



Review article

Clays for Efficient Disinfection of Bacteria in Water



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ABSTRACT

Clay minerals are not only abundant in nature but can be easily engineered to make highly efficient materials for disinfection of water. A combination of their abundance and efficiency makes them a sustainable source of material for water disinfection. Several works have reported the use of clay minerals in modified form to make the removal of harmful pathogens from water sustainable and more efficient. This article reviews the various modified clay minerals that have been developed for the removal of these harmful pathogens from water. It also considers several operating factors that moderates the efficiencies of these materials during the pathogen removal process, techniques for measuring interaction between bacteria and clay-based adsorbents and future perspectives on their use in the treatment of potable water. It is believed that this will spur some interest in the quick development of very efficient and sustainable clay-based materials that will be useful for disinfection of water and wastewater in the near future.

1. Introduction

The need for the development of effective and efficient water purification techniques is necessary given the various inadequacies associated with currently employed water purification techniques. Chemical purification (Chlorination, Ozonation); biological treatment (Activated sludge); physicochemical treatment (Flocculation, coagulation) and membrane systems (Ultra-filtration, reverse osmosis) are some of the currently employed treatment techniques, but each has its shortcomings.

Most of the current outbreaks of diseases in the world are as a result of water and food-borne enteric bacteria, such as cholera (caused by *Vibrio cholera*), diarrhoea, dysentery (caused by *Escherichia coli*), food poisoning and typhoid (caused by *Salmonella typhi*). These pathogens have shown to be the cause of diseases leading to morbidity and mortality in developing world. About 88% of diarrhoea disease is linked to unsafe water supply and hygiene (Jyoti and Pandit, 2001). It has been reported recently that > 1.3 million deaths of children are caused by diarrhoeal illness worldwide every year (Liu et al., 2013a; Ma et al., 2014).

Enteric bacteria, also known as faecal coliform bacteria, are bacteria which occur naturally in the intestines of warm-blooded animals. Human sources of these bacteria include failing septic tanks, and leaking sewer lines combined with sewer overflow. Animal source of these bacteria includes manure spread from livestock on land, in run-off

or streams, and improper disposal of farm animal wastes. It has been observed that the source of infection may be partly due to the transportation of manure to ground water by leaching and precipitation (Hong et al., 2012; Bradford et al., 2013; Ferguson et al., 2013).

Water Disinfection is the removal, deactivation or killing of pathogenic microorganisms in water. Water disinfection could occur by either or both chemical and physical means. A number of techniques have been applied for the removal of bacteria from water including physical processes e.g. adsorption, distillation and filtration (Xue et al., 2012), biological processes which include activated sludge and biological trickling filters, physicochemical processes such as flocculation or lime softening, chlorination and ozonation (Ma et al., 2014), electro-magnetic radiation (Ambashta and Sillanpaa, 2010) and photocatalytic process (Nie et al., 2014).

Chemical agents such as chlorine and its compounds are most widely used in water treatment because of their effectiveness, low cost and their extra protection against re-growth of bacteria and pathogens (Amin et al., 2014). However, the addition of these chemicals to water do alter the taste of the water and also react with various constituents in natural water to form disinfection by-products (DBPs), many of which are carcinogens (Villanueva et al., 2007). It is well known that chemical treatment of water with chlorine results in harmful and carcinogenic DBPs (Nieuwenhuijsen et al., 2009). In addition, bacteria have developed chlorine-induced antibiotic resistance (Xi et al., 2009; Yuan et al., 2015) in which case high dosage of the disinfectant will be required

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leading to the formation of a significant amount of DBPs. The alternative chemical agent is Ozone which requires the use complicated equipment and also leads to the formation of organic DBPs. With UV-irradiation, there is the possibility of bacterial re-growth (Wang et al., 2015). Besides, UV-irradiation will be difficult to deploy in several developing countries where constant power supply is a serious issue.

Membrane filtration, though very effective for disinfection of water, suffers from fouling which results in frequent replacement of the membranes that raises the cost of the entire water treatment process. Adsorption technique is a favoured method for removal of bacteria from potable water and wastewater owing to its simplicity, high efficiency, low-cost of operation, ease of regenerating the adsorbent and ease of upscaling the process (Nassar et al., 2012). Furthermore, adsorption processes do not produce by-products as is found with chemical disinfection processes like chlorination which gives it an edge over other purification techniques. Adsorbents used for bacterial removal from water can be organic (Rabea et al., 2003; Qi et al., 2004), inorganic (Zhang et al., 2010) and organo-inorganic (Undabeytia et al., 2014) in nature.

Several adsorbents have been developed in the recent years including nanoparticles and nanocomposites (Farkas et al., 2015; Abdolmaleki et al., 2017), graphene (Deng et al., 2014; Sharma et al., 2015), membranes (Papaphilippou et al., 2015) and double-layered hydroxides (Jin et al., 2007) for the removal of pathogenic organisms from water. Nanomaterials (nanoparticles and nanocomposites) especially silver-mediated nanoparticles have been found to be very effective in killing bacteria in water but there is growing concern about their toxicity both to humans and the environment (Savage and Diallo, 2005; Fewtrell, 2014). Graphene and its modified forms are also very effective in capturing bacteria from water, but they are very expensive to prepare.

Clay minerals are another class of adsorbents that offer themselves naturally as antimicrobials. Clay minerals have been used for medicinal applications throughout recorded history. They have been used as a mineral remedy for ailments such as diarrhoea, dysentery, tapeworm, hookworm, wounds, and abscesses (Otto and Haydel, 2013). They have also been used as excellent adsorbents for bacteria removal in water which has practical applications in wastewater treatment (Hrenovic et al., 2009) and environmental bioremediation (Muter et al., 2012). The advantage possessed by clay minerals over other adsorbents is their relative abundance in nature, low-cost and environmental friendliness in their applications. Furthermore, they have large specific surface areas, high porosity, surface charge and surface functional groups which qualify them as useful adsorbents (Yuan et al., 2013).

Nevertheless, with its known advantages in the removal of pathogens from water (Barr, 1957; Nováková, 1977), clay minerals suffer from the fact that they are difficult to recover from aqueous solution after use which makes it practically impossible to utilise them on a large scale for water disinfection. However, engineering their surfaces and sometimes their layers does enhance their usefulness especially in disinfection of water.

There exist a large body of data from decades of research on the removal of heavy metal ions and organic pollutants from water (Adebowale et al., 2006; Unuabonah et al., 2007; Unuabonah et al., 2013a,b; Moyo et al., 2014; Gupta and Bhattacharyya, 2014; Abdolmaleki et al., 2017). However, there is a largely disproportional amount of data on disinfection of water by adsorbents when compared with those of heavy metals and other organic pollutants in water except for the long-standing technique that utilises chlorine. There are even articles that discussed the interaction of clay minerals with bacteria for the purpose of understanding the role of certain bacteria in the formation and transformation of these clay minerals. These articles have been well discussed in a review article by Mueller (2015). The present article is devoted to discussing the development of clay minerals and their modified analogues for bacterial removal from water in recent years, the mechanism of bacterial removal from water and future

perspectives on the use of these clay-based adsorbents for bacterial removal in water. It is hoped that this article will generate more interest in the development of more low-cost, efficient and sustainable clay-based adsorbents and materials for the capture and possible degradation of bacteria in water that will be useful for large-scale water treatment in the near future.

2. Clay-based materials used in water disinfection

Several clays and modified clay minerals have been used for the removal of bacteria in water. Pyrophyllite, a hydrous aluminosilicate clay mineral with the chemical composition of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, was used to removed 94% of *E. coli* in solution even in the presence of 10 mM of NaHCO_3 at solution pH of 7.1 (Kang et al., 2013). A blend of clay-polymer composites using Bentonite and commercial polymers were used to remove *E. coli* from solution (Undabeytia et al., 2014). Clay-polyvinyl pyridinium matrix prepared by copolymerization of γ -methacryloxypropyltriethoxy silane, bonded covalently to clay with 4-vinylpyridine and subsequent quaternization with benzyl halides had high antibacterial properties against *E. coli* in aqueous solution (Seckin et al., 1997). Shtarker-Sasi et al., (Shtarker-Sasi et al., 2013) used micelles of the organic cations, Benzyltrimethylhexadecylammonium (BDMHDA), or Octadecyltrimethylammonium complexed with the Montmorillonite clay mineral to remove gram-negative (*Escherichia coli* K-12), gram-positive (*Bacillus megaterium*), and a protozoan parasite, *Cryptosporidium parvum* from water and reduced their concentration in water by 3–6 orders of magnitude. A mixture of clay soil (75%) and filter media such as sand, zeolite, vermicompost and charcoal (25%) were used to effectively remove faecal coliform from water within a range of 82–99% with the mixture of clay soil and charcoal given the best removal (Khamkure et al., 2016). Liu et al. (2016) developed magnetic nanoparticles from Fe_3O_4 , exfoliated Montmorillonite and Mica which were used to remove gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria from solution efficiently. It was observed that Bentonite in NaCl (5 and 25 mM ionic strengths) and CaCl_2 (5 mM ionic strength) electrolytes, captured more gram-negative strain *E. coli* DH5 α and gram-positive strain *Bacillus subtilis* than when Bentonite was used alone (Yang et al., 2012) with CaCl_2 electrolyte producing a better effect. Kaolinite was found to adsorb more *Pseudomonas putida* than Montmorillonite, and the adsorption capacity for this bacteria increased with increasing temperature from 15 to 35 °C (Jiang et al., 2007; Rong et al., 2008) since the activity of *P. putida* is optimum in this temperature range. The interaction between Cu^{2+} and Montmorillonite was harnessed for the removal of *Aeromonas hydrophila* bacteria from water which is known to be the cause of motile aeromonad septicaemia in fish, and *E. coli* K₈₈ (Hu et al., 2005; Hu and Xia, 2006). Wu et al. (2011) intercalated Montmorillonite, Vermiculite, Palygorskite and Kaolin with quaternary phosphonium salt and their antibacterial properties were measured against *E. coli* ATCC 25922 and *Staphylococcus aureus* ATCC 6538. Wu et al. (2011) also suggested that the antimicrobial activity of phosphonium intercalated clay minerals depend on three factors; the amount of phosphonium surfactant released, the surface charge of the adsorbents and particle size of the organoclay minerals. They opined that the increasing amount of phosphonium surfactant released, increasing zeta potential (positive charges) and the narrow particle size distribution of the modified clay adsorbents, enhances the antimicrobial efficiency of the adsorbent.

Only recently, a new bacteriostatic hybrid clay composite was developed from a combination of kaolinite, *Carica papaya* seeds and ZnCl_2 . This composite was used to remove *Vibrio cholerae* efficiently and *Salmonella typhi* from water with a breakthrough time of 400 and 700 min for the removal of 1.5×10^6 cfu/mL *S. typhi* and *V. cholerae* from water respectively (Unuabonah et al., 2017a). Kaolinite clay mineral modified with chitosan have also been found to be very effective in the removal of bacteria from water with its disinfection efficiency for *E. coli* being 103.07 mg/g (7.93×10^7 cfu/mL = 2.64×10^{10} cfu/g)

and for *V. cholerae* being 154.18 mg/g (1.19×10^8 cfu/mL = 3.97×10^{10} cfu/g) using the Brouers-Sotolongo isotherm model (Unuabonah et al., 2017b).

The use of modified clay-polymer composites for removal of bacteria in water has been extensively discussed in a review by Unuabonah and Taubert (Unuabonah and Taubert, 2014).

3. Mechanisms of bacteria removal by clay-based materials

There are two main modes by which clay-based materials disinfect bacteria-laden water: adhesion and killing.

3.1. Adhesion

Both solid adsorbents and microbial cell surfaces are important in determining how the bacteria adheres to material surfaces, which is an essential step to understanding the mechanism of removal of these bacteria from water. The adhesion process as a primary stage of bacteria removal is controlled by both chemical and physical interactions between the surface of the material and the bacteria (Zupan et al., 2009; Hori and Matsumoto, 2010). These interactions may be attractive or repulsive, depending on the complex interplay of the chemistries between the bacteria and substrate surfaces, and the aqueous phase (Katsikogianni and Missirilil, 2004).

At the molecular level, these interactions are not fully understood although it is thought to be by both specific and non-specific modes (Heilmann et al., 1996). However, three theoretical approaches have been advanced for the physicochemical interactions between adsorbents and bacteria: the DLVO (Derjaguin, Verwey, Landau and Overbeek) model, the thermodynamic approach and the extended DLVO theory. The DLVO theory has been used to describe the net interaction between a bacteria cell and an adsorbent's surface as a balance between two additive factors: one of which is an attractive interaction governed by van der Waals interaction and the other is a repulsive interaction resulting from the overlap between the electrical double layer of the bacteria cell and that of the adsorbent's surface (Coulomb interactions, generally repulsive due to the negative charge of bacteria cells and substratum). Although the strength of this theory lies in its ability to explain low levels of bacterial attachment to negatively charged surfaces, it has its limitation in its inability to explain the other variety of attachment behaviours observed with appreciable amounts of other types of surfaces or in solutions with appreciable electrolytes (Katsikogianni and Missirilil, 2004).

The thermodynamic approach takes into account the various types of attractive and repulsive interactions, such as van der Waals, electrostatic or dipole but expresses them collectively in terms of free energy. Under this theory, any of three other approaches can be used to help explain the interaction between bacteria and adsorbents: the *Neumann theory* that uses contact angle, the *polar dispersion theory* that assumes that matter interacts, symmetrically, through forces arising from permanent dipoles and the *electron donor-electron acceptor approach* which demonstrates that the permanent dipole contribution to intermolecular forces in bacteria-adsorbent interaction is negligibly small in acid-base systems and with H-bonding being responsible for the interactions (Katsikogianni and Missirilil, 2004).

Both DLVO and *Thermodynamic* approaches do not sufficiently explain the bacteria-adsorbent interaction. Both models focus only on hydrophilic interactions. Hence, the Extended DLVO theory was suggested which accounts for both hydrophilic and hydrophobic interactions (Garrett et al., 2008). The extended DLVO model seems to be a promising way to study bacterial adhesion especially when organo-inorganic materials like organo-clays are involved. However, it needs to be tested rigorously.

Aside from the theoretical approaches, there are useful data to support any proposed adhesion mode in the bid to describe the bacteria-adsorbent interaction. For example, the bacteriostatic clay

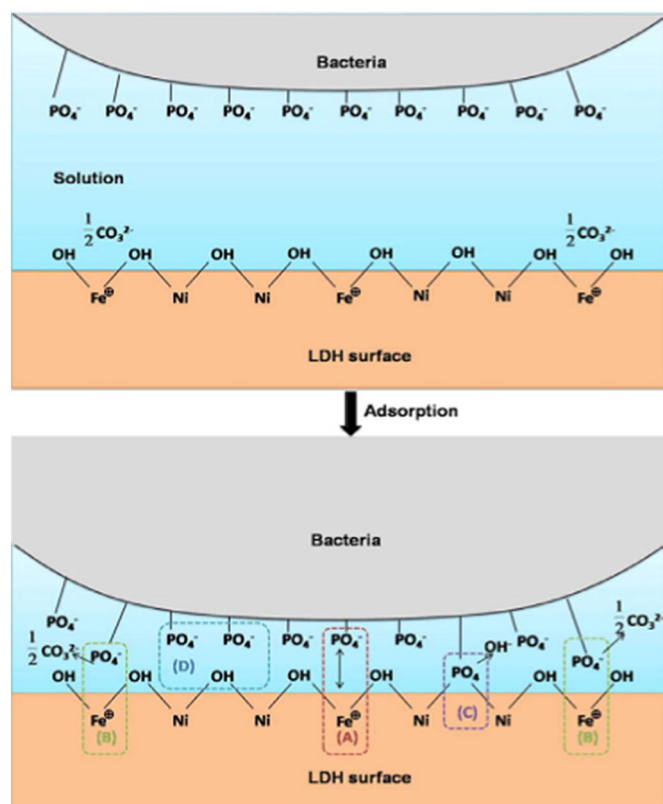


Fig. 1. Mechanism of *B. subtilis* adhesion onto NiFeCO₃-LDH. (A) Electrostatic interactions, (B) anion exchange, (C) OH replacement and (D) H-bond and polar interactions (Reproduced from Liu et al. (2013b)).

composites prepared by Unuabonah et al. (2017a), were shown to possess positive charges from the presence of ZnO in the clay mineral phase at a pH lower than the isoelectric point pH of ZnO (pH 9.0–10.0). This was established using the pH_{pzc} analysis. It is believed that this electrostatic interaction between the bacteria and modified clay mineral occur between pH range of 4.0 to 8.0 in which the bacterium is negatively charged due to the presence of PO_4^{3-} and COO^- on its surface which interacts with the positive charge on the surface of the modified clay adsorbents via electrostatic mechanism. Liu et al. (2013b) suggested three more possible mechanisms for the interaction of bacteria with clay minerals and modified clay mineral surfaces using Layer-Double Hydroxide (LDH). They suggested that there could be an ion-exchange between the bacterium and anions on the surface of the adsorbent (as shown in B in Fig. 1), a substitution of $-OH$ groups on the adsorbent's surface with PO_4^{3-} groups on the bacterium (as shown in C in Fig. 1) and H-bonding and polar attractions with or without the bridge of H_2O molecules that further encourages bacterial adhesion onto the adsorbent's surface (as shown in D in Fig. 1). Malachová et al. (2009) attributed the driving force of adhesion of *E. coli* cells to the modified Montmorillonite to the presence of fimbriae (thin flagella-like appendages or attachment) found on the cell wall.

Various factors influence the adhesion of bacteria onto adsorbent surfaces or their eventual lysis. They include properties or features of the bacteria, properties of the adsorbent surface (surface chemistry, surface charge, composition), environmental properties (which can be proteins of the serum present, roughness and bacteria hydrophobicity) and flow conditions if interaction is carried out in a fixed bed mode (Katsikogianni and Missirilil, 2004; Di Bonaventura et al., 2008; Kouider et al., 2010).

3.1.1. Bacteria-adsorbent hydrophobicity

Hydrophobicity stimulates bacteria adsorption to adsorbents'

surfaces especially when the surfaces are primarily organic in nature. In an experiment carried out by Gilbert et al. (1991), it was shown that in the attachment of hydrophobic organisms to a surface, irrespective of the charge on the surface, hydrophobicity rules. In general, bacteria having hydrophobic features prefer material surfaces that are hydrophobic while the ones with hydrophilic properties prefer surfaces that are hydrophilic. It has been shown that increasing shear stress and growth rate of bacteria does influence the adhesion of bacteria on adsorbents' surfaces (Vacheethasane et al., 1998; Stevik et al., 2004). It has been suggested that the contact between *E. coli* and the surface of a silicate layer is enhanced via increase in hydrophobicity and the electrostatic force from the intercalation or insertion of an organic molecule in the silicate. A typical example to illustrate this is the insertion of Chlorhexidini Acetas (N,N'-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecanediamidine di(acetate)) into Montmorillonite for the removal of *E. coli* from aqueous solution (He et al., 2006). The increase in hydrophobicity from the presence of Chlorhexidini Acetas molecule in the clay mineral enhanced the affinity of Montmorillonite for *E. coli* cells, while the electrostatic interaction of the residual positive charge on the silicate surface and the negative charge of the *E. coli* cell wall, inactivated the bacteria.

3.1.2. Surface charge of the bacteria and adsorbent

Bacterial cell wall has a negative charge. The bacteria cell wall does possess amphoteric properties due to the presence of the cationic and anionic groups. In gram-positive bacteria, the reason for the negative charge is the presence of teichoic acids linked to either the peptidoglycan or to the underlying plasma membrane. These teichoic acids are negatively charged because of the presence of phosphate in their structure. The gram-negative bacteria have an outer covering of phospholipids and lipopolysaccharides. The lipopolysaccharides impart a strongly negative charge to the surface of gram-negative bacteria cells (Ejaz, 2012).

Modification of the surface of clay minerals can be employed in adjusting the mode of disinfection of clay-based adsorbents: killing and/or adhesion. This modification can be achieved via physical or chemical means which can lead to changes in the surface area, structure and surface functionalities of the clay mineral and the alteration of the mineral composition of the clay material (Londono and Williams, 2016).

The surface charge on clay-based materials can be tuned by modifying the composition of the clay minerals with moieties that are likely to confer positive charges to the clay minerals or produce radical oxygen or hydroxyl groups that can damage bacterial cell wall. The charge on the clay mineral surface can also be altered by adjusting the pH of the solution either below or above its point of zero charge (pH_{pzc}). The surface of the clay mineral adsorbent attains a positive charge due to the protonation of the surface at pH values lower than the pH_{pzc} , and a negative charge at pH values higher than the pH_{pzc} of the modified clay mineral. With this feature, a clay-based adsorbent can be engineered for efficient removal of both gram-negative and gram-positive bacteria (Pina and Cervantes, 1995).

Rong, et al. (2008) reported that the quantity of the microorganism adsorbed onto Kaolinite and Montmorillonite clay minerals decreases with increase in pH of solution due to an increase in the repulsive force between the clay mineral and the bacteria. Zhang et al. (2015) suggested that adsorption of *E. coli* O157: H7 onto Kaolinite was pH dependent. However, it is proposed that the reason for *E. coli*'s stronger preference for the surface of Kaolinite to that of montmorillonite is because of the surface charge heterogeneity of Kaolinite with anisotropic properties on the basal and edge surfaces (Tombác and Szekeres, 2006; Cai et al., 2013) while that of *P. putida* is due to its smaller size and less negative surface charge (Wu et al., 2014).

It has been suggested that the weakly acidic functional groups of bacteria membranes attract H^+ or other positively charged metal ions in solution, which can displace the Ca^{2+} and Mg^{2+} in the cell

membrane, leading to an alteration in the stability of the cell membrane and an increase in the number of acid functional groups that can react with groups present on the modified clay mineral (Borrok et al., 2005). Indeed, some of these interactions between bacteria cells and clay minerals have been found to lead to morphological changes in the microorganism. Under pH conditions that confers neutral surface charge on the clay mineral, non-electrostatic forces such as hydrogen bond, Van der Waals force and hydrophobic interactions have been reported to account for the antimicrobial activity of some clay minerals (Rong et al., 2008; Liu et al., 2016). This type of interaction can be confirmed by analysing the bacteria-loaded clay adsorbents using Attenuated Total Reflectance (ATR)-Fourier Transformed Infra-Red (FTIR). The spectrum of this adsorbent will depict certain signature peaks unique to bacteria on an adsorbent's surface. Hydrogen bonding of the bacteria onto the clay-based adsorbents can be observed in the shifting of the O–H vibration to a lower frequency (Santhiya et al., 2000) and the Amide I band contribution from the bacteria at around 1628 cm^{-1} .

There are certain chemical interactions between functionalities of clay-based adsorbents and the bacteria that results in inactivation and death of the bacteria. These interactions are based on the mineral composition of the clay and redox state of the hydrated clay during its application in water treatment. While some pristine clay minerals and modified clay adsorbents do not possess soluble metal species with antimicrobial activity, modification of clay minerals with biocidal metal species that are not very harmful to man (Cu, Mn, Zn) can enhance the antimicrobial activity of clay mineral triggering inactivation and possible death of the bacteria (William and Haydel, 2010; Unuabonah and Taubert, 2014).

When exposed to high metal concentrations, microbes express different metal uptake mechanism (Nies, 1999), which includes intracellular metal efflux, alteration of internal redox condition, and complexation (Parikh and Chorover, 2006). Once the metal is taken in by the bacteria, its species in solution forms complexes with the phosphate on the bacteria. This alters the lipid-protein interactions, inhibiting membrane transport of proteins that leads to an imbalance in the membrane electrical potential in the bacteria which can lead to inactivation of the bacteria (Pina and Cervantes, 1995; Xu et al., 2012). Morrison et al. (2013) observed that antibacterial clays like the blue clay from Oregon Mineral Technologies (OMT) clay deposits in the Cascade Mountains in the United States do have high amounts of Fe that makes it biocidal as the clay mineral easily kill bacteria in solution through the leaching of Fe into the solution containing bacteria.

Asadishad et al. (2013) further showed that the presence of electrolytes in solution does influence bacterial adhesion and inactivation on modified clay minerals. Also, electrolyte type and concentration also play significant roles in bacteria adhesion onto modified clay minerals (McWhirter et al., 2002; Jiang et al., 2007). Asadishad et al. (2013) observed that lower ionic strength of electrolytes does favour higher inactivation rates of bacteria with inactivation rates of bacteria in KCl solution being higher than in $CaCl_2$ solution.

3.1.3. Flow conditions

Flow conditions are important as they strongly influence the attachment of bacteria to surfaces (Isberg and Barnes, 2002). Decreasing quantity of attached bacteria on a surface could be because of increased detachment forces one of which is high shear rates (Chang et al., 1991). To consider the balance between the force acting on the attached bacterium and the rate of bacteria-laden solution delivery, it is important to know that there is a peak flow rate for bacteria attachment (Liu and Tay, 2002). There is proof that bacteria dispersed on the surface of an adsorbent can react to shear stress by changing its size/density, growth rate, metabolism and morphology (Liu and Tay, 2002). Lower growth yield and increased dehydrogenase activity are attained when the shear rate is increased. Hiremath, (2014) observed that adhesion of *Listeria innocua* to Mica and polystyrene surfaces under laminar flow showed lower adhesion values in comparison with those

under static settings.

3.2. Killing

Another mode of removal of bacteria from water by different modified clay minerals is the inactivation and subsequent killing mechanism. For instance, Kleyi et al. (2016), modified Montmorillonite using Quaternary imidazolium salts with alkyl chains, (Octyl and Decyl) and used them for disinfection of drinking water (distilled, borehole and river water inoculated with *E. coli*). The mechanism of inactivation of *E. coli* on this modified clay mineral was suggested to be by rupturing of the bacteria cell membrane with subsequent leaking out of the cytoplasm, resulting in cell death. However, Motshekga et al. (2015) in their study of the antibacterial activity of chitosan-based nanocomposites containing bentonite-supported silver and zinc oxide nanoparticles for water disinfection, suggested that it is possible for an adsorbent to utilise both adhesion and killing mechanisms simultaneously for the removal of bacteria in water. With organo-clay modified with phosphonium surfactant, Wu et al. (2011) in their study of the antimicrobial activity of organo-clay minerals concluded that the following steps best describe the antibacterial mechanism of phosphonium organo-clay:

(1) Organo-clay minerals adsorb onto the bacterial cell by electrostatic attraction, and there is a slow release of phosphonium surfactant from organo-clay mineral (2) released phosphonium surfactant interacts with bacterial cells, and diffuses through the cell wall; (3) the cytoplasmic membrane coagulates and is disrupted by phosphonium surfactant; (4) phosphonium surfactant is continuously released and reacts with cytoplasmic constituents of the bacteria; and (5) The normal physiological activity of the bacterial cell is interfered with and the cell dies.

Ping et al. (2016) observed that surface modification of Montmorillonite with Metronidazole (MTZ) only provides the clay mineral with the ability to effectively interact with bacteria electrostatically. However, a further modification of Montmorillonite-MTZ material with Polyethylenimine (PEI) provides the clay mineral with the capacity to kill bacteria. It was suggested that the modified clay mineral first targets bacteria through extracellular polymeric substances-mediated adhesion and subsequently anchors the bacteria membrane. The PEI arms then promote membrane disruption to allow the free diffusion of Metronidazole inside the bacterial cytoplasm, thereby killing the bacteria.

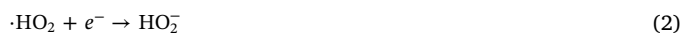
Recently, a deposit of blue and green clay minerals containing a mixed layer of illite-smectite, pyrite, Ca-plagioclase and quartz was found in the French Massif Central region of Oregon, United States of America (Morrison et al., 2016). These clay minerals are thought to mimic the ‘Trojan Horse’ attack mode such that two elements work in concerted effort to kill bacteria. Chemically reduced Fe, required in small amounts by a bacterial cell for nutrition, deceives the bacteria cell into opening its wall while the other element, Al, opens the cell wall, allowing a large amount of Fe to enter the cell. The excess of Fe then poisons the cell, killing it as the reduced Fe becomes oxidised. Fig. 2 shows the antibacterial mechanism of the blue and green clay minerals.

In another instance, dead bacteria cells killed by a toxic metal (Ag^+) are thought to become biocidal, with the ability to kill other living bacteria cells around them. This phenomenon has been termed the ‘zombie effect’ (Wakshlak et al., 2015). The scheme of reaction is shown to be.

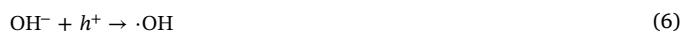
1. $\text{Ag}_{(\text{aq})}^+ + \text{Bacterium} \rightarrow \text{Ag-killed Bacterium}$
2. $\text{Ag-killed Bacterium} \leftrightarrow \text{Ag}^+ + \text{Killed Bacterium}$
3. $\text{Ag}_{(\text{aq. from 2})}^+ + \text{viable bacterium} \rightarrow \text{Ag-killed Bacterium}$

Death of bacteria cells could also occur via photocatalytic means, where the materials in contact with the bacteria cells possess one or more semiconductors which when irradiated by light generates electron-hole pairs depending on if the incident photons have equivalent or excess energy to the band gap (the void energy region which separates

the valence band from the conduction band). Once excited, an electron (e^-) will leap from the valence band into the conduction band, leaving behind a hole (h^+) in the valence band. The photo-generated electron-hole pairs (e^-h^+) which are then separated, migrate to the surface or interface of the photocatalyst, where a variety of redox reactions take place with the generation of various Reactive Oxygen Species (ROSs). Typically, the photo-generated e^- is trapped by dissolved O_2 in water to produce $\cdot\text{O}_2^-$, while the photo-generated h^+ reacts with surface $\text{H}_2\text{O}/\text{OH}^-$ to generate $\cdot\text{OH}$. Both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are highly active oxidants and are responsible for the decomposition of organic pollutants.



At the valence band, the photo-generated h^+ is expected to react with surface $\text{H}_2\text{O}/\text{OH}^-$ to produce $\cdot\text{OH}$ (Eqs. (5)–(6)). The $\cdot\text{OH}$ may also combine to form H_2O_2 (Eq. (7))



These, h^+ , $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and H_2O_2 , are regarded as reactive oxygen species (ROSs). It is suggested that they do oxidize the cell walls of bacteria and induce cell lysis. It is yet to be proven which one of these ROSs plays a significant role in the oxidation process that inactivates the bacteria. Aside from photocatalytic oxidation, it has been reported that bacteria inactivation can also occur through photocatalytic reduction where the photo-generated e^- plays a major role in the inactivation by preventing the recombination of e^-h^+ especially in an anaerobic condition (Chen et al., 2011; Wang et al., 2013).

4. Tools for studying the mechanism of bacteria-adsorbent interaction

There is the need to confirm exactly by what mechanism are the bacteria captured from solution and held on the surface of the adsorbent or killed by the adsorbent and what kind of chemical bonds are formed between the bacteria and the adsorbent when they are held on the adsorbent's surface. None of these can be readily determined by simple analytical techniques. They require microscopic or spectroscopic techniques and most times a combination of both.

4.1. Fourier transform infrared (FT-IR) spectroscopy

To understand the Fourier Transformed Infrared (FT-IR) spectra of bacteria laden surfaces, some fundamental knowledge of the bacteria cell surface characteristics and bacteria cell chemical composition is a prerequisite. The infrared spectra of bacterial cells reflect the biochemical composition of the cellular constituents of bacteria that include water, fatty acids, proteins, polysaccharides, and nucleic acids to create unique biochemical ‘fingerprints’ for different bacterial strains (Goodacre et al., 1996; Al-Quadiri et al., 2006; Lin et al., 2013). Several scientists have utilised the FT-IR tool to study the interaction of bacteria on clay minerals like in the interaction of *Pseudomonas putida* with Kaolinite and Montmorillonite (Rong et al., 2008) and the adsorption of *E. coli* by Chlorhexidini Acetas-modified montmorillonite (He et al., 2006). The Attenuated Total Reflectance-Fourier Transformed Infrared (ATR-FTIR) spectroscopy is preferred because it does not require any sample preparation that does destroy the pristine nature of the interaction between the bacteria and the adsorbent and hence the final result obtained.

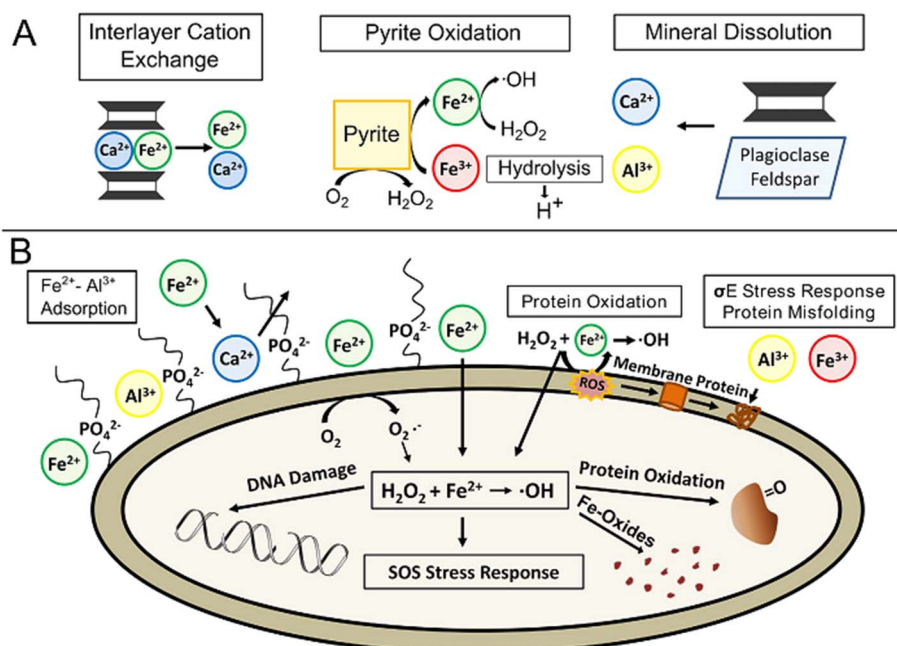


Fig. 2. Schematic showing the antibacterial mechanism of the Oregon Blue clays. (A) Illite-smectite interlayer cation exchange, pyrite oxidation and mineral dissolution (plagioclase feldspar and I-S) provide soluble Fe^{2+} , Fe^{3+} , Al^{3+} and Ca^{2+} , while generating H_2O_2 . Hydrolysis and precipitation of Fe^{3+} and Al^{3+} sustain the acidic environment. (B) Fe^{2+} and Al^{3+} out compete Ca^{2+} binding to phosphate rich lipopolysaccharides on the outer membrane of *E. coli*, which results in protein misfolding and oxidation, activating the σ^F -stress response. Hydrogen peroxide generated extracellularly by clay suspensions diffuses through the cell envelope and reacts with intracellular Fe^{2+} , forming radicals that oxidize proteins and DNA, activating the SOS-response. Fe^{3+} -oxide precipitates coincident with cell death. Through extended metal release and H_2O_2 production, the Oregon blue clays simultaneously stress multiple cellular systems unlike traditional antibiotics [Reproduced from Morrison et al. (2016)]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
ATR-FTIR assignment of absorption bands typically for bacteria (Reproduced from Yu and Irudayaraj, (2005)).

Wavenumber (cm^{-1})	Assignment	Biomolecule contributor
2957	$\nu(\text{CH}_3)$	Asymmetric fatty acids
2919	$\nu(\text{CH}_2)$	Asymmetric fatty acids
2872	$\nu(\text{CH}_3)$	Symmetric fatty acids
2852	$\nu(\text{CH}_2)$	Symmetric fatty acids
1790–1750	$\nu(\text{C}=\text{O})$ affected by Cl, etc.	Not clear
1741	$\nu(\text{C}=\text{O})$	Lipid esters
1708	$\nu(\text{C}=\text{O})$, H-bonded	RNA, DNA
~1695	Amide I band components resulting from antiparallel pleated sheets & β -turns	Proteins
~1670	$\nu(\text{C}=\text{N})$	RNA/DNA bases
~1655	Amide I of α -helical structure	Proteins
~1637	Amide I of β -sheets	Proteins
1548	Amide II	Proteins
1515	Aromatic –C–C–	Proteins
1457	$\delta(\text{CH}_2)$	Lipids, proteins
1415	C–O–H in-plane bending	Carbohydrates, DNA/RNA, proteins
1402	$\delta_c(\text{CH}_3)_2$ symmetric	Lipids, carbohydrates, proteins
1312	Amide III	Proteins
1284	Amide III	Proteins
1240	$\nu(\text{P}=\text{O})$ asymmetric	Phospholipids
~1160	$\delta(\text{COP})$, $\nu(\text{CC})$, $\delta(\text{COH})$	DNA & RNA backbones
~1120	$\nu(\text{CC})$ skeletal <i>trans</i> Conformation	DNA & RNA backbones
1200–1000	C–O–C, C–O dominated by ring vibrations	Carbohydrates
1085	$\nu(\text{P}=\text{O})$ symmetric	DNA & RNA, phospholipids
1076	$\nu(\text{CC})$ skeletal <i>cis</i> conformation	DNA and RNA backbones
900–800	C=C, C=N, C–H in ring structure	Nucleotides

ν = stretch; δ = deformation.

A typical spectrum of a bacterium held onto an adsorbent will exhibit some unique bands. These bands and their assignments are shown in Table 1. Note that there could be some shift in the frequency of

absorption of certain bands depending on the type of surface the bacteria is on.

The structural alterations of bacteria exposed to clay minerals and their modified forms can be characterized in four finger print regions of the FTIR spectrum. These regions are mainly placed between 3100 and 2800 cm^{-1} for fatty acids, 1800 and 1500 cm^{-1} for proteins and peptides, 1200 and 900 cm^{-1} for carbohydrates, and 900 and 600 cm^{-1} for the fingerprint region (Lasch and Naumann, 2015). The interaction between bacteria and nanoparticles have been fully studied by (Faghihzadeh et al., 2016).

However, it is important to mention that with the adhesion of bacteria onto an adsorbent surface; these absorption bands will shift slightly depending on the type of bonding that may have occurred between the bacteria and the adsorbent. A change in peak intensity could suggest a possible interaction between the bacteria and the clay mineral adsorbent (Parikh and Chorover, 2006).

4.2. Electron microscopy (EM)

Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) have been used to study the adhesion of bacteria onto surfaces. These techniques do provide information on the actual mechanism of bacterial removal from solution-adhesion or killing. For example, Morrison et al. (2013), using the SEM tool, showed that the Blue antibacterial clay mineral did not cause cell lysis on the bacterial held onto its surface. However, they observed that there were textural differences in the response of the gram-negative *E. coli* and the gram-positive *S. epidermidis* on this surface (Fig. 3).

With the modification of Mica with Fe_3O_4 , Liu et al. (2016) observed that there was significant cell disruption of *S. aureus* (Fig. 4) and *E. coli* (Fig. 5) bacterial which is vivid from shrinkage of cells. This condition indicates loss of intracellular cell content.

Similarly, to prove the killing nature of exfoliated Montmorillonite modified with both Polyethylenimine and Metronidazole, Ping et al. (2016) employed the SEM tool as shown in Fig. 6a which suggests that there was more cellular disruption with the modified clay mineral than with only the exfoliated clay mineral. The Fluorescence spectroscopic tool was further used to confirm this (Fig. 6b).

To determine the elemental composition of intracellular and the interaction between the Blue clay and the bacteria, the Scanning

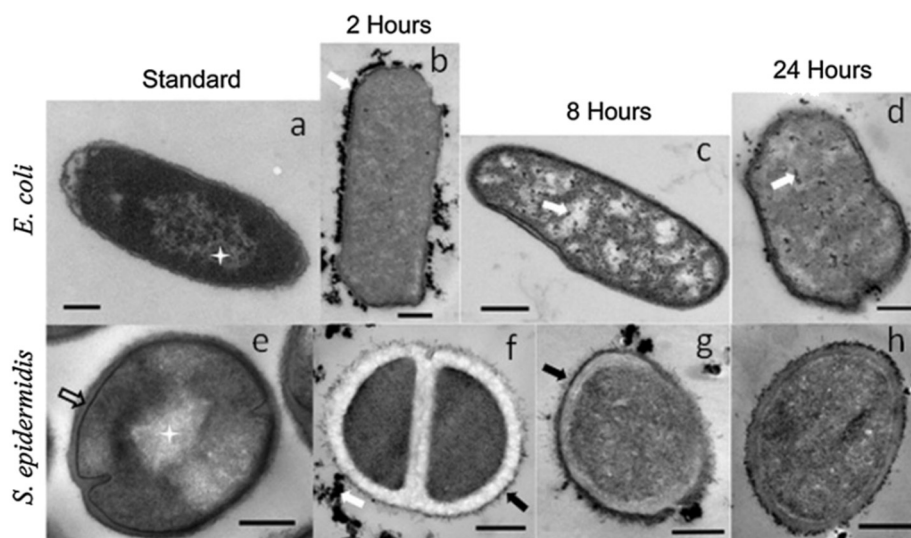


Fig. 3. SEM images of gram-negative *E. coli* and gram-positive *S. epidermidis* reacted with 100 mg/mL OMT Blue 1 mineral suspensions (Scale bars 250 nm). White stars indicate bacterial nucleoid (a, e). Hollow black arrow shows peptidoglycan layer (e). Solid white arrows indicate mineral particles and electron dense particles within the cytoplasm (c, d, f). Solid black arrows point to thread-like appendages coated with electron dense particles (f, g). Reproduced from Morrison et al. (2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Tunnelling Electron Microscopy (STEM) was utilised by Morisson et al. (2013). They observed from the STEM images that with *E. coli* on the surface of the Blue Clay, there was the presence of O–K edge and Fe–L edge spectra which suggest the accumulation of the clay particles in the bacteria cells (Fig. 7). The STEM images also showed that other elements like Al, Ag, Cu and Zn present in the clay which could play a role in antibacterial processes were not detected intracellularly.

TEM analysis was also used by Kleyi et al. (2016) to evaluate the mechanism of inactivation of *E. coli* using Montmorillonite modified with quaternary imidazolium salts. The TEM results showed that the mechanism of inactivation of the bacteria occurred through rupturing of the cell membrane after the *E. coli* cells came in contact with the modified clay mineral adsorbents (Figs. 8 and 8b).

In the absence of TEM or SEM, fluorescence microscopy technique could be employed. This technique together with a bacterial viability staining test using the LIVE/DEAD BacLight™ Bacterial Viability Kit (Life Technologies, USA) for confocal fluorescence analysis, can be used to directly quantify surface cell density and viability of bacteria on the adsorbent's surface (Wu et al., 2014).

5. Atomic force microscopy

Atomic force microscopy (AFM) is an established but very powerful technique for imaging the surfaces of clay minerals (Bickmore et al., 1999) or microbial cells (Dufrêne, 2004) and probing the forces driving cell-mineral adhesion (Bowen et al., 1998; Lower et al., 2000; Huang et al., 2015). Very recently, AFM has been used to study the 1) nanoscale surface morphology of bacteria-clay mineral aggregates 2) force-distance curves for bacterial cells approaching and retracting

clay-sized goethite particles and 3) the surface topographies of biofilms on clay-sized minerals as a function of time and nutrient availability. The clay minerals tested were Kaolinite, Montmorillonite and Goethite which were used as representative minerals for 1:1 and 2:1 layer silicates and metal oxides, respectively. Their study revealed that there are different association mechanisms between bacteria and minerals as stated earlier in this article. They further observed that bacteria do form more extensive biofilms on minerals (Fig. 8) under low rather than high nutrient conditions.

6. X-ray photoelectron spectroscopy (XPS)

The X-ray Photoelectron Spectroscopy (XPS) can be used to study the atoms involved in bonding between the bacteria cell and the clay-based materials in the bacterial inactivation mechanism, the type of bonding and where these atoms are located in the mineral phase and in the bacterium. Even though there are several reports on the use of XPS to characterise mineral surfaces and other solid surfaces interacting with bacteria, this tool is yet to be sufficiently used in studying the interaction between bacteria and clay-based adsorbents. A few examples of the use of XPS in bacteria-solid interaction includes the study from Asadishad et al. (2013) who used this technique to investigate the bonding between gram-negative and gram-positive bacteria on SiO_2 , Al_2O_3 and Fe_2O_3 surfaces. They observed the presence of C-metal and O-metal bonds which were covalently bonded to these surfaces which were suggested to mean that toxic hydroxyl radicals could not have been responsible for the loss of cell membrane integrity but due to bacteria-surface chemical bonding. Dalai et al. (2014) used the XPS technique for studying adsorbent (TiO_2)-bacteria interaction where

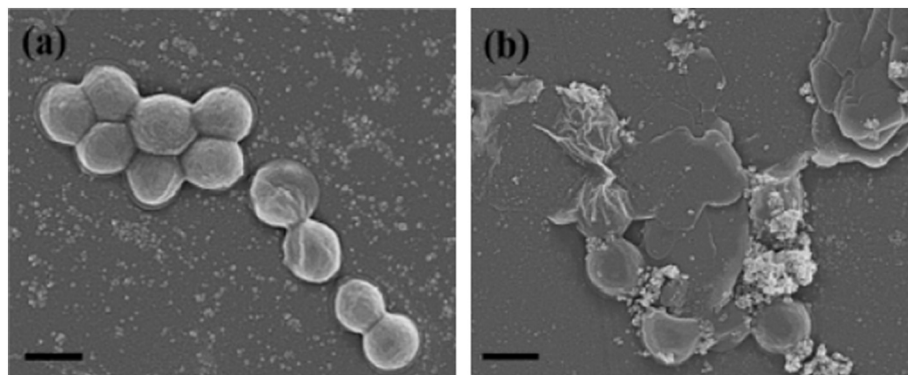


Fig. 4. SEM images of (a) pristine *S. aureus*, (b) after treatment with Fe_3O_4 /Mica, (scale bar: 1 μm). Reproduced from Liu et al. (2016).

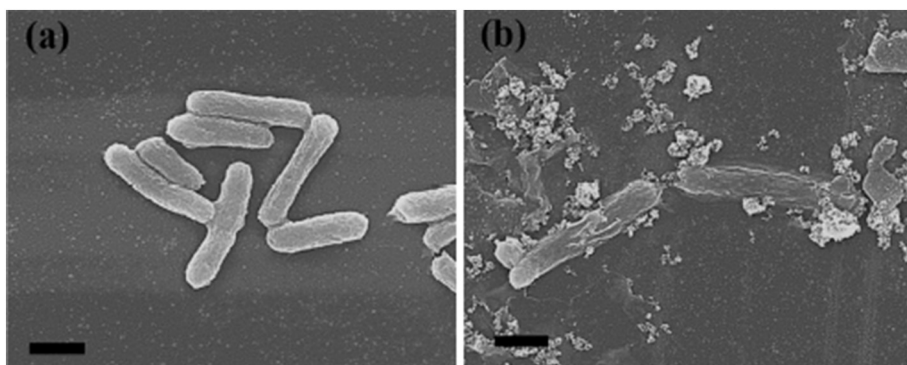


Fig. 5. SEM images of (a) pristine *E. coli*, (b) after treatment with $\text{Fe}_3\text{O}_4/\text{Mica}$, (scale bar: 1 μm). Reproduced from Liu et al. (2016).

they observed that a redox reaction (that reduces Ti(IV) to Ti(III)) could lead to radical generation that leads to the oxidative degradation of cell membrane of the bacteria. Pradier et al. (2005) used this tool to show the presence of C, O and N in different bacteria strains. Furthermore, they use the XPS tool to differentiate between N of amine and amide and that from a protonated amine. Besides, the XPS tool has been used to study the chemical composition and bonding between atoms on the surface of Gram-positive bacteria *Bacillus subtilis* (Leone et al., 2006).

7. Other tools

Organic matter including cells, exopolymers, intracellular organelles, or ultra structures is very sensitive to vacuum-induced dehydration at the microscope stage (Schaedler et al., 2008; Dohnalkova et al., 2011). Furthermore, traditional preparation of thin sections for TEM imaging (embedding in a resin after fixation and dehydration) can alter the configuration of organic matter in a sample (Miot et al., 2014) and may, therefore, lead to loss of authentic information about the presence of such organic matter in the sample. Cryo-electron Microscopy (cryo-EM) offers a way out of this limitation by rapidly freezing the sample in vitreous (i.e., amorphous) ice, thereby maintaining the microbe-mineral assemblages in an aqueous, near-native state. In a cryo-EM analysis, a drop of the sample is deposited onto a standard carbon-coated TEM grid, rapidly frozen in liquid ethane (or an ethane/propane mixture) while being cooled by liquid nitrogen, and then transferred to a TEM (Fig. 9) for imaging. Whole frozen cells can be visualised by cryo-electron tomography technique (Milne and Subramaniam, 2009). Thin sections can be produced by cryo-ultramicrotomy of frozen hydrated samples (i.e., cryo-electron microscopy of vitreous sections, or CEMOVIS) (Adrian et al., 1984; Matias et al., 2003). A limit of this method, however, is its inadequacy for preparing thin sections from brittle or hard samples. The cryo-Focused Ion Beam (cryo-FIB) method effectively circumvents this drawback with CEMOVIS. The cryo-FIB is a promising approach for imaging microbe-mineral interfaces. Recently, there is tremendous progress made in combining cryo-EM with light microscopy such as the combination of

confocal laser scanning microscopy with cryo-EM, which allows the retrieval of phylogenetic and metabolic information.

Scanning Transmission X-ray Microscopy (STXM) is another scientific tool to characterise the microbe-clay mineral interface at the microorganism scale (Cosmidis and Benzerara, 2014). It is a synchrotron-based transmission microscopy method that provides images with spatial resolution of approximately 25–50 nm. It uses soft X-rays (< 4 keV), provide information about the speciation of elements from carbon (C K-edge) to arsenic (As L-edge), i.e., of light elements interacting with the organic (microbe) portion and of heavier elements from the clay mineral portion (Miot et al., 2014).

8. Future perspectives

It is interesting to note that disinfection of water other than with the traditional use of Chlorine is now of serious interest among scientists because of the presence of disinfection by-products (which are carcinogens) in treated water and the increasing resistance of these bacteria to chemical treatments. However, to ensure that sustainable, affordable and very efficient materials are developed for disinfection of water in the near future, a few things need to be noted:

- Several of the very new materials developed have shown excellent efficiencies but have suffered some drawbacks which have largely hindered their successful upscaling. For examples, membranes have a unique capacity to remove bacteria from water including viruses but suffer severely from fouling which does require continuous replacement of the membrane filters that makes the entire water treatment process very expensive. At the moment there are concerted efforts to develop antifouling agents which could be used to modify these membranes and increase their ability to withstand fouling. While this is encouraged, it is suggestive to say that these membranes could be developed from clay minerals (i.e. ceramic membranes which are by far more resistant to fouling than polymeric membranes). They will provide for cheap and sustainable materials for disinfection of water.

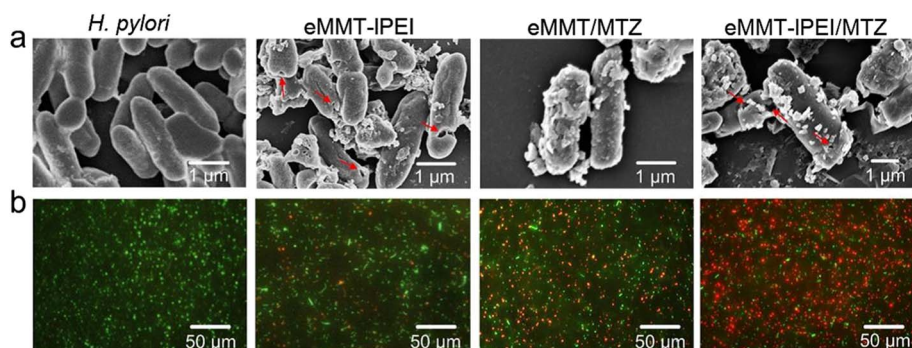


Fig. 6. a) SEM images of *H. pylori* incubated with exfoliated Montmorillonite (eMT) nanoparticles for 4 h. The red arrows denote transmembrane pores formed by eMT-Polyethylenimine. b) Fluorescence micrographs of *H. pylori* and *H. pylori* treated with different eMT nanoparticles for a period of 2 h. Native bacteria with green fluorescence represent live bacteria, whereas those in red represent dead bacteria. Live and dead *H. pylori* were stained by LIVE/DEAD BacLight bacterial viability kits. Reproduced from Ping et al. (2016).

Note: eMT-exfoliated Montmorillonite; PEI = Polyethylenimine; MTZ = Metronidazole.

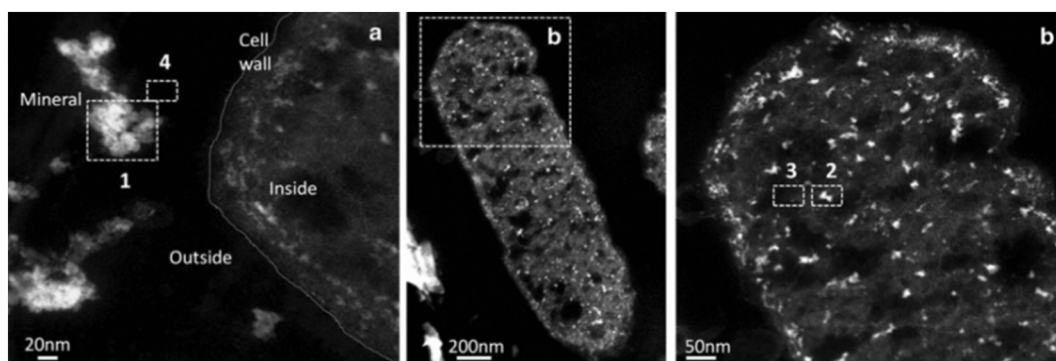


Fig. 7. STEM dark field images (contrast reversed from TEM images, Fig. 5) and electron energy loss (EELS) in eV of *E. coli* reacted with a 100 mg/mL Blue 1 mineral suspension for 24 h. (a) Mineral particles outside the cell range in size from 20 to 100 nm; (b) intracellular particles (~ 10 nm) are shown in two separate images with 200 and 50 nm scale bars. Reproduced from Morrison et al. (2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- The toxicity concerns raised by the use of nano-materials for water treatment especially with silver-mediated nano-materials could be resolved with the development of clay-based composite materials that are possibly modified with less toxic metal ions, like Cu and Zn, known also to be bactericidal but yet will be useful to the human body at very low concentrations in the event that they leach into the treated water from the materials. Furthermore, it is important that materials development scientists in their research into and development of clay-based materials for disinfection of water, check for the presence of certain components of these materials in the treated water. This is necessary as these components could leach into the treated water and cause health problems for humans when ingested. In addition, sensors or simple tools could be developed to detect the likely presence of these clay-based bactericides in treated water. Several of these clay based bactericides are nanocomposites that could find their way into treated water and become harmful to cells in vivo when ingested with treated water.
- The development of visible-light photocatalytic clay-based adsorbents or materials for degradation of bacteria in water and wastewater treatment will provide a sustainable and efficient route

to disinfection of water that will ultimately reduce the overall cost of water treatment and ensure that potable water is available to all in the near future. This will eventually reduce the increasing incidence of Antimicrobial Resistance (AMR) to drugs currently observed among humans as the visible-light photocatalytic material should be able to disinfect a broad spectrum of pathogens and at the same time degrade a large number of antibiotic contaminants in water to less harmful products. The development of these highly efficient bactericidal photocatalytic clay-based materials will feed into the Sixth Sustainable Development Goals of the United Nations that prescribes access to safe water which is essential to human health and economic prosperity. However, the impact of cell content of bacteria that leaks off after degradation, on human health or the quality of the treated water should be studied as well as the influence of certain other organics present in the water on the efficiency of the photocatalyst.

- Going forward, there is a need for further studies to be undertaken on some of the new antibacterial adsorbents developed, to establish the influence of certain common anions (e.g., SO_4^{2-} , NO_3^- , Cl^- , etc.) and humic acid in water on the efficiency of these clay-based

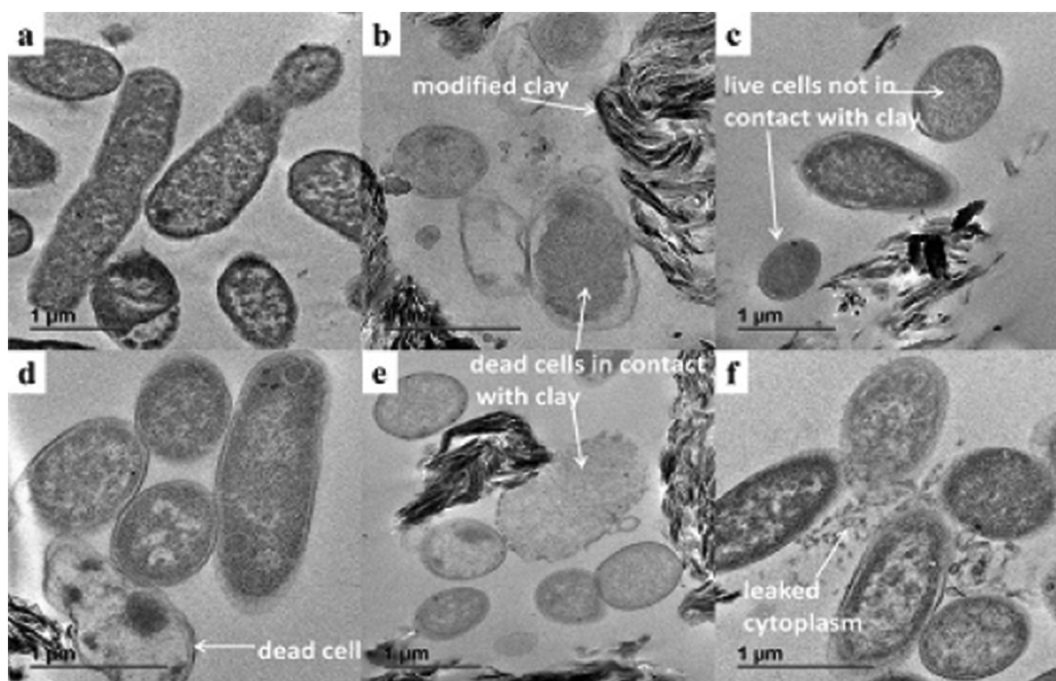


Fig. 8a. TEM micrographs showing the mechanism of inactivation of the modified Montmorillonite against *E. coli*: (a) *E. coli* (control) and (b–f) *E. coli* treated with Quaternary Imidazolium Montmorillonite with Octyl chain. Reproduced from Kleyi et al. (2016).

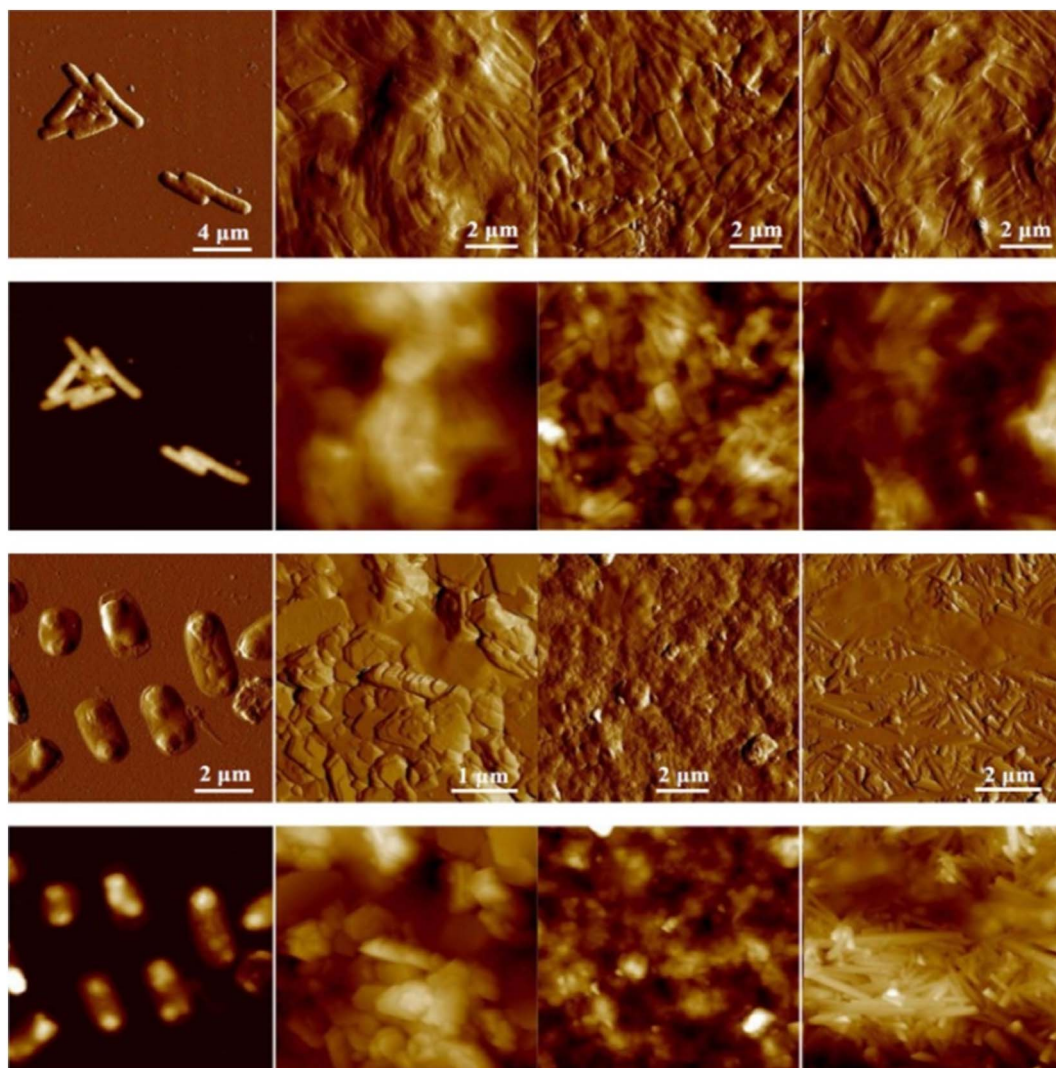


Fig. 8b. AFM peak force error and height images of *E. coli* biofilm formed on coverslips (the first column), kaolinite (the second column), montmorillonite (the third column) and goethite (the fourth column) surfaces after 2 days in M9 (the upper two rows) and LB medium (the lower two rows). Reproduced from Huang et al. (2015).

antibacterial adsorbents for disinfection of water. This study will be useful in understanding the mechanism of these adsorbents when in contact with bacteria in aqueous solution especially because recent studies have shown that bacteria like *Bacillus subtilis* and *Pseudomonas fluorescense* reduced the adsorption of PO_4^{3-} onto Fe

and Al (hydr) oxides, Geothite and Gibbsite (Hong et al., 2015; Hong et al., 2016). On the contrary, Humic acid was found to inhibit bacteria adhesion to Montmorillonite and Goethite while it enhances adsorption onto Kaolinite by altering the surface charge of the clay mineral.

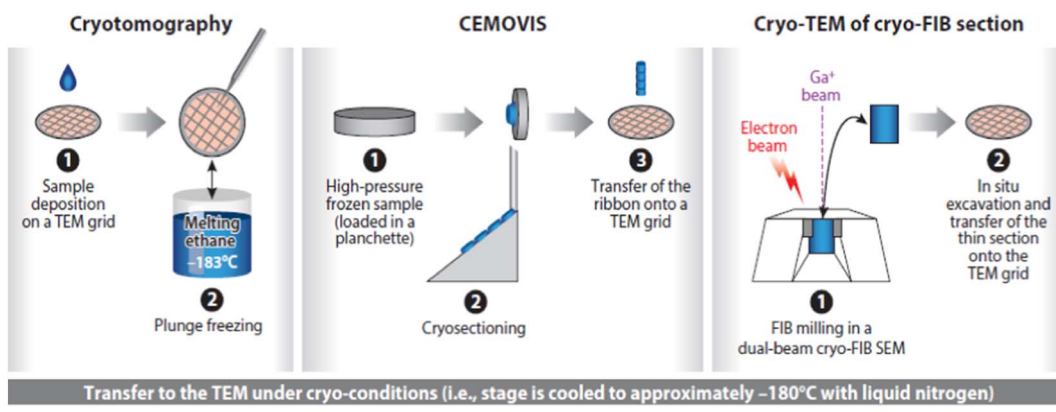


Fig. 9. Overview of some Cryo-Electron Microscopy methods adapted to the imaging of microbe-mineral interfaces in their hydrated near-native state (Reproduced from Miot et al. (2014)).

- Regeneration is an important aspect of an adsorption process. Without the rejuvenation of the adsorbents, the adsorption process will altogether be very expensive. The restoration of the efficiency of clay-polymer composites using either HCl or NaClO has been suggested (Undabeytia et al., 2014). Furthermore, it has been suggested that with clay minerals modified with Fe₃O₄, e.g., Mica, an alternating current applied to bacteria-loaded adsorbent generates a high-frequency magnetic field which is transmitted as energy in the form of rapidly localised inductive heat that destroys the bacteria bound to the magnetic nanoparticles (Liu et al., 2016). Unuabonah et al. (2017a) successfully used steam regeneration to renew the efficiency of bacterial-laden hybrid clay adsorbents. So far just a handful of works has reported the regeneration of bacteria-loaded clay based adsorbents. With sufficient regeneration data, it will be possible to adequately estimate the economic and industrial value of these potential antibacterial adsorbents in the treatment water.
- Recent studies show that more of Kaolinite, Montmorillonite and Bentonite and their modified forms have been used as antibacterial clay minerals. Although, there is a very recent study on the use of Palygorskite and Sepiolite for the removal of *P. putida* in soil (Tavanaei et al., 2016), yet it will be helpful to try out other clay minerals like Halloysite and even Palygorskite, and Sepiolite and their modified forms in the removal of several bacteria from water. They could prove to be more efficient than those currently in studied.
- There is need to also study the rate of uptake of these bacteria as well as the thermodynamics of the bacteriostatic or bacteriocidal activities of these clay minerals or their modified forms.
- At the moment it is quite difficult to compare the efficiency of these clay-based adsorbents for removal of bacteria in water with those of other materials. The reason is that there is still no uniform way of quantifying these bacteria on the surface of these clay-based adsorbents. It is quite important that an accurate and consistent mathematical model or expression is established to enable proper evaluation of antibacterial efficiencies of these adsorbents.
- The latest discovery of blue and green clays that kill bacteria (Morrison et al., 2016) may provide an economical route for the removal of harmful bacteria from water using these clay minerals only if they are in such quantity that can sustain its future use in the treatment of large volumes of water. On the contrary, however, with this discovery, it is possible to suggest that natural clays could be engineered to have the two elements (Fe, Al) implicated in the killing of bacteria in such sufficient amount that clays become sustainable materials for treatment of water.

9. Conclusion

Given the preceding discussion, adsorption of bacteria from water and wastewater is currently the most attractive technique for cleaning of pathogenic polluted water. There is currently a dearth of information on clay minerals and modified clay minerals for water disinfection. Development of clay-based adsorbents with high efficiency to capture bacteria from water will certainly be worthwhile due to their ready availability, low-cost and ease of preparation. Clay-based visible-light photocatalyst for degradation of these bacteria in water is also worth considering as a future option for disinfection of water.

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References

- Abdalmaleki, A., Mallakpour, S., Mahmoudian, M., Sabzalian, M.R., 2017. A new polyamide adjusted triazinyl-β-cyclodextrin side group embedded magnetic nanoparticles for bacterial capture. *Chem. Eng. J.* 309, 321–329.
- Adebowale, K.O., Unuabonah, E.I., Olu-Owolabi, B.I., 2006. The effect of some operating variables in the adsorption of lead and cadmium ions onto modified kaolin clay. *J. Hazard. Mater.* B134, 130–139.
- Adrian, M., Dubochet, J., Lepault, J., McDowell, A.W., 1984. Cryo-electron microscopy of viruses. *Nature* 308, 32–36.
- Al-Quadiri, H.M., Al-Holy, M.A., Lin, M., Alami, N.I., Cavinato, A.G., Rasco, B.A., 2006. Rapid detection and identification of *Pseudomonas aeruginosa* and *Escherichia coli* as pure and mixed cultures in bottled drinking water using Fourier transform infrared spectroscopy and multivariate analysis. *J. Agric. Food Chem.* 54, 5749–5754.
- Ambashta, R.D., Sillanpaa, M., 2010. Water purification using magnetic assistance: a review. *J. Hazard. Mater.* 180, 38–49.
- Amin, M.T., Alazba, A.A., Manzoor, U., 2014. A review of removal of pollutants from water/wastewater using different types of nanomaterials. *Adv. Mater. Sci. Eng.* <http://dx.doi.org/10.1155/2014/825910>. (Article ID 825910).
- Asadishad, B., Ghoshal, S., Tufenkji, N., 2013. Short-term inactivation rates of selected gram-positive and gram-negative bacteria attached to metal oxide mineral surfaces: role of solution and surface chemistry. *Environ. Sci. Technol.* 47, 5729–5737.
- Barr, M., 1957. Adsorption studies on clays II. The adsorption of bacteria by activated attapulgite, halloysite, and kaolin. *J. Am. Pharm. Assoc.* 46, 490–492.
- Bickmore, B.R., Hochella, M.F., Bosbach, D., Charlet, L., 1999. Methods for performing atomic force microscopy imaging of clay minerals in aqueous solutions. *Clay Clay Miner.* 47, 573–581.
- Borrok, D., Turner, B., Fein, J., 2005. A universal complexation framework for modelling proton binding on bacterial surfaces in geologic settings. *Am. J. Sci.* 305, 826–853.
- Bowen, W.R., Hilal, N., Lovitt, R.W., Wright, C.J., 1998. Direct measurements of the force of adhesion of a single biological cell using an atomic force microscope. *Colloids Surf. A Physicochem. Eng. Asp.* 136, 231–234.
- Bradford, S.A., Morales, V.L., Zhang, W., Harvey, R.W., Packman, A.I., Mohanram, A., Welty, C., 2013. Transport and fate of microbial pathogens in agricultural settings. *Crit. Rev. Environ. Sci. Technol.* 43, 775–893.
- Cai, P., Huang, Q., Walker, S.L., 2013. Deposition and survival of *Escherichia coli* O157:H7 on clay minerals in a parallel plate flow system. *Environ. Sci. Technol.* 47, 1896–1903.
- Chang, H.T., Rittmann, B.E., Amar, D., Heim, R., Ehlinger, O., Lesty, Y., 1991. Biofilm detachment mechanisms in a liquid-fluidized bed. *Biotechnol. Bioeng.* 38, 499–506.
- Chen, Y., Lu, A., Li, Y., Zhang, L., Yip, H.Y., Zhao, H., An, T., Wong, P.-K., 2011. Naturally occurring sphalerite as a novel cost-effective photocatalyst for bacterial disinfection under visible light. *Environ. Sci. Technol.* 45, 5689–5695.
- Cosmidis, J., Benzerara, K., 2014. Soft X-ray scanning transmission micro-spectroscopy. In: *Handbook of Biomineralization*. Taylor and Francis, London.
- Dalai, S., Pakrashi, S., Chakravarty, S., Hussain, S., Chandrasekaran, N., Mukherjee, A., 2014. Studies on interfacial interactions of TiO₂ nanoparticles with bacterial cells under light and dark conditions. *Bull. Mater. Sci.* 37, 371–381.
- Deng, C.H., Gong, J.L., Zeng, G.M., Niu, C.G., Niu, Q.Y., Zhang, W., Liu, H.Y., 2014. Inactivation performance and mechanism of *Escherichia coli* in aqueous system exposed to iron oxide loaded graphene nanocomposites. *J. Hazard. Mater.* 276, 66–76.
- Di Bonaventura, G., Piccolomini, R., Paludi, D., D'Orio, V., Vergara, A., Conter, M., Lanieri, A., 2008. Influence of temperature on biofilm formation by *Listeria monocytogenes* on various food-contact surfaces: relationship with motility and cell surface hydrophobicity. *J. Appl. Microbiol.* 104, 1552–1561.
- Dohnalkova, A.C., Marshall, M.J., Arey, B.W., Williams, K.H., Buck, E.C., Fredrickson, J.K., 2011. Imaging hydrated microbial extracellular polymers: comparative analysis by electron microscopy. *Appl. Environ. Microbiol.* 77, 1254–1262.
- Dufrène, Y.F., 2004. Using nanotechniques to explore microbial surfaces. *Nat. Rev. Microbiol.* 2, 451–460.
- Ejaz, B., 2012. Does bacterial cell wall have any charge? If so what is the charge? https://www.researchgate.net/post/Does_bacterial_cell_wall_have_any_charge_If_so_what_is_the_charge [Accessed 29th May, 2017].
- Faghizadeh, F., Anaya, N.M., Schiffman, L.A., Oyanedel-Craver, V., 2016. Fourier transform infrared spectroscopy to assess molecular-level changes in microorganisms exposed to nanoparticles. *Nanotechnology for Environ. Eng.* 1, 1–16.
- Farkas, K., Varsani, A., Pang, L., 2015. Adsorption of rotavirus, MS2 bacteriophage and surface-modified silica nanoparticles to hydrophobic matter. *Food Environ. Virol.* 7, 261–268.
- Ferguson, C., Husman, A.M.R., Altavilla, N., Deere, D., Ashbolt, N., 2013. Fate and transport of surface water pathogens in watersheds. *Crit. Rev. Environ. Sci. Technol.* 33, 299–361.
- Fewtrell, L., 2014. Water Disinfection and Toxicity. www.who.int/water_sanitation_health/dwq/chemicals/Silver_water_disinfection_toxicity_2014v2.pdf Centre For Research into Environment and Health, pp. 1–53.
- Garrett, T.R., Bhakoo, M., Zhang, Z., 2008. Bacterial adhesion and biofilms on surfaces. *Prog. Nat. Sci.* 18, 1049–1056.
- Gilbert, P., Evans, D., Evans, E., Duguid, I., Brown, M., 1991. Surface characteristics and adhesion of *Escherichia coli* and *Staphylococcus Epidermidis*. *J. Appl. Bacteriol.* 71, 72–77.
- Goodacre, R., Timmins, E.M., Rooney, P.J., Rowland, J.J., Kell, D.B., 1996. Rapid identification of *Streptococcus* and *Enterococcus* species using diffuse reflectance absorbance Fourier transform infrared spectroscopy and artificial neural networks. *FEMS Microbiol. Lett.* 140, 233–239.
- Gupta, S.S., Bhattacharyya, K.G., 2014. Adsorption of metal ions by clays and inorganic

- solids. RSC Adv. 4, 28537–28586.
- He, H., Yang, D., Yuan, P., Shen, W., Frost, R.L., 2006. A novel Organoclay with antibacterial activity prepared from montmorillonite and Chlorhexidini Acetas. J. Colloids Interface Sci. 297, 235–243.
- Heilmann, C., Schweitzer, O., Gerke, C., Vanittanakom, N., Mack, D., Gotz, F., 1996. Molecular basis of intercellular adhesion in the biofilm-forming *Staphylococcus epidermidis*. Mol. Microbiol. 20, 1083–1091.
- Hiremath, N., 2014. Adsorption and Bacterial Adhesion Characteristics of Proteins, Microbial Growth Media and Milk on Abiotic Surfaces under Static and Laminar Flow Conditions. Department of Food Science and Agricultural Chemistry. McGill University, Montreal.
- Hong, Z., Rong, X., Cai, P., Dai, K., Liang, W., Chen, W., Huang, Q., 2012. Initial adhesion of bacillus subtilis on soil minerals as related to their surface properties. Eur. J. Soil Sci. 63, 457–466.
- Hong, Z., Li, J., Jiang, J., Liu, Z., Xu, R., 2015. Presence of bacteria reduced phosphate adsorption on goethite. Eur. J. Soil Sci. 66, 406–416.
- Hong, Z.N., Li, J.Y., Jiang, J., Li, Z.L., Xu, R.K., 2016. Competition between bacteria and phosphate for adsorption sites on gibbsite: an in situ ATR-FTIR spectroscopic and macroscopic study. Colloids Surf. B: Biointerfaces 148, 496–502.
- Hori, K., Matsumoto, S., 2010. Bacterial adhesion: from mechanism to control. Biochem. Eng. J. 48, 424–434.
- Hrenovic, J., Ivankovic, T., Tipljas, D., 2009. The effect of mineral carrier composition on phosphate-accumulating bacteria immobilization. J. Hazard. Mater. 166, 1377–1382.
- Hu, C.H., Xia, M.S., 2006. Adsorption and antibacterial effect of copper-exchanged montmorillonite on *Escherichia coli* K₈₈. Appl. Clay Sci. 31, 180–184.
- Hu, C.H., Xu, Z.R., Xia, M.S., 2005. Antibacterial effect of Cu²⁺-exchanged montmorillonite on *Aeromonas hydrophila* and discussion on its mechanism. Veterinary Microbiol. 109, 83–88.
- Huang, Q., Wu, H., Cai, P., Fein, J.B., Chen, W., 2015. Atomic force microscopy measurements of bacterial adhesion and biofilm formation onto clay-sized particles. Sci. Rep. 5, 16857–16868.
- Isberg, R.R., Barnes, P., 2002. Dancing with the host: flow-dependent bacterial adhesion. Cell 110, 1–4.
- Jiang, D., Huang, Q., Cai, P., Rong, X., Chen, W., 2007. Adsorption of *Pseudomonas putida* on clay minerals and iron oxide. Colloids Surf. B: Biointerfaces 54, 217–221.
- Jin, S., Fallgren, P.H., Morris, J.M., Chen, Q., 2007. Removal of bacteria and viruses from waters using layered double hydroxide nanocomposites. Sci. Technol. Adv. Mater. 8, 67–70.
- Jyoti, K.K., Pandit, A.B., 2001. Water disinfection by acoustic and hydrodynamic cavitation. Biochem. Eng. J. 7, 201–212.
- Kang, J.-K., Lee, C.-G., Park, J.-A., Kim, S.-B., Choi, N.-C., Park, S.-J., 2013. Adhesion of bacteria to pyrophyllite clay in aqueous solution. Environ. Technol. 34, 703–710.
- Katsikogianni, M., Missirilisi, Y.F., 2004. Concise review of mechanisms of bacterial adhesion to biomaterials and of techniques used in estimating bacteria-material interactions. Eur. Cell Mater. 5, 37–57.
- Khamkure, S., Cervantes, E.P., Melo, P.G., Gonzalez, A.Z., 2016. Effect of clay soil content on fecal bacteria removal in an intermittent media infiltration system. Environ. Eng. Manag. J. 15, 113–121.
- Kleyi, P., Ray, S., Abia, A., Ubomba-Jaswa, E., Wesley-Smith, J., Maity, A., 2016. Preparation and evaluation of quaternary imidazolium-modified montmorillonite for disinfection of drinking water. Appl. Clay Sci. 127–128, 95–104.
- Kouider, N., Hamadi, F., Mallouki, B., Bengourram, J., Mabrouki, M., Zekraoui, M., Latrache, H., 2010. Effect of stainless steel surface roughness on *Staphylococcus Aureus* adhesion. Int. J. Pure Appl. Sci. 4, 1–7.
- Lasch, P., Naumann, D., 2015. Infrared Spectroscopy in Microbiology. Encyclopedia of Analytical Chemistry.
- Leone, L., Loring, J., Sjöberg, S., Persson, P., Shchukarev, A., 2006. Surface characterization of the gram-positive bacteria *Bacillus subtilis*-an XPS study. Surf. Interface Anal. 38, 202–205.
- Lin, S., Huang, R., Cheng, Y., Liu, J., Lau, B., Wiesner, M., 2013. Silver nanoparticle-alginate composite beads for point-of-use drinking water disinfection. Water Res. 47, 3565–3599.
- Liu, Y., Tay, J.-H., 2002. The essential role of hydrodynamic shear force in the formation of biofilm and granular sludge. Water Res. 36, 1653–1665.
- Liu, C., Xie, X., Zhao, W., Liu, N., Maraccini, P.A., Sassoubre, L.M., Boehm, A.B., Cui, Y., 2013a. Conducting nanosponge electroporation for affordable and high-efficiency disinfection of bacteria and viruses in water. Nano Lett. 13, 4288–4293.
- Liu, J., Duan, C., Zhou, J., Li, X., Qian, G., Xu, Z.P., 2013b. Adsorption of bacteria onto layered double hydroxide particles to form biogranule-like aggregates. Appl. Clay Sci. 75–76, 39–45.
- Liu, T.-Y., Chen, C.-L., Lee, Y.-C., Chan, T.-Y., Wang, Y.-L., Lin, J.-J., 2016. First observation of physically capturing and maneuvering bacteria using magnetic clays. ACS Appl. Mater. Interfaces 8, 411–418.
- Londono, S.C., Williams, L., 2016. Unraveling the antibacterial mode of action of a clay from the Colombian Amazon. Environ. Geochem. Health 38, 363–379.
- Lower, S.K., Tadanier, C.J., Hochella, M.F., 2000. Measuring interfacial and adhesion forces between bacteria and mineral surfaces with biological force microscopy. Geochim. Cosmochim. Acta 64, 3133–3139.
- Ma, X., Zhou, W., Fu, Z., Cheng, Y., Min, M., Liu, Y., Zhang, Y., Chen, P., Ruan, R., 2014. Effect of wastewater-borne bacteria on algal growth and nutrients removal in wastewater-based algae cultivation system. Bioresour. Technol. 167, 8–13.
- Malachová, K., Praus, P., Pavličková, Z., Turicová, M., 2009. Activity of antibacterial compounds immobilised on montmorillonite. Appl. Clay Sci. 43, 364–368.
- Matias, V.R., Al-Amoudi, A., Dubochet, J., Beveridge, T.J., 2003. Cryo-transmission electron microscopy of frozen-hydrated sections of *Escherichia coli* and *Pseudomonas Aeruginosa*. J. Bacteriol. 185, 6112–6118.
- McWhirter, M.J., McQuillan, A.J., Bremer, P.J., 2002. Influence of ionic strength and pH on the first 60 min of *Pseudomonas aeruginosa* attachment to ZnSe and to TiO₂ monitored by ATR-IR spectroscopy. Colloids Surf. B: Biointerfaces 26, 365–372.
- Milne, J.L., Subramaniam, S., 2009. Cryo-electron tomography of bacteria: progress, challenges and future prospects. Nat. Rev. Microbiol. 7, 666–675.
- Miot, J., Benzerara, K., Kappler, A., 2014. Investigating microbe-mineral interactions: recent advances in X-ray and electron microscopy and redox-sensitive methods. Annu. Rev. Earth Planet. Sci. 42, 271–289.
- Morrison, K.D., Underwood, J.C., Metge, D.W., Eberl, D.D., Williams, L.B., 2013. Mineralogical variables that control the antibacterial effectiveness of a natural clay deposit. Environ. Geochem. Health 36, 613–631.
- Morrison, K.D., Misra, R., Williams, L.B., 2016. Unearthing the antibacterial mechanism of medicinal clay: a geochemical approach to combating antibiotic resistance. Sci. Rep. 6, 19043.
- Motshekga, S.C., Ray, S.S., Onyango, M.S., Momba, M.N.B., 2015. Preparation and antibacterial activity of chitosan-based nanocomposites containing bentonite-supported silver and zinc oxide nanoparticles for water disinfection. Appl. Clay Sci. 114, 330–339.
- Moyo, F., Tandlich, R., Wilhelm, B.S., Balaz, S., 2014. Sorption of hydrophobic organic compounds on natural sorbents and Organoclays from aqueous and non-aqueous solutions: a mini-review. Int. J. Environ. Res. Public Health 11, 5020–5048.
- Mueller, B., 2015. Experimental interactions between clay minerals and bacteria: a review. Pedosphere 25, 799–810.
- Muter, O., Potapova, K., Nikolajeva, V., Petrina, Z., Gribo, T., Patmalnieks, A., Svinka, R., Svinka, V., 2012. Comparative study on bacteria colonization onto ceramic beads originated from two Devonian clay deposits in Latvia. Mater. Sci. Appl. Chem. 26, 134–139.
- Nassar, R., Browne, E., Chen, J., Klivanov, A., 2012. Removing human immune deficiency virus (HIV) from human blood using immobilized heparin. Biotechnol. Lett. 34, 853–856.
- Nie, X., Li, G., Gao, M., Sun, H., Liu, X., Zhao, H., Wong, P.K., An, T., 2014. Comparative study on the photo-electrocatalytic inactivation of *Escherichia coli* K-12 and its mutant *Escherichia coli* BW25113 using TiO₂ nanotubes as a photoanode. Appl. Catal. B Environ. 147, 562–570.
- Nies, D.H., 1999. Microbial heavy-metal resistance. Appl. Microbiol. Biotechnol. 51, 730–750.
- Nieuwenhuijsen, M.J., Grellier, J., Smith, R., Iszatt, N., Bennett, J., Bset, N., Toledano, M., 2009. The Epidemiology and possible mechanisms of disinfection by-products in drinking water. Phil. Trans. R. Soc. A 367, 4043–4076.
- Nováková, J., 1977. Effect of clays on the microbial adsorption. Zentralblatt für Bakteriologie, Parasitenkunde, Infektionskrankheiten und Hygiene. Zweite Naturwissenschaftliche Abteilung: Allgemeine, Landwirtschaftliche und Technische Mikrobiologie 132, 418–422.
- Otto, C., Haydel, S., 2013. Microbicidal clays: composition, activity, mechanism of action, and therapeutic applications. In: Méndez-Vilas, A. (Ed.), Microbial Pathogens and Strategies for Combating them: Science, Technology and Education, Badajoz, Spain, pp. 1169–1180.
- Papapillipou, P., Vyrides, L., Mpekris, F., Stylianopoulos, T., Papatryfonos, C., Theocharis, C., Christoforou, T., 2015. Evaluation of novel, cationic electrospun microfibrillar membranes as adsorbents in bacteria removal. RSC Adv. 5, 67617–67629.
- Parikh, S.J., Chorover, J., 2006. ATR-FTIR spectroscopy reveals bond formation during bacterial adhesion to iron oxide. Langmuir 22, 8492–8500.
- Pina, R.G., Cervantes, C., 1995. Microbial interactions with aluminum. Biometals 9, 311–316.
- Ping, Y., Hu, X., Yao, Q., Hu, Q., Amini, S., Miserez, A., Tang, G., 2016. Engineering bioinspired bacteria-adhesive clay nanoparticles with a membrane-disruptive property for the treatment of *Helicobacter pylori* infection. Nano 8, 16486–16498.
- Pradier, C., Rubio, C., Poleunis, C., Bertrand, P., Marcus, P., Compere, C., 2005. Surface characterization of three marine bacterial strains by Fourier transform IR, X-ray photoelectron spectroscopy, and time-of-flight secondary-ion mass spectrometry, correlation with adhesion on stainless steel surfaces. J. Phys. Chem. B 109, 9540–9549.
- Qi, L., Xu, Z., Jiang, X., Hu, C., Zou, X., 2004. Preparation and antibacterial activity of chitosan nanoparticles. Carbohydr. Res. 339, 2693–2700.
- Rabea, E.I., Badawy, M.E.-T., Stevens, C.V., Smagghe, G., Steurbaut, W., 2003. Chitosan as antimicrobial agent: applications and mode of action. Biomacromolecules 4, 1457–1465.
- Rong, X., Huang, Q., He, X., Chen, H., Cai, P., Liang, W., 2008. Interaction of *Pseudomonas putida* with kaolinite and montmorillonite: a combination study by equilibrium adsorption, ITC, SEM and FTIR. Colloids Surf. B: Biointerfaces 64, 49–55.
- Santhiya, D., Subramanian, S., Natarajan, K.A., 2000. Surface chemical studies on galena and sphalerite in the presence of *Thiobacillus thiooxidans* with reference to mineral beneficiation. Miner. Eng. 13, 747–763.
- Savage, N., Diallo, M.S., 2005. Nanomaterials and water purification: opportunities and challenges. J. Nanopart. Res. 7, 331–342.
- Schaedler, S., Burkhardt, C., Kappler, A., 2008. Evaluation of electron microscopic sample preparation methods and imaging techniques for characterization of cell-mineral aggregates. Geomicrobiol. J. 25, 228–239.
- Seckin, T., Onal, Y., Yesilada, O., Gultek, A., 1997. Preparation and characterization of a clay-polyvinylpyridinium matrix for the removal of bacterial cells from water. J. Mater. Sci. 33, 5993–5999.
- Sharma, V.K., McDonald, T.J., Kim, H., Grag, V.K., 2015. Magnetic graphene-carbon nanotube iron nanocomposite as adsorbents and antibacterial agents for water purification. Adv. Colloid Interf. Sci. 225, 229–240.
- Shtarker-Sasi, A., Castro-Sowinski, S., Matan, O., Kagan, T., Nir, S., Okon, Y., Nasser,

- A.M., 2013. Removal of bacteria and *Cryptosporidium* from water by micelle–montmorillonite complexes. *Desalin. Water Treat.* 51, 7672–7680.
- Stevik, T.K., Aa, K., Ausland, G., Hanssen, J.F., 2004. Retention and removal of pathogenic bacteria in wastewater percolating through porous media: a review. *Water Res.* 38, 1355–1367.
- Tavanaei, M., Shirvani, M., Bakhtiari, S., 2016. Adhesion of *Pseudomonas putida* onto palygorskite and sepiolite clay minerals. *Geomicrobiol. J.* <https://doi.org/10.1080/01490451.2016.1238982>.
- Tombácz, E., Szekeres, M., 2006. Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. *Appl. Clay Sci.* 34, 105–124.
- Undabeytia, T., Posada, R., Nir, S., Galindo, I., Laiz, L., Saiz-Jimenez, C., Morillo, E., 2014. Removal of waterborne microorganisms by filtration using clay–polymer complexes. *J. Hazard. Mater.* 279, 190–196.
- Unuabonah, E.I., Taubert, A., 2014. Clay–polymer nanocomposites (CPNs): adsorbents of the future for water treatment. *Appl. Clay Sci.* 99, 83–92.
- Unuabonah, E.I., Adebawale, K.O., Olu-Owolabi, B.I., 2007. Kinetic and thermodynamic studies of the adsorption of lead (II) ions onto phosphate-modified kaolinite clay. *J. Hazard. Mater.* 144, 386–395.
- Unuabonah, E.I., Olu-Owolabi, B.I., Taubert, A., Omolehin, E.B., Adebawale, K.O., 2013a. SAPK: a novel composite resin for water treatment with very high Zn^{2+} , Cd^{2+} and Pb^{2+} adsorption capacity. *Ind. Eng. Chem. Res.* 52, 578–585.
- Unuabonah, E.I., Guenter, C., Weber, J., Lubahn, S., Taubert, A., 2013b. Hybrid clay: a new highly efficient adsorbent for water treatment. *ACS Sustain. Chem. Eng.* 1, 966–973.
- Unuabonah, E.I., Kolawole, M.O., Agunbiade, F.O., Omorogie, M.O., Koko, D.T., Ugwuja, C.G., Ugege, L.E., Oyejide, N.E., Guenter, C., Taubert, A., 2017a. Novel metal-doped bacteriostatic hybrid clay composites for point-of-use disinfection of water. *J. Environ. Chem. Eng.* 5, 2128–2141.
- Unuabonah, E.I., Adewuyi, A., Kolawole, M.O., Omorogie, M.O., Olatunde, O.C., Fayemi, S.O., Günter, C., Okoli, C.P., Agunbiade, F.O., Taubert, A., 2017b. Disinfection of water with new chitosan-modified hybrid clay composite adsorbent. *Heliyon* 3, e00379.
- Vacheethasane, K., Temenoff, J.S., Higashi, J.M., Gary, A., Anderson, J.M., Bayston, R., Marchant, R.E., 1998. Bacterial surface properties of clinically isolated *Staphylococcus epidermidis* strains determine adhesion on polyethylene. *J. Biomed. Mater. Res. A* 42, 425–432.
- Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castaño-Vinyals, G., Marcos, R., Rothman, N., Real, F.X., Dosemeci, M., Kogevinas, M., 2007. Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. *Am. J. Epidemiol.* 165, 148–156.
- Wakshlak, R.B.-K., Pedahzur, R., Avnir, D., 2015. Antibacterial activity of silver-killed bacteria: the "zombies" effect. *Sci. Rep.* 5. <http://dx.doi.org/10.1038/srep09555>.
- Wang, W., Yu, J.C., Xia, D., Wong, P.K., Li, Y., 2013. Graphene and g-C₃N₄ nanosheets wrapped elemental α -sulfur as a novel metal-free heterojunction photocatalyst for bacterial inactivation under visible-light. *Environ. Sci. Technol.* 47, 8724–8732.
- Wang, W., Huang, G., Jimmy, C.Y., Wong, P.K., 2015. Advances in photocatalytic disinfection of bacteria: development of photocatalysts and mechanisms. *J. Environ. Sci.* 34, 232–247.
- William, L.B., Haydel, S.E., 2010. Evaluation of the medicinal use of clay minerals as antibacterial agents. *Int. Geol. Rev.* 52, 745–770.
- Wu, T., Xie, A.-G., Tan, S.-Z., Cai, Z., 2011. Antimicrobial effects of quaternary phosphonium salt intercalated clay minerals on *Escherichia coli* and *Staphylococcus aureus*. *Colloids Surf. B: Biointerfaces* 86, 232–236.
- Wu, H., Chen, W., Rong, X., Huang, Q., 2014. Adhesion of *Pseudomonas putida* onto kaolinite at different growth phases. *Chem. Geol.* 390, 1–8.
- Xi, C., Zhang, Y., Marrs, C.F., Ye, W., Simon, C., Foxman, B., Nriagu, J., 2009. Prevalence of antibiotic resistance in drinking water treatment and distribution systems. *Appl. Environ. Microbiol.* 75, 5714–5718.
- Xu, J., Campbell, J.M., Zhang, N., Hickey, W.J., Sahai, N., 2012. Did mineral surface chemistry and toxicity contribute to evolution of microbial extracellular polymeric substances. *Astrobiology* 12, 785–798.
- Xue, M.Q., Li, J., Xu, Z.M., 2012. Environmental friendly crush-magnetic separation technology for recycling metal-plated plastics from end-of-life vehicles. *Environ. Sci. Technol.* 46, 2661–2667.
- Yang, H., Tong, M., Kim, H., 2012. Influence of bentonite particles on representative gram-negative and gram-positive bacterial deposition in porous media. *Environ. Sci. Technol.* 46, 11627–11634.
- Yu, C., Irudayaraj, J., 2005. Spectroscopic characterization of microorganisms by Fourier transform infrared microspectroscopy. *Biopolymers* 77, 368–377.
- Yuan, G.D., Theng, B.K.G., Churchman, G.J., Gates, W.P., 2013. Chapter 5.1-clays and clay minerals for pollution control in handbook of clay science. In: Bergaya, F., Lagaly, G. (Eds.), *Development in Clay Science*, 2nd ed. Elsevier.
- Yuan, Q.-B., Guo, M.-T., Yang, J., 2015. Fate of antibiotic resistant bacteria and genes during wastewater chlorination: implication for antibiotic resistance control. *PLoS One* 10 (3), e0119403.
- Zhang, D., Li, G., Jimmy, C.Y., 2010. Inorganic materials for photocatalytic water disinfection. *J. Mater. Chem.* 20, 4529–4536.
- Zhang, T., Yang, W., Zhu, X., Wang, H., Brookes, P.C., Xu, J., 2015. The pH dependence of *Escherichia coli* O157:H7 adsorption on kaolinite and goethite surfaces. *J. Soils Sediments* 15, 106–116.
- Zupan, J., Mavri, J., Raspor, P., 2009. Quantitative cell wall protein profiling of invasive and non-invasive *Saccharomyces cerevisiae* strains. *J. Microbiol. Methods* 79, 260–265.