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Article in *Agricultural Reviews* · May 2018

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Potentials of zinc and magnetite nanoparticles for contaminated water treatment

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Received: 19-06-2017 Accepted: 15-04-2018

ABSTRACT

Water contamination is an issue requiring continuous remedy on daily basis because of the high demand for clean quality water. Scientists have proffered numerous ways of making this possible but the techniques involved is often difficult to replicate at small scale. For this reason, easier and cheaper techniques for contaminated water treatment are often sought after. One way of actualizing this is via nanotechnology, which involves the use of smaller particles (< 100 nm in size) to coagulate suspended substances and inhibit microbial growth in the targeted water. The mechanisms involved have been presented for zinc and magnetite nanoparticles in this write-up. This technology provides way of getting clean quality water for domestic, agricultural and industrial applications.

Key words: Contamination, Health, Magnetite nanoparticles, Water treatment, Zinc nanoparticles

Water contamination is a form of environmental degradation occurring when waste products are discharged into water bodies without adequate treatment to remove harmful substances (Banerjee *et al.*, 2006; Kumar and Sagwal, 2000). Quality assurance is necessary in water management practice to ensure safety in water application. Certain practices including poor agricultural waste management can contaminate water and adversely affect its quality. Applying contaminated water in domestic, industrial and agricultural activities is capable of posing serious health issue (Ebner *et al.*, 1999). For instance, handling of crops with contaminated water can easily spread pathogens (Ambika *et al.*, 2010; Hirano, 2009; Meshalkin and Bgatova, 2008). Fruit or vegetables handled with contaminated water can cause waterborne illnesses when consumed by humans. It is possible to spread pathogens from irrigated crops imported from abroad, especially when strict crop handling practices are not enforced, and this too can cause foodborne health problems (Selvaraj *et al.*, 2014; Theron *et al.*, 2008).

Application of untreated water in animal husbandry might seemed ideal especially in feed formulation, but the high amount of microorganisms and minerals present in the water could be hazardous to the animals in the long run. It is usually not a healthy practice to breed animals with contaminated water, but if contaminated water is supplied to animals, chances are that they may develop low reproductive performance and their immune system may wane. In fact, the presence of certain chemicals like mercury

and nitrogen may seriously affect their metabolism and cause death of the animals in some cases. Presence of toxic blue-green algae, accidental oil spills, pesticides and fertilizers in water may also affect general performance of livestock. Thus, adequate amount of quality water supply for drinking is paramount in animal and aquatic managements (Obasohan and Oronsaye, 2008). This is to avoid the migration of pathogens from water into the body of the animals, especially when they drink from the same trough. Thus, water quality analysis and treatment prior to intake by the animals is necessary to ensure safety.

Water entering an industrial plant needs adequate treatment to meet specific requirements and application. Problems such as biofouling, corrosion of metals, and scale formation may result if contaminated water is applied in the industrial process operations, as shown in Figure 1. The microorganisms in contaminated water may multiply so rapidly to such an extent leading to a situation called biofouling when the water becomes unfit for industrial use. Cooling systems and hot water circuits frequently provide ideal habitats for micro-organisms such as bacteria, fungi, algae and protozoans, while systems using sea water may suffer from fouling by larger creatures such as barnacles and mussels. Also, metal parts in contact with the contaminated water may become oxidized electrochemically to cause corrosion and eventual production of traces of permanent oxides in the production line. Moreover, some insoluble compounds in the contaminated water may be precipitated to cause scale and sludge formation under the conditions

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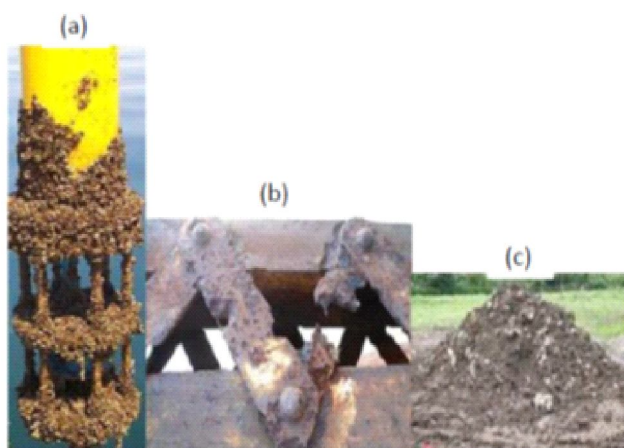


Fig 1: Typical problems associated with contaminated water in the industry

(a) Biofouling (b) Metal corrosion (c) Industrial process sludge

prevailing at the point of deposition. This typically occurs in industrial food processing plants, like in large heat exchange plant and cooling tower pond, which requires high temperature in operation.

Many processes of treating contaminated water for domestic, agricultural and industrial applications have been reported in literature (Chon *et al.*, 2010; Di *et al.*, 2012; Sangeetha and Baskar, 2016). For example, activated sludge process has been used to absorb and adsorb organic matter and pathogens in contaminated water via the action of colony of microorganisms (Karn *et al.*, 2009; Zhang *et al.*, 2003). Another technique commonly used in treating contaminated water is nanoremediation (Bardos *et al.*, 2014; Latha *et al.*, 2004; Zhang *et al.*, 2015). The technique involves bringing nanoparticles (< 100 nm in size) in contact with a target contaminate to cause coagulation and disinfection either via pump-and-treat or *in situ* application (Meshalkin and Bgatova, 2008). Potential nanoparticles for use in water disinfection include, silver, copper, zinc, magnetite, titanium, and cobalt in order of strength. Since silver, titanium, cobalt and copper are quite expensive compared to zinc and magnetite, the application of the latter in water disinfection cannot be over emphasized.

Application of some readily abundant nano-metal ions in contaminated water treatment can greatly influence water quality (Addleman *et al.*, 2005; Fadeyibi *et al.*, 2017). Research is on-going to apply zinc and magnetite nanoparticles in the removal chemical contaminants and microorganisms from contaminated water. According to Fadeyibi *et al.* (2017) and Chen *et al.* (1998), zinc and magnetite nanoparticles exhibit anticorrosive, antibacterial, antifungal and ultra-violet filtering behaviors; and these have often helped in treating contaminated water via nanotechnology. Synthesis of zinc and magnetite nanoparticles used in coagulating suspended solids and removing impurities from contaminated water have been

reported (Glushchenko and Skalny, 2010). The method was generally effective for water disinfection, simple, quite affordable and does require high skill to operate (Chen *et al.*, 1998). Despite the opportunities presented by nanotechnology in this sector, very little is known about the application of zinc and magnetite nanoparticles in Nigerian water treatment authorities. Millions of Naira are often needlessly spent on purchase of sophisticated and complex water treatment technology to make water available to the people. It is possible to address the problems associated with water quality at small scale using this approach because of the small size of the nanoparticles, which presents good reactive surface against the activities of microbial contaminants in the water. There is therefore the need to review the potentials of zinc and magnetite nanoparticles as contaminated water treatment alternative. Thus, this review focuses on the potentials of zinc and magnetite nanoparticles as treatment agents for contaminated water for domestic, industrial and agricultural applications.

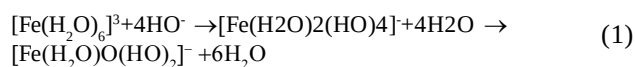
Preparations of magnetite and zinc nanoparticles: The synthesis of magnetite and zinc nanoparticles normally involves complex processes because of their colloidal nature. Depending on the nature of contaminants and purpose of treatment, the methods of preparation of the nanoparticles differ. Some of the methods presented are expensive and requires high skill to operate. There are however few approaches that are easy to replicate, inexpensive and those not involve the formation of complexes, as shown in Table 1. For contaminant removal applications, a proper surface modification of the nanoparticles is a critical aspect regarding their water stability and subsequent reclamation.

Potential treatment of contaminated water using magnetite nanoparticles: Magnetite nanoparticles have potential for application in treatment of contaminated water. The particles have been reported to have unique features that aided its suitability for water treatment. According to Blaney (2007), magnetite nanoparticles can successfully remove suspension and pathogenic contaminant from drinking and wastewater streams. It is also possible to remove carcinogenic metals and radioactive chemicals from contaminated water using magnetite nanoparticles (Navratil, 2003). The mechanism involved in removing metals from the process usually results in the formation of hydroxide complexes due to their low solubility. Dzombak (1990) corroborated this, as a matter of fact, when he reported that magnetite nanoparticles are suitable scavenger for many heavy metal contaminants in water treatment process. A simple magnetite water treatment mechanism can be described when magnetite (Fe^{3+}) reacts with the basic hydroxide ion (OH^-) in a contaminated water to form a floc of magnetite hydroxide ($\text{Fe}(\text{OH})_2$) or more precisely formulated as $\text{FeO}(\text{OH})^-$, which is capable of

Table 1: Methods of preparation of magnetite and zinc nanoparticles

s/n	Treatment Agent	Method	Pros	Cons	Reference
1	Magnetite Nanoparticles	Micro-emulsion technology	(a) 10-100 nm particle size	-Requires skill	Zhou <i>et al.</i> (2001)
		Hydrothermal reactions	(b) Size can be controlled	-Process expensive	Fried <i>et al.</i> (2001)
		Chemical synthesis	(a) Remove contaminants	-Requires skill	Lee <i>et al.</i> (2005)
			(b) 2- 10 nm particle size	-Process expensive	Tang <i>et al.</i> (2003)
			(a) Inactivate contaminants	-Chemical residue	Anuku (2012)
			(b) 3- 8 nm particle size	-Process expensive	Fadeyibi <i>et al.</i> (2017)
		Co-precipitation	(a) Remove contaminants	-Easily oxidized	Laurent <i>et al.</i> (2008)
			(b) 5-100 nm particle size	-Process expensive	
		Plasma assisted molecular beam	(a) No chemical usage	-Process expensive	Chen <i>et al.</i> (1998)
			(b) < 10 nm particle size	-Process laborious	
		Hydrothermal growth technique	(a) No hazard involved	-Requires skill	Brush and Dutta (2009)
			(b) Remove heavy metals	-High temperature	
		Sol-gel method	(a) Simple process	-Chemical residue	Fadeyibi <i>et al.</i> (2016)
			(b) 4-6 nm particle size	-Use a lot of water	
2	Zinc Nanoparticles				

removing microorganisms and suspended materials, as expressed in Eq. (1).



In situ and preformed magnetite methods can be employed in contaminated water treatment application (Boyd, 1986; Glushchenko *et al.*, 2010). The *in situ* approach involves addition of ferrous ions to the contaminated water sample at 80°C followed by the addition of a suitable base and subsequent oxidation in sufficient amount of oxygen to form magnetite. In the preformed approach, ferrite is prepared separately using the *in situ* procedures and later added in slurry form to the contaminated water (Boyd, 1986). Furthermore, the application of magnetite in contaminated water treatment, whether *in situ* or preformed, is much more effective than the conventional flocculation techniques for removal of heavy metal, suspension and pathogens (Kochen and Navratil, 1997). The ferromagnetic feature of magnetite permits magnetic separation of metals from contaminated water samples. Thus, metallic impurities can be removed conveniently without subjecting the samples to further process, unlike the conventional approach which requires additional process to remove impurities (Navratil, 1988). Also, magnetite technique does not require expensive chemicals like the conventional method, since oxidation of iron to magnetite can easily be achieved within the batch (Ibanez *et al.*, 2003). Therefore, magnetite nanoparticles, when separately used or in conjunction with other processes, can effectively treat contaminated water.

Potential treatment of contaminated water using zinc nanoparticles: Zinc nanoparticles also have potential in the treatment of contaminated water. This is possibly because of the high reactivity, photolytic properties, and large surface area of the zinc nanoparticles (N. Ibanez *et al.*, 2003; Daneshvar *et al.*, 2004). The porous nanostructure nature of the nanoparticles, together with their high BET surface area for the adsorption of heavy metals (Ge *et al.*, 2012; Kumar *et al.*, 2013), might also have contributed to their potential in treating contaminated water. Already zinc nanoparticles have been reported to adequately remove traces of copper in contaminated water with high removal efficiency (Wang *et al.*, 2010). Baruah and Dutta (2009) also reported zinc nanoparticles as attractive material for water treatment in solar photo-catalysis. Kumar *et al.* (2013) and Bokare *et al.* (2013) also observed high removal efficiencies, by zinc nanoparticles, of traces of lead and cadmium in contaminated water, respectively. Moreover, research results of Janotti *et al.* (2011) and Kim and Yong (2012) to examine the potential impacts of zinc nanoparticles on contaminated water in conventional activated sludge process showed that the nanoparticles can significantly inhibit nitrifying activity.

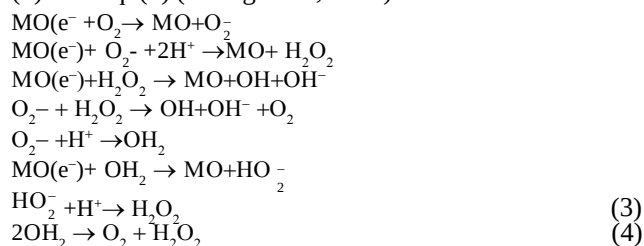
As observed by Fadeyibi *et al.* (2017) and Haritha *et al.* (2011), zinc nanoparticles have received significant attention due to their unique antifungal, antibacterial, ultra-violet filtering properties, and high photochemical and catalytic activities. The antibacterial activity performances of zinc nanoparticles against *Bacillus subtilis* and *Escherichia coli* have been studied by Haritha *et al.* (2011). The particles are able to negatively influence the growths of *Bacillus subtilis* and *Escherichia coli* in contaminated water samples. It is possible to integrate zinc nanoparticles into membrane treatment at some points so as to achieve treatment goal in a single process (Li *et al.*, 2008). This way, the membranes process becomes more functional while minimizing fouling to human and ecosystem (Wiesner *et al.*, 2006).

Photo-catalysis using zinc nanoparticles can be an attractive method of treating contaminated water, as it shows great potential of removing chemical and biological contaminants (Baruah, and Dutta, 2011; Jongnavakit *et al.*, 2012). The process also offers large surface areas to volume ratios which in turn allows higher adsorption of contaminate. The prospect of using photo-catalysis in detoxifying industrial and agricultural liquid wastes has also been reported (Baruah, and Dutta, 2009). Application of this process in the purification of contaminated water for municipal purpose has been reported (Baruah, and Dutta, 2011). The mechanism involved in photo-catalytic treatment of contaminated water using zinc nanoparticles was outlined by Baruah *et al.* (2012), as shown in Fig. 2. Water purification is achieved through dissolution of zinc oxide to release zinc ions and subsequent formation of reactive oxygen molecules through photo-catalysis. This way and in the presence of light as catalyst, pairs of electron and holes are formed, which in turn moves up to the conduction band while the hole drifts to the bottom of the valence band. Degradation process is subsequently initiated by the action of the electron-hole pair causing a change in redox potential. Almost all types microbial and inorganic contaminants can be degraded by this change in redox (Baruah, and Dutta, 2009). The fundamental expression in the photo-catalysis process is given in Eq. (2).



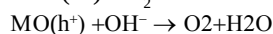
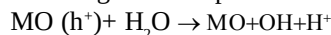
where, MO represents zinc oxide.

The electrons generated further assisted in the formation of O_2^- , H_2O_2 , OH , HO_2^- and HO_2 , as shown in Eq. (3) and Eq. (4) (Zhang *et al.*, 2005).



(4)

Also, the holes generated further assisted in oxidizing zinc nanoparticles as shown in Eq. (5) and Eq. (6).



The reactions are terminated as:



It is important to note the role played by high surface area of the zinc nanoparticles in the reaction process. The adsorption of the target contaminates in the water is high because of this, thus promoting the efficiency of the photo-catalytic reaction. One advantage of this process is the fact that it is able to remove all categories of contaminates, including chemical, bacteria, fungi, virus, molds and so on. However, photo-catalytic inactivation of bacteria, fungi and virus is usually complex to actualize and this ultimately depends on type, concentration and physical state of the microbes. Besides, the morphology of the nanoparticles can also influence the rate of microbe inactivation in the contaminated water (Huang *et al.*, 1998; Krishna *et al.*, 2008). Research results of Huang *et al.* (1998) and Krishna *et al.* (2008) showed that photo-catalytic process can effectively be used to inactivate diarrhea causing *Escherichia coli* from contaminated water. The inactivation of *Bacillus subtilis* and *Staphylococcus aureus* by photo-catalytic process in conjunction with zinc nanoparticles has also been reported (Sapkota *et al.*, 2011). Therefore, zinc nanoparticles, when separately used or in conjunction with other processes, can effectively treat contaminated water.

CONCLUSION

Pathogens contained in contaminated water can cause serious physiological issue to irrigated crops and health issue to human and livestock. Nanotechnology has provided avenue for preventing the activities of pathogens in

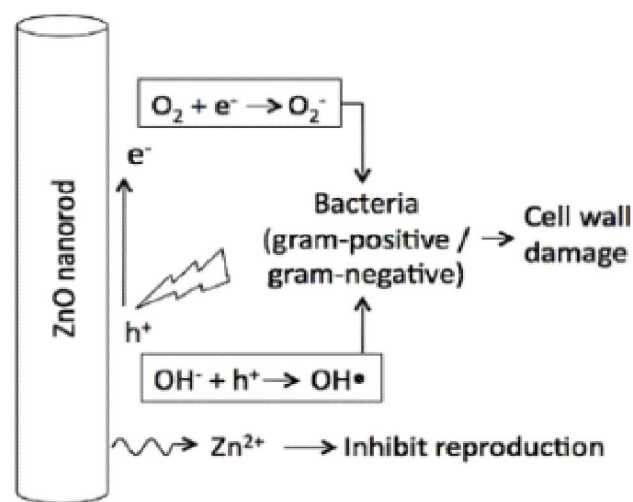


Fig 2: Photo-catalytic treatment of contaminated water and bacteria immobilization via zinc nanoparticles (Baruah *et al.*, 2012)

contaminated water. This is usually achieved when nanoparticles are brought into contact with the target contaminant to prevent infection process to take place. This article presented the potential of zinc and magnetite

nanoparticles as treatment agents for contaminated water resulting from agricultural activities. It can be seen that zinc and magnetite nanoparticles are alternative treatment means for contaminated water.

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