

Nanotechnology and its Application in Water Treatment: A Review

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Abstract— Environmental pollution, mainly caused by toxic chemicals, includes air, water, and soil pollution. This pollution results not only in the destruction of biodiversity, but also the degradation of human health. Pollution levels that are increasing day by day need better developments or technological discoveries immediately. In this sense, Nanotechnology, is the production and art of operating matter at the nanoscale (1–100 nm), offers the potential of novel nanomaterials for treatment of surface water, groundwater, and wastewater contaminated by toxic metal ions, organic and inorganic solutes, and microorganisms. Nanotechnology has three main capabilities that can be applied in the fields of environment, including the cleanup (remediation) and purification, the detection of contaminants (sensing and detection), and the pollution prevention. Different nanomaterials and their application in water treatment, purification and disinfection is reviewed in this article.

Keywords— Nanotechnology, Nanoparticles, Water Purification, Water Remediation, Wastewater treatment.

I. INTRODUCTION

In this day and age where enterprises have been modernized and propelled, our condition is filled with different kinds of toxins transmitted from human exercises or mechanical procedures. Instances of these toxins are carbon monoxide (CO), chlorofluorocarbons (CFCs), substantial metals (arsenic, chromium, lead, cadmium, mercury and zinc), hydrocarbons, nitrogen oxides, natural mixes (unpredictable natural mixes and dioxins), sulfur dioxide and particulates. Human exercises, for example, oil, coal and gas burning, can possibly change outflows from regular sources. Notwithstanding air contamination, there is additionally water contamination brought about by different elements, including waste removal, oil slicks, spillage of manures, herbicides and pesticides, results of modern procedures and burning and extraction of petroleum products.

Contaminants are for the most part discovered blended noticeable all around, water and soil. Along these lines, we need an innovation that can screen, recognize and, if conceivable, clean the contaminants from the air, water and soil. Right now, offers a wide scope of capacities and innovations to improve the nature of existing condition.

Nanotechnology is additionally used to forestall the arrangement of toxins or contaminants by applying the material innovation, mechanical procedures and others. Consequently, three significant utilizations of nanotechnology in the fields of condition can be classified, to be specific

- 1) Restoration (remediation) and purification of contaminated material,
- 2) Pollution detection (sensing and detection) and
- 3) Pollution prevention.

With rapid increment of pollutant species and concentration, the development of instruments that able to treat and prevent it is necessary.

II. NANOTECHNOLOGY FOR CLEAN WATER

About 30% of all water on the Earth is not surrounded in the ice or glaciers and only 0.08% of it is clean water (Krantzberg *et al.*, 2010), a similarity of 1 teaspoon of water versus a 5 litre container of water. As of late, water has become a vital

issue, and it is very difficult to tackle the related issues. The advancement of nanotechnology can be utilized to improve water quality. A few strategies that can utilize nanotechnology use responsive media for separation and filtration, bioremediation and disinfection.

Remediation is the method to evacuate, minimize or neutralize the water contaminants that can harm human wellbeing or environments. Remediation technologies can be divided into three classifications, in particular

- 1) Thermal method
- 2) Physicochemical method and
- 3) Biological method

Most customary strategies, for example, extraction, adsorption and oxidation are less effective, costly and tedious, whereas the more environmentally friendly biological degradation is inexpensive, but very time-consuming. A propelled technique that can be utilized is nanomaterials, with improved affinity, capacity and selectivity for heavy metals and other contaminants. The benefits of utilizing nanomaterials are their higher reactivity, larger surface contact and better removal ability. There are a few instances of nanoparticles and nanomaterials that can be utilized for remediation of water, for example zeolites, carbon nanotubes (CNTs), self-amassed monolayers on mesoporous bolsters, biopolymers, single-enzyme nanoparticles, nanoparticles of zero valent iron (ZVI), among others.

III. NANOTECHNOLOGIES FOR WATER REMEDIATION

The use of metals and chemicals in process industries has resulted in the generation of large quantities of effluent that contain high levels of toxic heavy metals, whereas mining and mineral processing operations also generate toxic liquid wastes (Coetser *et al.*, 2007). Moreover, groundwater is often contaminated by spills, agricultural practices, past waste disposal practices and leaking underground storage tanks (Kemper 2004; Foley *et al.*, 2005). The presence of different organic and heavy metal contaminants in these, as well as other environmental water sources has a large environmental, public health and economic impact. In addition to highly toxic metallic cations such as arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), and mercury (Hg) (Jarup 2003; Lee *et al.*, 2005), inorganic anions such as nitrate (NO_3^-) and perchlorate (ClO_4^-) are also of concern. Whereas high levels of nitrates in drinking water may be harmful to newborn babies and contribute to cancer (Yang and Lee 2005), perchlorate, which has emerged as a high profile contaminant and has consequently received considerable regulatory attention (Cheng *et al.*, 2007), has been reported to lead to hypothyroidism in adults (Blount *et al.* 2006). Moreover, almost all of the chlorinated aromatic compounds exhibit high toxicity and several of these compounds are carcinogenic (Xu *et al.*, 2005b). Notably, trichloroethene (TCE) is considered to be one of the most common hazardous organic contaminants found in groundwater and has been linked to liver damage and impaired pregnancies in humans (Nutt *et al.*, 2006). In addition, halogenated aromatic compounds have become a serious environment contamination problem because they have a long life, are chemically stable and are non-biodegradable (Keum and Li 2004).

Most of the traditional technologies such as solvent extraction, activated carbon adsorption, and common chemical oxidation, whilst effective, very often are costly and time consuming (Schwarzenbach *et al.*, 2006). Biological degradation is environmentally friendly and cost-effective; but it is usually time-consuming (Ahluwalia and Goyal 2007). Thus, the ability to remove toxic contaminants from these environments to a safe level and doing so rapidly, efficiently, and within reasonable costs is important (Savage and Diallo 2005). Nanotechnology could play an important role in this regard. An active emerging area of research is the development of novel nanomaterials with increased affinity, capacity, and selectivity for heavy metals and other contaminants. The benefits from use of nanomaterials may derive from their enhanced reactivity, surface area and sequestration characteristics (Zhang 2003; Li *et al.*, 2006). A variety of nanomaterials are in various stages of research and development, each possessing unique functionalities that is potentially applicable to the remediation of industrial effluents, groundwater, surface water and drinking water (Table 1).

TABLE 1
EXAMPLES OF NANOSTRUCTURED AND NANO-REACTIVE MEMBRANES FOR USE IN WATER FILTRATION

Membrane	Pollutant	Reference
Nanostructured membranes		
Carbon nanotubes	Carbon nanotubes	Srivastava <i>et al.</i> (2004)
Nanoreactive membranes		
Alumina membrane formed from A-alumoxane	Synthetic dyes	DeFriend <i>et al.</i> (2003)
Alumina membranes functionalized with poly(styrene sulfonate) or poly(allylamine hydrochloride)	Divalent cations	Stanton <i>et al.</i> (2003)
Silica and cellulose-based membranes functionalized with amino acid homopolymers	Metal ions	Bhattacharyya <i>et al.</i> (1998)
Polycarbonate track-etched membranes functionalized with amino acid homopolymers	Metal ions	Hollman and Bhattacharaya (2004)
Pt/Fe laden cellulose acetate film	Trichloroethylene (TCE)	Meyer <i>et al.</i> (2004)
Zero-valent Fe laden cellulose acetate membrane	TCE	Wu <i>et al.</i> (2005)
Ni/Fe or Pd/Fe laden polyacrylic acid/polyether sulfone composite membranes	TCE	Xu <i>et al.</i> (2005a)
Ni/Fe laden cellulose acetate membrane	TCE	Wu and Ritchie (2006)
Alumina or polymeric membranes with gold nanoparticles	4-nitrophenol	Dotzauer <i>et al.</i> (2006)
Polymer-impregnated ceramic TiO ₂ filters	Polycyclic aromatic hydrocarbons (PAHs)	Arkas <i>et al.</i> (2006)
Polymer-impregnated ceramic alumina & silicon-carbon filters	Trihalogen methanes, PAHs, pesticide	Allabashi <i>et al.</i> (2007)

3.1 Water remediation with iron nanomaterial

A typical framework that has been created throughout the years to remediate water is known as a 'pump and treat' system (Tratnyek and Johnson, 2006). The system is intended to pump water from the soil to the surface, to deal with it and afterward to infuse it once more into the ground (Fig 1). Until 1998, the pump and treat system was as yet utilized as an approach to remediate water. Another approach to remediate water is by utilizing permeable reactive barrier (PRB). PRB cleans subsurface groundwater and remediate without the need to carry the water to the surface (Fig. 2). This treatment can be utilized to tidy up contaminations, for example, chlorinated hydrocarbons, aromatic nitro compounds, polychlorinated biphenyls (PCBs), pesticides and chromate compounds (Yunus *et al.*, 2012).

The PRB technique (Fig.2), which is expected to replace the pump and treat method, has some disadvantages, such as its cost (it is very expensive) and there is no definite time of replacement. Once in a while the reactivity of iron is reduced due to the presence of impurities in the form of metal hydroxide and metal carbonate compounds. Several alternative methods have been done to overcome these shortcomings. In the early 1990s, it was found that some zero-valent metals such as iron (ZVI), proposed as a filter material of PBR, can handle or diminish perilous contaminants in the water in large quantities (Uyttebroek, *et al.*, 2010). The small particle size makes nano-iron capable of multifunctional use for remediation purposes. In general, ZVI is classified into two types:

- 1) Nnanoscale ZVI (nZVI) and
- 2) Reactive nanoscale iron product (RNIP).

They are made using the fundamental techniques of nanotechnology. nZVI particles have a diameter of 100–200 nm composed of iron (Fe) with a valence of zero, though RNIP particles comprise of 50/50 wt% Fe and Fe₃O₄. Although real application data is not yet produced, the potential use of ZVI is good. Miehr *et al.* (2004) have identified that ZVI has high reactivity to a enormous number of contaminants, including Cu²⁺, chlorinated hydrocarbons, CrO₂²⁻ and NO₃⁻.

Notwithstanding the utilization in PRB, nano-iron can also be used by means of direct injection into the soil, sediment or solid waste. Try to blend the nanoparticles with water to form slurry. Once injected, the particles will remain in the form of a suspension and a treatment zone will be formed. Another way is to attach the nanoparticles to a solid matrix such as activated carbon which has proven very effective.

Nano-iron could be subbed with different metals. Metals, for example zinc and tin have the ability to reduce contaminants such as iron. Two metal alloys such as iron and iron–nickel–copper have been utilized to degrade trichloroethene and trichloroethane (Carroll *et al.*, 2012). The commonly used metals are palladium, silver, platinum, cobalt, copper and gold, while aluminum is used as an inert.

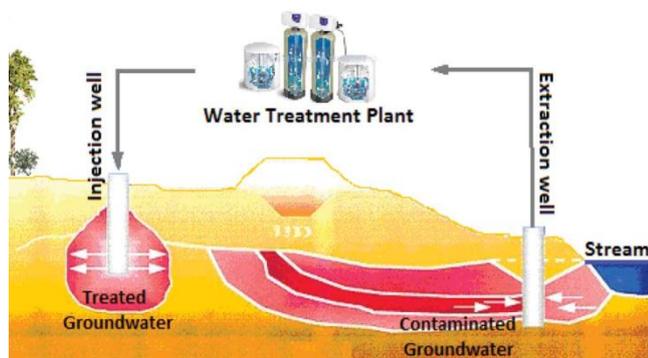


FIGURE 1: Pump and treat system

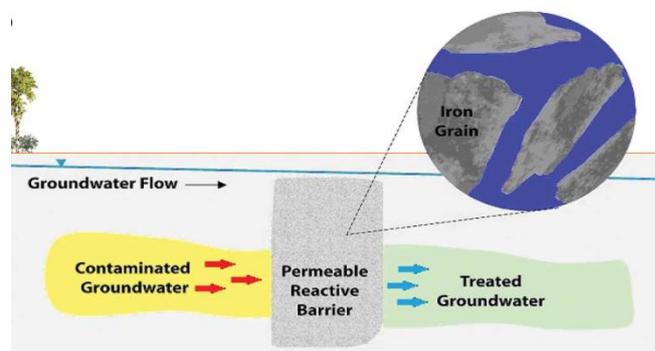


FIGURE 2: Permeable Reactive Barrier

3.2 Water remediation with ferritin

Ferritin is an iron-containing protein that is able of controlling the formation of mineralized structures. Ferritin can be found in animals and plants and its capacity is to store iron. Ferritin is formed when 24 polypeptides that are structurally similar to each other form a cage-like protein structure (Theil, 1987). Once the cage is formed, the iron molecules can enter the cavity through the protein shell, where the mineralization process transforms iron molecules into ferrihydrite nanoparticles.

Researchers have discovered the ability of ferritin to remediate toxic metals and chlorocarbon under visible light or solar radiation (Moretz, 2004). The advantages of ferritin over ordinary iron catalyst are:

- 1) Ferritin does not react under photoreduction; and
- 2) It is also more stable.

One obvious application of ferritin which has been proven in the laboratory is to change chromium Cr(VI) into Cr(III). Cr(VI) is carcinogenic pollutant that is generally contained in the industrial waste, while Cr(III) is formed naturally as a Cr compound, which is less poisonous and insoluble in water.

3.3 Water remediation with polymer nanoparticles

Polymer nanoparticles have different utilization, including water treatment and sunscreen. Using a similar principle as surfactant micelles, polymeric nanoparticles have amphiphilic properties, where every particle has hydrophobic and hydrophilic parts. When water is available, the polymer will form a polymer cell with a diameter of several nanometres inside the hydrophobic part, while the hydrophilic part is outside. On polymer nanoparticles, crosslink occurs prior to the aggregation of particles so that their stability is maintained. Amphiphilic polyurethane (APU) nanoparticles have good prospects as a remediation agent. Tungittiplakorn *et al.* (2004) used a poly urethane acrylate anionomer (UAA) and poly (ethylene glycol) modified urethane acrylate (PMUA) as the reactant/precursor chains.

In the application, polymeric nanoparticles offer a solution for commonly used conventional surfactants to improve remediation of hydrophobic organic contaminants using a pump and treat system. These contaminants are generally classified into nonaqueous-phase liquid which adheres firmly to the ground so that it is difficult to cleanse, leading the remediation process to be less and less effective. In this manner, a surfactant is needed to tidy up these contaminants.

3.4 Water remediation with zeolites

Zeolites are inorganic crystalline porous materials that have a highly ordered structure and are generally comprised of silicon (Si), aluminium (Al), and oxygen (Cambor *et al.*, 1998). Their physicochemical characteristics such as high mechanical and chemical resistance in addition to their high surface area have formed the basis for their widespread use in catalysis, separation, and ion-exchange (Tavolaro *et al.*, 2007). Although conventional synthesis methods produce zeolites on the scale of 1 to 10 μm , nanoscale zeolites, which comprise discrete, uniform crystals with dimensions ranging from 5 to 100 nm, have been synthesized successfully (Ding and Zeng 2007). Compared to micron-scale zeolites, the nanocrystalline

zeolites exhibit greater external surface areas, smaller diffusion path lengths and a greater aversion to coke formation. The Si/Al ratio of zeolites can be varied either during synthesis or post-synthetically and, in general, zeolites have a low Si/Al ratio and therefore a high ion-exchange capacity. Conversely, if the Al content and thus the ion-exchange capacity of a zeolite is reduced, it becomes more hydrophobic or organophilic in its adsorptive characteristics (Tavolaro *et al.*, 2007).

In contrast to nanocrystalline zeolites, micron-scale zeolites have been tested for a variety of environmental applications. NaP1 zeolites, which can be synthesized inexpensively by alkaline hydrothermal activation of coal fly ash in 1–2 M NaOH solutions, have been used successfully to remove heavy metals from acid mine wastewaters (Moreno *et al.*, 2001) and to remove Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II) from metal electroplating wastewaters (Alvarez-Ayuso *et al.*, 2003). Moreover, surfactant-modified zeolites (SMZ) have also been used to not only remediate water containing the radioactive species ^{137}Cs and ^{90}Sr found in nuclear plant wastewater, but also to adsorb both tetrachloroethene and chromate (CrO_2^-) from groundwater, and to remove petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylene from oilfield wastewater (Bowman 2002). In contrast, nanocrystalline zeolites appear to be in the research phase and no specific water remediation processes have been proposed. The synthesis of nanocrystalline NaY zeolites capable of absorbing Ca. 10% more toluene and Ca. 30% more nitrogen dioxide relative to commercial NaY zeolites have, however, been described (Song *et al.* 2005). In addition, nanocrystalline ZSM-5 zeolites, with a particle size of 15 nm, have been reported to adsorb Ca. 50% more toluene than ZSM-5 samples with larger particle sizes (Song *et al.*, 2004), furthermore suggesting that such nanoscale zeolites may be potentially superior to traditional micron-scale zeolite sorbents

3.5 Water remediation with carbon nanotubes

Carbon nanotubes (CNTs) are cylinder-shaped macro- molecules of which the walls of the tubes are made up of a hexagonal lattice of carbon atoms and they are capped at their ends by one half of a fullerene-like molecule (Iijima 1991). CNTs can be divided essentially into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) based on the principle of hybridized carbon atom layers in the walls of CNTs. Whereas SWCNTs have diameters ranging from 0.3 to 3 nm, the MWCNTs are composed of a concentric arrangement of many cylinders and can reach diameters of up to 100 nm (Iijima and Ichihashi 1993). Since their discovery, carbon nanotubes have attracted considerable attention which stems from their outstanding structural, mechanical, and chemical properties (Popov 2004; Miyagawa *et al.* 2005). In addition to their potential application in electronics, chemical and biological sensing, catalysis, and reinforced composite materials (Polizu *et al.*, 2006), their large surface area and tubular structure also make CNTs a promising adsorbent material.

Carbon nanotubes (CNTs) have been evaluated for the sorption of 1, 2-dichlorobenzene (DCB) and it was reported that they can be used in a wide pH range of 3 to 10 and that sorption of DCB onto the CNTs took 40 min to reach equilibrium with a maximum sorption capacity of 30.8 mg/g. More recently, novel sorbents with high surface areas (in excess of $189 \text{ m}^2/\text{g}$) have been developed that consists of cerium oxide supported on either carbon nanotubes (CeO_2 -CNT) (Peng *et al.*, 2005) or on aligned carbon nanotubes (CeO_2 -ACNTs) (Di *et al.*, 2006). Although the CeO_2 -CNTs were effective sorbents for As(V), addition of the divalent cations Ca(II) and Mg(II) at concentrations ranging between 1 and 10 mg/l was reported to increase the amount of sorbed As(V) (from 10 to 82 mg/g) (Peng *et al.*, 2005). The CeO_2 -ACNTs exhibited high Cr(VI) adsorption efficiency from drinking water at a pH range of 3 to 7.4. The largest Cr(VI) adsorption capacity reached was 30.2 mg/g at pH 7.0, which was ca. two times higher than that of activated carbon and Al_2O_3 (Di *et al.*, 2006).

Nanoporous activated carbon fibers (ACFs), prepared by electrospinning of CNTs, with surface areas ranging from 171 to $483 \text{ m}^2/\text{g}$, have been synthesized. Their organic sorption capability was compared to granular activated carbon and in all cases, the ACFs had much higher organic sorption equilibrium constants for benzene, toluene, xylene, and ethylbenzene than granular activated carbon (Mangun *et al.*, 2001)

Multiwalled carbon nanotubes (MWCNTs), pre-treated with nitric acid, have been used successfully for the sorption of different heavy metal ions, including Pb(II) (97.08 mg/g), Cu(II) (24.49 mg/g), and Cd(II) (10.86 mg/g) from an aqueous solution. These sorption capacities were three and four times higher than those of powder and granular activated carbon, respectively (Li *et al.*, 2003).

Salipira *et al.*, (2007) reported that copolymerization of cross-linked nanoporous polymers with functionalized CNTs resulted in novel polymers capable of efficient removal of organic pollutants from water. These novel polymers removed p-nitrophenol by 99% from a 10 mg/l spiked water sample, whereas granular activated carbon removed only 47%. Moreover, these polymers removed trichloroethylene (10 mg/l spiked sample) to non-detectable levels (detection limit <0.01 parts per billion (ppb)) compared to 55% for granular activated carbon.

In addition to their ability to sorb heavy metals and organic compounds, CNTs may also be useful as adsorbents for toxins and herbicides in environmental water. Based on a report by Long and Yang (2001), indicating that significantly higher dioxin removal efficiency is found with CNTs than with activated carbon, MWCNTs have subsequently been used successfully as the sorbent for the preconcentration and separation of chlorophenols and different herbicides, including triazine herbicides, DDT and its metabolites, as well as sulfonyleurea herbicides, from river, tap and lake water samples. The ability of CNTs to adsorb MC-RR and LR, the most prevalent microcystin (MC) toxins produced by cyanobacterial bloom, has also been evaluated. Cyanobacteria blooms in natural waters have become a growing environmental problem worldwide due to the increased discharge of nitrogen- and phosphorus-containing wastewater into rivers and lakes, and MC-RR and LR have been found in fresh water bodies as well as in oceans (Haider *et al.*, 2003). Generally, MCs are very stable in the water body and resistant to removal from drinking water by traditional water treatment technology. Compared to wood-based activated carbon and clays (sepiolite, kaolinite and talc), the adsorption amounts of MCs in lake water by CNTs, of which the outer diameters ranged from 2 to 10 nm, were four times higher (Yan *et al.*, 2006), suggesting that CNTs may be a potentially promising nanomaterial for the removal of MCs from drinking water.

Whilst the above studies indicate that CNTs are potentially efficient adsorbents for a variety of pollutants in both drinking and environmental waters, their practical application may be hampered by their high cost, as well as their poor solubility and the difficulty in collecting them from their dispersing medium. It is therefore interesting to note that in a recent study, Lu *et al.*, (2007) performed statistical analyses on the replacement cost of NaClO-oxidized SWCNTs and MWCNTs, both of which had been reported to be effective Zn(II) sorbents and could be reused through 10 cycles of water treatment and regeneration. The results of their analyses revealed the use of such reusable carbonaceous sorbents can indeed be cost-effective in spite of their high unit cost at the present time. Moreover, Jin *et al.*, (2007) reported a simple method for fabricating magnetic Fe nanoparticle functionalized MWCNTs, which not only displayed improved water solubility, but could also be recovered easily from the water by magnetic separation. The functionalized water-soluble MWC-NTs (Fe-MWCNT-CH₂COONa) were also tested as a sorbent using four model aromatic compounds. The results indicated that addition of 10 mg of Fe-MWCNT-CH₂COONa to aqueous solutions containing 8.6 ppb of the corresponding model compound, adsorbed benzene (79%), toluene (81%), dimethylbenzene (83%), and styrene (88%) very effectively. Notably, after being washed several times with methanol and dried in vacuum, the Fe-MWCNT-CH₂COONa could be reused.

IV. CONCLUSION

Water plays a role in day to day of human activity, it is becoming an increasingly scarce resource in many parts of the world. Besides utilization of non-traditional sources for production of high-quality freshwater and the conservation and protection of water bodies from pollution, equally important is the development of innovative new technologies and materials whereby challenges associated with the provision of safe potable water can be addressed. It is widely recognized that nanotechnology and its applications play an important role in resolving issues relating to water shortage and water quality. Due to large surface areas of nano particles, size and shape dependent catalytic properties, significant efforts are started to explore uses of nanomaterials in applications such as membrane separations, catalysis and adsorption. In addition, nanomaterials can be functionalized with different chemical groups to increase their attraction toward a given compound, thus resulting in ligands that are not only recyclable but also have a high capacity and selectivity for organic and inorganic solutes, just as lethal metal ions and inorganic anions in aqueous solutions.

While much consideration has been focused on the development and potential benefits of nanomaterials in water treatment processes, concerns have also been raised regarding their potential human and environmental toxicity. Undoubtedly, contemplates have demonstrated that the similar properties of nanomaterials that make them alluring (e.g., size, shape, structure, reactivity) may likewise make them be lethal. It is difficult, however, to assess the effect of nanomaterials on health and the environment because the methods and tools for such a task have not been well developed yet. In addition, common frameworks for risk research, risk assessment, and risk management are lacking at present. It is vital that these processes be developed and investigated to ensure that nanomaterials are as safe as possible, while reaching their full potential. Despite these information gaps, it is sure that new nanomaterials, particularly in water and wastewater treatment, will play key roles in guaranteeing adequate and good quality water to satisfy the ever-increasing need for consumable water.

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