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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), electromagnetic 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 addtion, 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 $Al_2Si_4O_{10}(OH)_2$, 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, Benzyldimethylhexadecylammonium (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* DH5α 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* K_{88} (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 *Staphylococci 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 *Samonella 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)