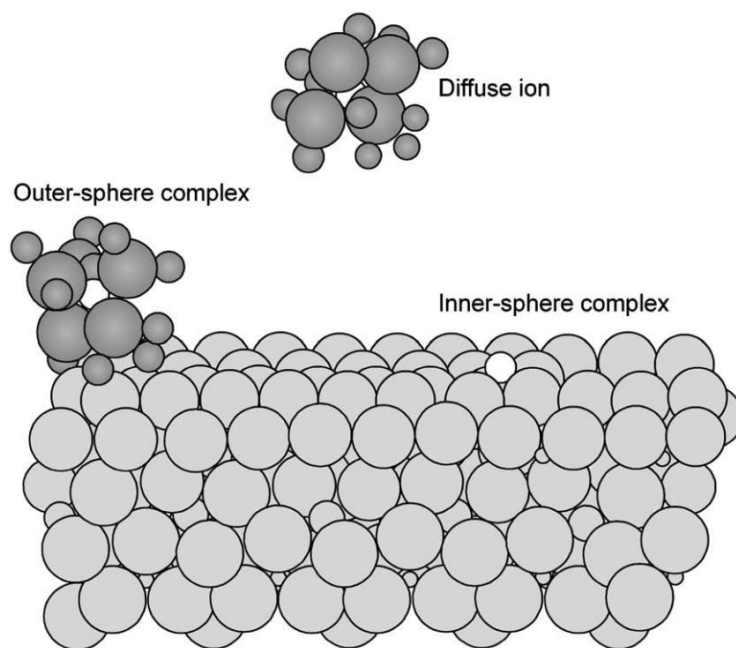


Figure (5) represents the diffusion of ions into the outer and inner surface compels (imported by Sposito, 1992)

Environmental factors are affecting the sorption mechanism in an ecosystem such as pH, ionic strength, and the presence of complexing agents (Baïoumy & Ismael, 2014). The major characteristics that affect the efficiency of specific adsorbents in sorption process are surface charge, surface area, pore size, functional group type, the surrounding solution pH, and the contaminant (adsorbate) concentration.

In study suggested by Baioumy & Ismael (2014), Na-bentonite was highly reactive than Ca-bentonite, in sorption of Ni, Cr and Zn from electroplating process wastewaters due to low exchange cation charge of Na than Ca. Jackson (1998) described that, the affinity of clay minerals to divalent cation is specific according to the clay mineral type. Jackson (1998) found that Montmorillonite affinity to divalent cations as follows $\text{Ca}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$, while Kaolinite affinity $\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ and, Illite $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+}$ according to the hydroxyl groups affinity in each type.

Different natural and modified clay mineral adsorbent types had proven its efficiency in water decontamination process such as calcite, bentonite, gibbsite, Kaolinite, China clay and hydrotalcite (Wang & Peng 2010). For example, hydrotalcite clay is positively charged clay with high pH_{pzc} (point of zero charge) ranges from 8 to 12, have a good sorption efficacy to anionic and oxyanionic pollutants (Goh et al., 2008). Hydrotalcite clay was found to be efficiently adsorbing negatively charged contaminants as fluoride (Mandal et al., 2009a), phosphates (He et al., 2010), and arsenic (Türk et al., 2009)

Several studies have investigated the role of clay minerals in wastewater decontamination of PTE's. Bhattacharyya & Gupta (2008) exhibited the role of natural kaolinite and Montmorillonite and their derivatives on PTE's removal from contaminated water resources. Moreover, other clay mineral such as Zeolites, diatomite, Kaolinite, and clay were evaluated to be efficient sorbents to different heavy metals (Apiratikul & Pavasant, 2008b; Sheng et al., 2009; Gu & Evans, 2008; Al-Jilani & Alsewailem, 2009). In study reported by Jiang et al. (2010), Kaolinite clay application in agricultural drainage water contaminated by various PTE's resulted in removal of various heavy metals metallic ions as Cd, Cu and Pb. Their study exhibited that, the maximum adsorbate removal was in the first 30 minutes of the process, with optimum reduction of Pb ions available concentration from 160 ppm to 8 ppm at the end of the experiment.

Common clay minerals adsorbents that are frequently used in agricultural drainage water treatment, modified probentonite and proKaolinite to retain the organic and inorganic pollutants from the surrounding ecosystem. In study reported by Wang et al. (2021), on acid treated Montmorillonite for heavy metals removal from automobile effluent, the modified Montmorillonite proved to be efficient in

heavy metals removal with expansion of the porous structure of Montmorillonite. Moreover, Wang et al. (2021) reported that, the sorption of the heavy metals to the clay minerals surface depends on the heavy metals initial concentration in the effluent, while the rate of sorption and the reaction equilibrium effected by metal ions ionic radii measurement.

Modified Montmorillonite such as, chitosan coated Montmorillonite had been investigated by Gecolet al. (2006) studies, for the removal of tungsten from drinking water in Nevada, USA. The coating process resulted in changing the clay minerals charge into positively charge to which tungsten anions was attached to the active sites. Also, the study detected that the net charge decreases as the tungsten concentration increases due to most of the tungsten anions were already occupying the active polymer sites. Another study reported by Aytas et al. (2009) detected that, thermal activation of natural bentonite at 400^oC, cause the highest adsorption of uranium (VI) which decreases while the Calcination temperature increases. In South Africa, wastewater studies detect the high concentration of heavy metals in the wastewater streams due to agricultural and industrial activities. A research study investigated by Sajidu et al.(2006) on the use of mixed clay minerals from Tundulu site from the removal of cadmium, chromium, copper, mercury, lead, zinc, and arsenic. The mixed clay structure was composed of Kaolinite, Illite and other minerals. The study exhibit that the heavy metal removal is pH dependent mechanism, where pH 5 removed most of the chromium with total removal 90%, while pH 7 removed most of zinc ions with a best removal of 93%. Arsenit and arsenate were removed by modified Montmorillonite (T- pillared) in study reported by Na et al. (2010).

Kaolinite and Montmorillonite were evaluated by the study of Angove et al. (1998) to be efficient for cobalt removal with Langmuir capacity of 1.5mg g⁻¹, while Bhattacharyya & Gupta (2008) estimated it to be 11.2mg g⁻¹ for Kaolinite and 28.6 mg g⁻¹for Montmorillonite respectively. Copper ions was removed efficiently in study reported by Yavuset al. (2003) with Langmuir capacity of 11.0mg g⁻¹

According to Sen Gupta & Bhattacharyya (2006), Cadmium (II) was removed from liquid solution by Kaolinite and Montmorillonite and their tetrabutylammonium and poly zirconium derivatives. They study concluded that, the sorption activity is fast in the beginning which slowed progressively indication the diffusion of the ions in the interlayers of the particles. The study also estimated that, the sorption process is pH

dependent where it is very poor when the pH is acidic and increased to reach optimum conditions in the alkaline pH. Another study reported by Sen Gupta & Bhattacharyya (2006) reported the removal of copper ions from aqueous solution by Kaolinite and Montmorillonite and their derivatives, their study exhibited that although the modifications enhanced the sorption efficiency, but the pillaring wasn't suitable for clay structure. The Langmuir isotherm with adsorption capacity ranging from, 3.0 to 28.8 mg g⁻¹. Ferronato et al. (2015), described the role of Zeolites such as Clinoptilolite in heavy metals removal with efficiency ranging from 78 to 95% within 24hrs with main conclusion of the probable use of this efficient low-cost sorbent in inorganic and PTE's contaminant removal. Another study was reported by Bedelea et al. (2009), Bentonites sample from deposit in Romania was applied for the removal of metal ions, cadmium, lead, and chromium from wastewaters effluent. In their study, bentonite sample proved to be efficient for heavy metal ions removal with special mention to lead ions that were completely removed with 100% removal efficiency.

In a study reported by Kabaryet et al. (2022), the efficiency of bentonite and Kaolinite and other Kaolinite derivatives (Aswan clay and Ball clay) were assessed for the removal of some heavy metals (Cd, Cu, Ni, Zn and As) and the decontamination of pathogenic bacteria in water samples collected from Belbies and Rahaway drains. Their study concluded that all clay mineral types removed Cd²⁺ completely from the water samples, while bentonite was most efficient in Cu²⁺ removal with 85% removal efficacy. The most effective removal treatment for Ni, Zn and As were detected in Kaolinite, Aswan clay and ball clay respectively, with removal percentage of 81.7, 98.75 and 100% for each, respectively.

Other inorganic and organic pollutants' removal by clay minerals

Different clay minerals were evaluated to have efficient sorption capacity for inorganic contaminants such as ammonium, nitrates, and salutes, as well as for organic contaminants such as dyes, pesticides, and some aromatic pollutants. Ferronato et al. (2015) reported the role of Clinoptilolite in NH⁴⁺ removal from aqueous solution using bed laminar flow system. Their study reported the higher sorption affinity of ammonium ions to Zeolite than Na ions. The affinity selectivity among salutes were ordered as following, Na⁺>Ca²⁺> K⁺> Mg²⁺> P. Fluoride ions were found to be desorbed by magnesium incorporated bentonite with 97% removal efficiency, reported by Thakre et al. (2010). Mena-Duran et al. (2007), studied the rate

of nitrate removal by calcium Montmorillonite activated by hydrochloric acid. Their study estimated the removal efficacy percentage increasing from 13.75% to 22.3%, when the stirring time were brought from 0.5 to 68 hours.

Various organic pollutants that are resistant to degradation were found to be transformed or partially degraded by clay minerals application in liquid solution. Gu et al. (2011) described the removal of dichloroacetic acid by bentonite based adsorptive ozonation process, followed by catalytic oxidation of Fe^{3+} . Their study concluded that the removal efficacy increased from 68% to 92% by increasing Fe^{3+} concentration from 0.5 to 5 mg L^{-1} . Carbon tetrachloride was sorped by ammonium modified bentonite with sorption efficiency 70%, exhibited by Lu & Pan (2010). Emerging contaminants such as salicylic acid, carbamazepine and naproxen were detected to be sorped to intercalated bentonite with efficiency values between 2.69 and 5.55 μmolg^{-1} exhibited by Rivera-Jimenez et al. (2011). Moreover, Senturket al. (2009), describe the sorption of phenol by CTAB (acetyl trimethyl ammonium bromide) modified bentonite, with removal value of 333 mg g^{-1} at alkaline pH 9. Another beneficial study reported by Gu et al. (2009), on the ability of bentonite to retain humic acid with efficiency percentage of 95% when combined with ozonation. Their study exhibited that adsorption efficiency enhanced when iron concentration increased from 0 to 10 mg L^{-1} . This study illustrates the effect of bentonite in the retention and slow release of organic carbon compounds which resulted in prolonged productivity and fertility when applied to agricultural soil.

Interactions between clay minerals and microorganisms

The interactions between microorganism and clay minerals play a vital role in geosphere elemental cycle (Dong, 2012). Clay minerals/microorganisms' interaction are necessary for organic matters retention and transformation (McMahon et al., 2016), as well as various elements cycles as Fe, Al, Mg, P, C, N, Si, etc., (Vogel et al., 2014). From another point of view, Vorhies & Gaines (2009), stated that Microbial secrets and metabolite can cause disintegration and dissolution of the clay mineral structure. Microorganism and their metabolites are considered as strong reducing agent which contributed to redox cycle of Fe^{3+} in sediments, soil and oceans which may be responsible for bioremediation of the contaminated sites (Playter et al., 2017). Wang et al. (2017) exhibited that, the bioavailability of heavy metals is greatly affected by the sequestering of the heavy metal ions on the clay minerals/bacterial

matrix and their intermediates derivatives. This evidence suggested that bacterial mineralization of clay minerals can participate as a strong candidate in pollutants removal (Cygan&Tazaki, 2014). Although fungi kind of microorganisms contribute to the overall biomineralization cycle, however bacterial influence is much significant in transformation, cycling and availability of mineral and elements.

The interaction of bacteria with 1:1 type of clay minerals such as Kaolinite, resulted in the transformation and purification of Kaolinite into kaolin. Moreover, bacterial extracellular polysaccharides and exudates can cause nucleation and further crystallization of Kaolinite (Freebairn et al., 2013). In another study explained by Fiore et al. (2011), Kaolinite was formed by bacteria through the precipitation of ammonium silicate by oxalate or microbial organic compounds including extrapolymerized polysaccharides (EPS), which was affected by environmental factors as temperature, pH, cations, or the nature of the functional group (Tazaki, 2013). While Kaolinite reactivity is low in comparison to other clay minerals, bacterial interaction increases Kaolinite particles reactivity through transformation of it into gibbsite or Illite, figure (6). In study reported by Andrade et al. (2018), Kaolinite was transformed to Illite through introduction of some metals as Si, Fe and Mg with further Fe reduction.

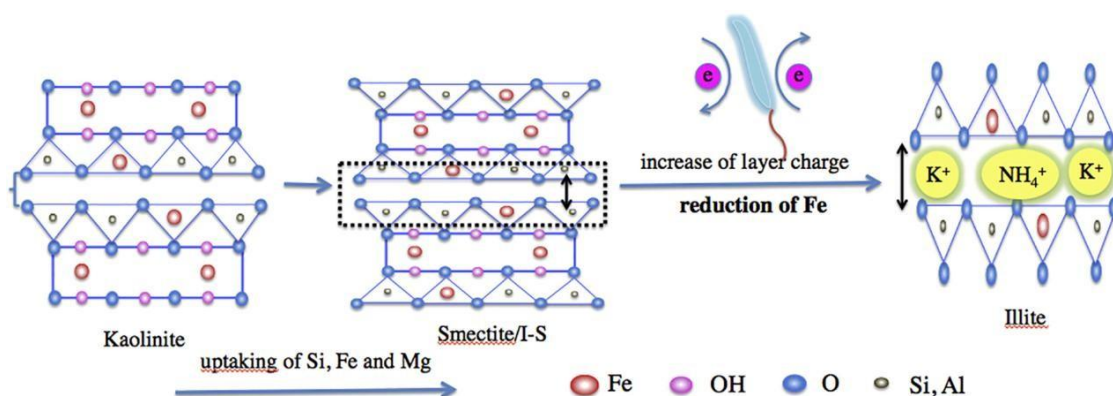


Figure (6) sequence of transformation of kaolinite into Illite (imported from Li et al., 2012) with Fe reduction.

On the other hand, bacteria can adhere to Kaolinite with the assets of bacterial exudates and polysaccharides (Poorni& Natarajan, 2013). However, the adherence of bacterial cell to Kaolinite particles depends on the properties of bacteria cells (as growth phase) reported by Hong et al. (2012), pH ranges from 3 to 10 described by Zhang et al. (2015), and ionization strength of the solution (when IS solution of solution increases the adherence of bacteria decreases) exhibited by Hong et al.

(2014). The interaction between Kaolinite and bacteria resulted in the reductive transformation of many metallic ions such as Cr(VI) and As(V), into Cr(III) and As(III), which known to be less toxic to human than their precursors, reported by Kang et al. (2015) and Ghorbanzadehet al.(2015), respectively.

The interaction between bacteria and 2:1 clay mineral type such as Smectite resulted in the bioreduction of Fe^{3+} in the Smectite structure and the formation of Fe-Illite complex figure (6), (Zhang et al., 2012). However, microbial interaction with Smectite with incorporation of bacterial EPS cause the dissolution of Smectite, and the degree of dissolution depends on the nature of the EPS and the microbial metabolites secrets in the same environment (Oulkadi et al., 2014). Zhao et al., (2017a,b), exhibited that, the process of microbial interaction with Smectite is reversible and can work in the two directions depends on the Fe redox potential in the environment. Either Smectite can transform to Illite with the bioreduction of Fe^{3+} , or it can transform to Kaolinite with reverse biooxidation of Fe^{3+} . The effect of these interactions on heavy metal and pollutants removal is inevitable. Heavy metals ions either trapped in the bacterial EPS/clay minerals complexfigure (7), reported by Qu et al. (2017) or subjected to transformation into more oxidized and less toxic forms, according to Bishop et al. (2014).

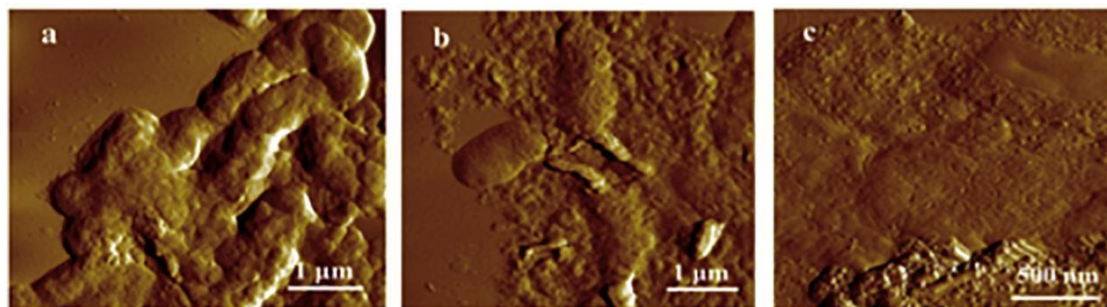


Figure (7) the interaction between Montmorillonite and *P. putida*, at pH 3 (a) and pH 7.5 (b), and pH 7.5 with 1mM Cu. Imported from Qu et al. (2017).

Clay minerals and wastewater disinfection

Globally, most of the pandemic diseases outbreaks happen due to the discharging of polluted water in nature water bodies which usually used by human for domestic and agricultural uses. The continuous natural or artificial disposal of the wastewaters in rivers, lakes, ground water, sediments, and oceans, resulted in the spread and proliferation of different pathogens such as bacteria, fungi, and protozoa. In aquatic science, the biological contamination of water bodies is measured by the

presence of specific microbial indicators such as enteric fecal bacteria count which expressed in CFU/g^{-x}, where “x” is the dilution factor of the environmental sample. Enteric bacteria are group of bacteria inhabit the stomach and intestine of warm-blooded animals, which existence indicates water pollution with domestic or livestock wastewater effluents. Several studies had explained the role of clay minerals and their modification in bacteria disinfection in wastewater. Undabeytia et al. (2014), exhibit the role of modified bentonite to remove *E. coli* from solution. Yang et al. (2012), described that, bentonite mixed with NaCl (5 and 25mM ionic strength) or CaCl₂ (5mM), increase the adsorption of gram negative (*E. coli*) and gram positive (*B. subtilis*) than unmixed bentonite.

The exact bactericidal/bacteriostatic mechanism of action of clay minerals on bacterial cell isn't fully understood under neutral conditions as both factors possess surface negative charge; however, it is influenced by different factors such as surface charge and chemistry of both bacteria and clay minerals as well as environmental factors such as pH, temperature. The adherence of bacteria to clay mineral surfaces can be enhanced through modifications of three parameters

1. Optimization of clay minerals particles hydrophobicity. bacterial cell is hydrophobic and their adherence to clay mineral particles can be increased through increasing clay minerals hydrophobicity properties by insertion of organic compounds as acids and their derivatives (He et al., 2006)
2. Modifications of bacteria or clay minerals' surface charge. As both bacteria and clay minerals particles are negatively charged, the adherence of bacterial cell to clay mineral particles can be enhanced through protonation of the clay mineral surface. In solution where pH value below the pH_{pzc} point of zero charge (specific for each clay type), clay minerals particles acquire more protons on their surfaces where their changed into positively charged, otherwise it is negatively charge. According to this theory both negative and positive bacteria attach to the clay minerals particles described by Pina & Cervantes (1995). In the case of bacteria, Borroket et al. (2005) reported that, the weakly acidic functional groups on the bacterial cell membrane may displace the important salutes as Ca²⁺ and Mg²⁺ with proton H⁺, which in turn affect the cell membrane structure stability and accelerate the cell death.

3. Bacterial cells flow condition on clay mineral surfaces. In study reported by Hiremath (2014), *Listeria innocua* adherence to metal surfaces were defected and decreased under Luminor flow condition than under static condition.

Inactivation and the subsequent death of the bacterial cell is another way of pathogen removal from wastewater. This mode of action was described by Motshekga et al. (2015), where inactivation of bacterial cells followed by rupture of cellular membrane and the leakage of cytoplasm took place by modified bentonite clay minerals. Wu et al. (2011), explained the role of phosphonium organo-clay minerals as antibacterial agent. Their study exhibited the successive steps of bacterial cell death as following, bacterial cell adheres to the clay mineral surface followed by the subsequent release of phosphonium group (PH^{+4}) across the cell wall to the cytoplasm, which disrupted consequently followed by cell death. Morrison et al. (2013) documented the successive steps of pathogenic bacteria death (*E. coli*) and (*S. epidermidis*) using SEM, showed in figure(8).

Kabaryet al. (2022), found that, the application of clay mineral types (Kaolinite, Bentonite, Ball clay and Aswan clay) after amalgamation with *Acidithiobacillus* + phosphate dissolving bacteria culture mixture, enhances the removal of Cd, Cu, Ni, Zn and As from wastewater drainage samples as well as fecal coliform bacteria in all amended treatments than control samples. Their study concluded that “T18” refer to bentonite treatment with the culture mixture, was the most efficient treatment in Cd, Cu, Ni, Zn, As and pathogenic bacteria removal with efficiency percentage of 100%, 46.25%, 81.43%, 91%, 100% and 61% for each of the contaminants, respectively.

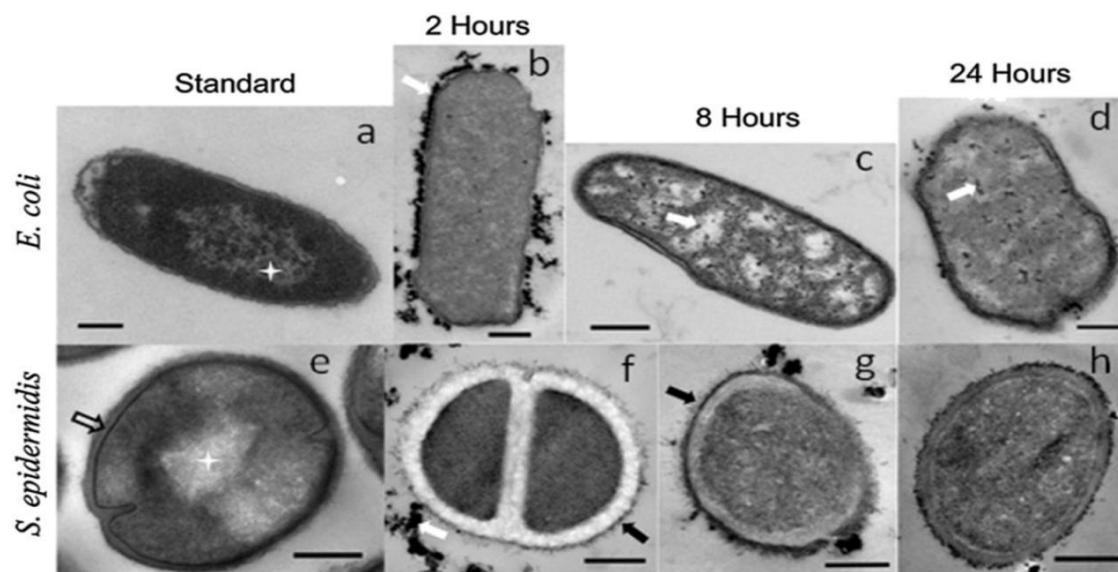


Figure (8) The fate of gram-negative (*E. coli*), and gram-positive bacteria (*S. epidermidis*), after exposure to blue clay-mineral during 24hrs exposure time. (Imported from Morrison et al. (2013)).

CONCLUSION AND FUTURE PROSPECTIVE

Although the role of clay minerals has proven to be very effective in different environmental necessitate aspects, its role in pollution control and contaminants removal is the most significant, not only due to its absolute efficiency but also because its low- cost, widely available characteristics with less hazardous effect detected.

The future prospective of this review of article is to discover more nature clay mineral types with the desirable properties needed for decontamination of wastewater from all contaminant types. Moreover, study the effect of chemical modifications as the solution ionization degree and introduction of organic acids, nanomaterials or other adsorbents on the overall clay mineral structure and their effectiveness in water decontamination process. Variations in environmental conditions such as pH, temperature, bacterial growth, and surface properties, is also of great importance to be deeply studied on both clay mineral structure and its interaction with both bacteria and other heavy metals implicated in the same environment.

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