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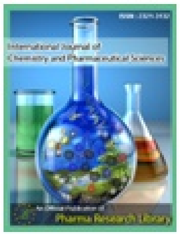

Microbial adsorption and inhibition mechanisms of Clay Minerals and Derived Materials: A Review

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ABSTRACT

The global health issues of antimicrobial resistant and instability of antibiotics and other antimicrobial agents have drawn the attention of researchers to developing alternative technologies for combating the epidemics of these health issues. Clay minerals in the past and present decades have been explored as cheap and effective materials to combat the problems of antimicrobial resistant with enhanced stability properties, both in their raw and modified forms as well as materials derived from them. The biogeochemical characteristics of clay minerals have drawn the interests of several researchers worldwide. Several synthetic and modification methods such as intercalation, adsorption and pillaring have been employed to derive materials from clay minerals. Clay minerals and derived materials possess diverse biological properties and play a vital role in microbial inhibition which is accompanied by diverse mechanisms that are driven by different factors such as pH, presence of metals and metal ions. Microorganisms also adhere to clay materials' surfaces by adsorption mechanisms that are influenced by medium chemistry, and this makes it possible for the materials to remove microbes from their respective contaminated medium. These properties make clay materials suitable for both biomedical and pharmaceutical applications. This mini review discusses various mechanisms by which microorganisms are inhibited and adsorbed by clay minerals, factors influencing the mechanisms as well as the interactions between clay minerals and microorganisms.

Keywords: adsorption; microbial inhibition mechanism; microorganisms; clay materials; biomaterials.

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1. Introduction

The global health issues of antimicrobial resistant and instability of antibiotics and other antimicrobial agents have drawn the attention of researchers to developing alternative technologies for combating these health issues. Chemical agents with several drawbacks that have been used to combat the endemic problems associated with microorganisms include metal complexes of shiffbase ligands, nitrogen and sulfur heterocyclic systems, plant extracts, compounds containing the pyrazoline ring and thiazole ring systems [1-4]. Free chlorine and chlorinated compounds are the most widely used chemicals in water treatment for the merits of their effectiveness, low cost and protection efficiency against re-growth of bacteria and other pathogenic microorganisms [5]. Alteration of taste and ability to react with various water constituents resulting to undesirable by-products are the major drawbacks associated with the use of chlorine in water treatment [6]. Clay minerals are generally composed of alumina and silica which are formed bytetrahedral and octahedral sheets that are linked together through sharing of apical oxygen atoms [7]. Recent advances in mineralogical and physicochemical characterization of clay minerals have enabled their classification into different groups *viz*: illite, kaolinite, vermiculite, smectite and chlorites [8-10]. Clay mineralogy has been studied for several years by many researchers which have led to advances in their applications. Architecture, construction, adsorption technology, ceramics, cosmetic, paints, medicine and pharmaceuticals are the major areas where clay minerals have been widely applied [11-14]. Both raw and modified clay minerals as well as materials synthesized from them have long been used in many parts of the world to treat several human diseases and ailments caused by pathogenic microorganisms [15, 16].

Clay minerals consist of various elements including the transition metals capable of interacting with microorganisms Adekeye et al. [17]. These elements may either be beneficial or toxic to microorganisms. Some elements may serve as sources of minerals for various biological functioning while others may be toxic [18-20]. The interactions between clay minerals and microorganisms are often influenced by medium chemistry. Several materials have been derived from clay minerals through different techniques which include intercalation, pillaring and ion exchange for effective inhibition and adsorption of microorganisms [13, 21-23]. Inhibition and adsorption are the two major modes by whichby which clay-based materials disinfect microbially-ladened substances. The mechanisms by which microorganisms are inhibited and adsorbed by clay minerals and their materials are discussed in this mini review.

2. Clay Minerals Microbes

Microorganisms have been identified as the most abundant living thing and a great proportion of them live in direct contact with mineral surfaces [24]. It has been estimated that approximately 50% of the earth's biological organisms corresponds to prokaryotes, of which of many of them lives on mineral surfaces [25]. Microfungi, free or in symbiosis with plants and algae, are also very numerous. About 25% of the entire biological mass is made up of fungi according to Miller [26], of which microscopic fungi are the largest components. Thus, it could be said that prokaryotes and microfungi make up about 75% of the biological mass in the planet. Microscopic algae are relatively abundant, but the numbers that live on or under mineral surfaces are less than that of prokaryotes and fungi. A great number of these microorganisms exist on and inhabit clay minerals surfaces [26-30].

3. Detection of Microorganisms in Clay Minerals

Several researches have been carried out to investigate microbial communities associated with geological materials including clay minerals [31-36]. Limitations of employed methodological approaches have been identified when isolating and characterizing clay-endemic microbes [37-41]. Several techniques have been developed and used for both detection and characterization of microorganism in clay mineral surfaces; scanning electron microscospy (SEM) and epifluorescence microscopy are considered the most commonly applied of these techniques. Both techniques, however, have limitations in observing bacteria that are associated with clay minerals [42]. The techniques are greatly marked with the inability to resolve clay-hosted bacterial cells resulting from the abundance of reflective and autofluorescent mineral grains within clay matrices; the requirement for large dilutions, and the presence of mineral grains of comparable size to bacteria are also considered major flaws of these techniques [42]. In a research conducted by Haveman et al. [37], they identified issues associated with the commonly applied fluorescent stains 4,6-diamino-2-phenylindole (DAPI) and acridine orange when used against fine-grained geologic media. A major issue identified by the researchers is discrepancy in cell count when cells were enumerated using DAPI versus acridine orange probes such that cell counts obtained using DAPI were morethan twice those determined by acridine orange [37]. Similar result was observed in the work reported by Kostka et al. [28]. They reported an inconclusive enumeration of bacterial cells against clay mineral matrices when using DAPI and acridine orange stains. More so, Fukanaga et al. [38] utilized the fluorescent probe carboxy fluoresceindiacetateacetoxymethyl ester (CFDA-AM) to detect the presence of living cells within bentonite clay samples. The authors confirmed the absence of artefacts associated with DAPI and acridine orange probes when using CFDA-AM by analyzing an autoclaved sample as a negative control.

Trends in limitations associated with these commonly applied probes and microscopy techniques resulted to quest of scientists in developing and sorting for alternative instrumentation and more sophisticated techniques for identification and analytical characterization of microbial cells affiliated with clay mineral matrices. Greater success was achieved in a work reported by Maurice et al. [43] who used atomic force microscopy (AFM) to examine kaolinite grains within a bacterial matrix from microbial growth experiments, supporting the utility of this powerful technique to resolve clay mineral-microbial associations. Lower et al. [44] proposed that biological force microscopy (BFM) may find application in understanding processes such as mineral dissolution, attachment of bacterial cells to mineral substrates, and biofilm development. Different studies using polymerase chain reaction (PCR) for the genetic identification of bacterial DNA in clay samples have been conducted [42, 45]. PCR was found to successfully identify bacterial DNA in clay samples at different depths within examined cored sections, and the technique was used to support the notion that a decline in cell count density is observed with increasing depth in undisturbed clay deposits [45]. In addition to the use of genetic DNA-based characterization through carbon utilization studies, Lawrence et al. [42] was able to show that cells of coccoid morphology dominated approximately 61% of microbial population at certain depth in an undisturbed clay deposit, although rod-shaped bacteria were shown to be approximately 39% whereas those of spiral morphology were absent. Their results also showed approximately 97% of the microbial populations were Gram-negative bacteria while 3% were characterized to be Gram-positive bacteria in approximation; moreover, numerous species of aerobes, actinomycetes, sulfur oxidizers, methanogens, and other anaerobic species were identified [42]. Boivin-Jahns et al. [45] was able to show that microbial population of clay minerals decreases with increasing depth.

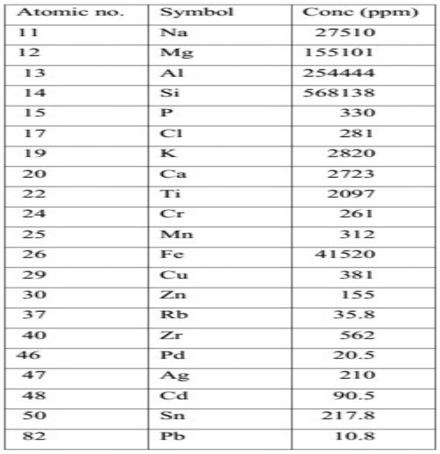
4. Factors Influencing the Survival of Microbes in Clay Minerals

There are several factors influencing the survival of microorganisms in clay minerals as they face numerous challenges living in the minerals deposits and several physical mechanisms have been identified which can cause the death of subject microorganisms. For instance, Rebata-Landa and Santamarina [46] stressed that physical processes such as puncture, (describing the impalement of bacterial cells by clay particles pressed at an angle into the cell wall) and tensional breakage(occurring when the space around a bacterial cell is reduced due to compression, causing axial deformation and tensional rupture of the cell wall) usually account for a number of bacterial death in mineral deposits of clay; this implies that both the shape and size of the minerals would significantly affect the survival of microbes. In 2005, Fukunaga et al., identified that a decline in moisture content at depth within bentonite clay may be responsible for the observed decrease in bacterial activity and survival [38]. This also shows that moisture content as a factor affects bacterial activities and survival. Entrapped bacteria within clay deposits usually undergo slow cell division, exist in low cell count densities and survive under nutrient-poor diffusion controlled conditions by drastically reducing metabolic activity [42, 45]. Boivin-Jahns et al. [45] explained that the degree of microbial diversity defining a clay deposit is heavily dependent upon the extent of confinement experienced within the particular environment. The influence of pore connectivity on bacterial diversity in soils was also studied by Carson et al. [41] and their results showed there is a relationship between pore connectivity and bacterial diversity in soil. They further explained that under the conditions of low water potential and high clay and silt content a soil exhibit low effective porosity, which can induce a decrease in bacterial mobility and substrate diffusion within the soil media. Elemental and other mineralogical compositions of clay may significantly affect the survival of microorganisms. Chemical effects such as pH of the clay minerals, presence and nature of metal ions in the minerals and presence of organic matter have been reported to influence the survival of microbes in clay minerals [23,24].

5. Clay Minerals-Microbes Interactions

Clay minerals are made up of different elemental composition that are either positively or negatively charged [10]. The particulate composition of clay minerals of different charges makes it possible for the minerals to interact well with a wide range of microorganisms. These interactions are driven by different mechanisms. The mechanisms can be understood in terms of adsorption influenced by electrostatic attraction and ion exchange which could influence mineral transformation, mineral weathering, microbial killings or microbial growth etc., [47-49]. Table 1 showed the elemental composition of a typical kaolinite clay determined by proton induced X-Ray emission technique [17].

Table 1: Elemental composition and concentration of Ire-Ekiti kaolinite clay soil



Atomic no.	Symbol	Conc (ppm)
11	Na	27510
12	Mg	155101
13	Al	254444
14	Si	568138
15	P	330
17	Cl	281
19	K	2820
20	Ca	2723
22	Ti	2097
24	Cr	261
25	Mn	312
26	Fe	41520
29	Cu	381
30	Zn	155
37	Rb	35.8
40	Zr	562
46	Pd	20.5
47	Ag	210
48	Cd	90.5
50	Sn	217.8
82	Pb	10.8

The interaction between clay minerals and microbes also depends on various minerals characteristics such as particle size distribution, particulate shape, clay content, hydrophobic properties of particle surface, moisture content, heterogeneity of soil matrix, density between soil matrix magnetic properties, and other conditions such as pH, temperature, elemental concentration, ionic properties, contact time and so on [38, 42, 46, 50]. Clay minerals-microbes interactions can be understood in different perspectives viz: the activities of microorganisms in clay minerals, activities of clay minerals on microorganisms and the mutual relationship that exist between clay minerals and microorganisms [51]. Actions of clay minerals on microorganisms have been much defined by the inhibitory effects of the minerals on microorganisms. However, mutual relationship is also enjoyed between clay minerals and microorganisms most especially in terms of ion exchange between clay minerals and microbes, mineral regeneration and formation for improved inhabitation. Phosphates, nitrates halides, sulphates, oxygen, hydrogen and carbon are chemical composition of clay that may be essential for biological processes and support the survival of microorganisms living on clay minerals. The potential inhibition of microorganisms by clay minerals is accompanied by different mechanisms which are further discussed in the later part of this review. The potency of clay minerals to inhibit microorganisms (bacteria, fungi, virus and protozoa) is majorly attributed to both physical processes and abiotic or chemical factors. These factors explain both the physical and chemical effects of clay on microorganisms.

6. Microbial Inhibition of Clay Minerals and Derived Materials

As discussed earlier that the mechanisms of inhibition of microbes by clay minerals depend on several factors that include pH and ion exchange capacity of the clay influenced by the presence of metals and metal ions. Adsorption capacity of the clay minerals is another factor that influenced the uptake or removal of microorganisms from their respective contaminated media. Adsorption is influenced by electrostatic attraction and repulsion between the clay positively charged surfaces and the negatively charged surfaces of microbial cell walls. This section discusses the factors influencing the inhibition and removal (adsorption) of microorganisms by clay and its derived materials as well as the processes by which the inhibition and removal are achieved.

Mechanistic Factors Influencing the Inhibition of Microbes by Clay Minerals and Derived Materials

Presence of metal and metal ions:

Microbiocidal metals are characterized by their growth inhibiting activities, morphology disruption, and biochemical activities alterations of microorganisms [52, 53]. It is well known that bio-toxicity of a given metal depends on its concentration, chemical speciation, lipophilic and lipophobic properties, as well as the nature of the host environment [54, 4]. The mechanisms by which microorganisms are inhibited by clay minerals or clay materials are mainly associated with their adsorptive and ion exchange properties. Improving the ion exchange and the surface binding properties of different clay minerals has been targeted in designing and developing various clay hybrid antimicrobial agents. Metal ion toxicity is directly linked to ion speciation changes that are influenced by different parameters such as the pH, ion solubility, osmotic strength, redox state, and temperature of the environment [48].Metal Ions like Ag, Cu and Fe etc., are known to possess mild antimicrobial properties and have been successfully loaded into clay materials through different processes like intercalation, adsorption and pillaring to improve their antimicrobial properties [16, 21, 22]. The mechanism of inhibition involves gradual release of the novel exchanged ions from the clay materials for long-term antimicrobial effects. Some of the biocidal metals responsible for microbial inhibition and their inhibiting mechanisms are discussed below.

Aluminium ions:

Most microorganisms thrive well in environments with pH near 7.0 [55]. Acidification of both marine and terrestrial environments may be influenced by the presence of metal ions that can alter the biogeochemical properties of the environments. Sparling and Lowe [56] suggested that the solubilisation or mobilization of toxic metals may be the primary cause of some adverse effects attributed to acidification of water and soil. It is well documented that aluminium ion Al^{3+} is toxic to living organisms, and thus, the toxicological effects of acidification are at least partially due to the action of released Al ions. Though the mechanism of aluminium toxicity is poorly understood, once inside the microbial cells, it is assumed that aluminium may affect metabolism by binding directly to enzymes (e.g. *phosphatases*) or to enzyme substrates resulting to alteration in their biochemical functioning [57]. However, Londono et al. [49] were able to show that Al toxicity plays a central role in the antimicrobial action of a kaolinite clay against a model *Escherichia coli* (ATCC 25922). The clay was reported to have buffered the media pH to approximately 4.6 and Eh values to +360 mV. Chemical analysis of the clay and the bacteria showed that P, Al, and transition metals (Fe, Mn, Cu, and Zn) were exchanged during incubation process at 37 °C. Only Al derived from the clay was shown to have exceeded the minimum inhibitory concentrations for *E. coli* under acidic conditions. Ion imaging analytical technique showed elevated Al levels in the bacterial membrane, and high intracellular Fe levels, as compared to those of untreated controls. The inhibition mechanisms reported in their study include Phosphorus depletion in the *E. coli* after reaction with the clay and evidence of membrane permeation, suggests that Al reacts with membrane phospholipids thereby enhancing intracellular transport of metals and thus amplifying the toxicity of transition metals in the microbe [49]. The antimicrobial action and mechanism of inhibition is shown below.

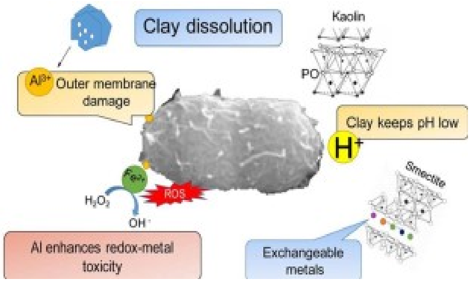


Fig 1: antimicrobial action of a kaolinite clay against a model *Escherichia coli* (ATCC 25922) [49].

Silver and silver ions:

Silver and silver-based nanomaterials have been shown to exhibit broad-spectrum microbicidal activities against fungi, bacteria and viruses [58]. The proposed mechanisms of action vary greatly and include the inhibition of respiration, generation of reactive oxygen species (ROS), cell membrane damage, and inactivation of iron-sulfur clusters of bacterial *dehydratases* involved in amino acid biosynthesis [58-61]. Proteomic analyses of *E. coli* exposed to silver ions and silver nanoparticles showed destabilization of the microbial outer membrane, accumulation of envelope protein precursors, and depletion of intracellular ATP, indicating the collapse of the membrane Su et al. [83]. A Study has also shown that silver interacts with the many membrane-bound proteins present in the cytoplasmic membrane [59]. Binding of silver metal to enzymes in the electron transport chain can uncouple the respiratory transport chain, resulting in the formation of hydroxyl and superoxide radicals [59, 61]. In this regard, the generation of ROS is likely a secondary consequence rather than the direct cause of silver toxicity. The silver ion is highly reactive in nature and can bind strongly to ligands containing oxygen, sulphur or nitrogen [62].

In order to enhance the antibacterial activity of a naturalsmectite clay, Parolo et al. [13] loaded the clay with silver ion after which the silver loaded clay showed improved antibacterial activity with a measurable zone of inhibition. The antibacterial activity of the silver loaded smectite clay was shown to have increase with increase in loading of the Ag^+ and thus, antibacterial properties of the material was attributed to the electrostatic force of attraction of the negatively charged membrane of the bacteria (*E. coli*) to the clay surface and thus enabling the silver ion to kill the bacteria or inhibit their replication [13].

Copper ions and copper surfaces:

Copper is a metal is known to possess antimicrobial properties. As a transition metal, it is thought to increase the bulkiness of a ligand upon complex formation thereby improving the lipophilic properties of the complex [52, 63]. The use of copper-coated materials has been proposed for surfaces exposed to human contact sto reduce infections caused by microorganisms. It is known that a copper ion catalyses reactions that produce ROS (hydroxyl radicals) via Fenton and Haber-Weiss reactions and cause oxidative damage to lipids, proteins and DNA [64, 65]. Bacterial killing by dry metallic copper surfaces have been shown by Santo et al. [66]. In their experiment, they noted that the death of the microbe was as a result of loss of cellular integrity and rapid cellular damage. The basis of copper toxicity at the molecular level could also occur via attack of bacterial iron-sulfur clusters in cytoplasmic *dehydratases*. Copper binds with the sulfur atoms of the cluster with high affinity, subsequently displacing the catalytic iron atoms, and consequently inactivating *the dehydratase* catalytic cluster [47]. Xia et al. [47] showed the effects of copper bearing montmorillonite clay on the growth performance, intestinal microflora and morphology of weanling pigs. The displacement of the iron ion in the iron-sulfur cluster terminates the functional activity and resulting to death of the microbes. This finding was also supported by the study reported by Macomber et al. [23]

Clay adsorption of microbes and mechanisms:

The presence of pathogenic bacteria in water has been attributed to the cause of diverse bacterial infectious diseases when consumed and this necessitates their uptake from aqueous solutions. The removal of bacteria could be achieved through the use of adsorbents because of interfacial forces of attraction that could be established between their surfaces. The attraction of bacteria cell onto adsorbent surfaces could be influenced by the medium chemistry, cell surface molecules, hydrophobicity and surface charges. Bacteria cell wall is known to compose of outer membrane proteins, lipopolysaccharides, extracellular polymeric substances and positively charged surfaces which could be accountable for the adhesive force established during interaction with alumino-silicates or clay materials [16, 67].

Several clay minerals in their raw and modified form have been used for the adsorptive removal of bacteria in water. Pyrophyllite, a hydrous alumino-silicateclay mineral, was reportedly used to remove *E. coli*in solution at solution pH of 7.1, and the amount of bacteria removed reached 94% (Kang et al., 2013). Adsorption complexes of montmorillonite clay mineral with organic cation Benzyldimethylhexadecylammonium (BDMHDA), was used to remove gram-negative bacteria (*E. coli* K-12) and gram-positive bacteria (B. magaterium) as well as a protozoan parasite (*Cryptosporidium parvum)* from their contaminated water medium. The results from the adsorption experiment showed reduced concentration of the contaminants [68]. A blend of clay soil (75%) and filter media including zeolite, sand, charcoal and vermicompost (25%) were used to remove faecal coliform from water. The technique was considered effective and the coliform removal ranged within 82–99% with the mixture of clay soil and charcoal showing the best removal efficiency [69]. Clay-polymer composites of bentonite and commercial polymers were also reportedly used to remove *E. coli*from solution (Undabeytia et al., 2014).Magnetic nanoparticles of exfoliated mica and montmorillonite were used to efficiently remove *S. aureus*and *E. coli* bacteria from solution [70]. Wu et al. [71] intercalated vermiculite, montmorillonite, kaolinite and palygorskite with quaternary phosphonium salt and their antibacterialproperties were evaluated against *Staphylococciaureus* **(**ATCC 6538) and *E. coli* **(**ATCC 25922). They suggested that the antibacterial activities of the phosphonium intercalated clay minerals were dependent on thesurface charge of the adsorbents, the amount of phosphonium surfactant released and particle size of the materials. Recently, agrogenic composite of *carica papaya* seeds and kaolinite clay, modified with ZnO was used to remove *Vibrio cholera* and *Samonellatyphi* [16]. The bacteriostatic agrogenic clay composite (adsorbent) was shown to possess positively charged particles at pH lower than the isoelectric point pH of ZnO (pH 9.0–10.0) established by using the pH point of zero charge (pzc) analysis. It is believed the adsorption of the bacteria onto the surfaces of the adsorbent was due to electrostatic mechanism that occur between the modified clay mineral and bacteria occur as the bacteria surfaces were negatively charged (due to the presence of PO_4^{3-} and COO^-) while the surfaces of the adsorbent were positively charged [16]. The bacteria were attracted to the positively charged surfaces of the adsorbent and became attached. Liu et al. [72] modified clay mineral surfaces using Layer Double Hydroxide (LDH) and suggested three possible mechanisms for the interaction of bacteria with the modified clay minerals to either be a substitution of OH groups on the adsorbent's surface with PO_4^{3-} groups on the bacteria, exchange of ions between the bacteria and the surface of the adsorbent or H-bonding and polar attractions that occur with or without the bridge of H_2O molecules which enhances bacterial adhesion onto the adsorbent's surface as shown in Figure 2.

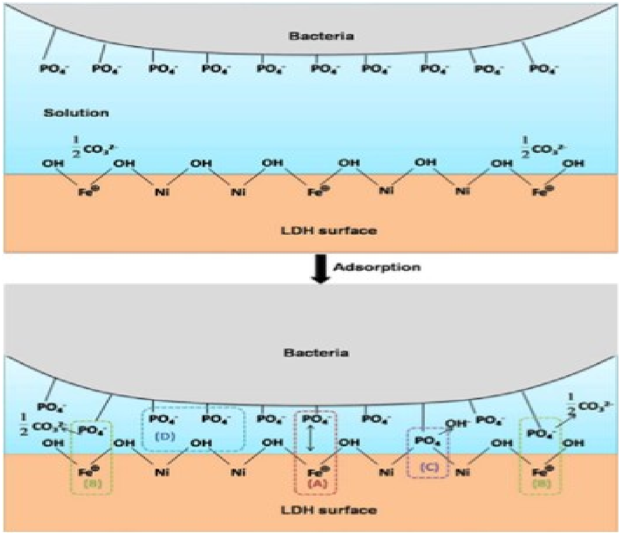


Fig 2: Mechanism of *B. subtilis* adhesion onto $NiFeCO_3$-LDH. (A) Electrostatic interactions, (B) ion exchange, (C) OH group replacement and (D) H-bond and polar interactions [72].

(N,N″-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecanediamidine di(acetate)) was intercalated into Montmorillonite for the removal of *E. coli* from aqueous solution and the mechanism of adsorption was attributed to the bacteria hydrophobicity, and electrostatic force of attraction that existed between the adsorbent and adsorbate (*E. coli*) [75]. Various factors that include surface and internal features of the bacteria and adsorbent’s surface chemistry have been shown to influence the adsorption and adhesion of bacteria onto clay materials’ surfaces [76-81]. Further experiments have shown that hydrophobicity and Van der Waals force account for the antimicrobial activities of some clay minerals [70, 82].

7. Conclusion

Clay minerals and derived materials have been shown by several researchers to possess mild antimicrobial activities. The bioactivities of clay materials are dependent on the type of minerals they contained, their physico-chemical and biogeochemical properties which are influenced by several factors such as pH, presence of metals and metal ions. Inhibition and adsorption are the two major modes by whichby which clay-based materials disinfect microbially laden substances. Susceptibility of a microorganism to inhibition by clay minerals and derived materials is influenced by several factors which include the microbial cell surface molecules, hydrophobicity and surface charges as well as the chemical composition, structural and morphological properties of the clay materials in use. Microbial adsorption is a phenomenon that describes the attachment of a microorganism to the surface of a clay material by electrostatic attraction which usually occurs between the clay positively charged surfaces and the negatively charged surfaces of microbial cell walls. There has been limited information on the bioactivity of microbially synthesized clay minerals and this could be an area for further research in bioapplication of clay minerals. Up till date, information regarding the use of natural clay materials in treating and managing plants diseases caused by pathogenic microorganisms is still mean.

Conflict of Interest

The authors of this work declare that there are no conflicts of interest

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