Affordable and Clean Drinking Water Using Nanomaterials

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Abstract

Realizing the molecular nature of contaminants in drinking water and the need to remove them at ultra trace levels, significant progress has been made in the recent past to utilize nanomaterials for water purification. This article summarizes our recent efforts to understand the chemistry of nanoscale materials for the purification of drinking water. The application of metal/metal oxide nanoparticles/graphene-based chemistry for drinking water purification can be summarized for three major types of contaminants: halogenated organics including pesticides, heavy metals such as arsenic and microorganisms. We were the first to introduce a nanomaterials-based purifier for drinking water to tackle pesticide contamination. Recent efforts for the removal, as well as ultralow concentration detection of such species, using a variety of nanostructures will be summarized. There are several materials emerging in the recent past and their chemistry may also be utilized for this application.

Keywords : Water purification, Nanomaterials, Graphene, Heavy metals, Sensors

1. Introduction

Water is absolutely necessary for life on earth. All living organisms require water for their creation, survival and evolution. Increased disposal of industrial, domestic and agricultural waste into water bodies and consequent pollution of water has become a major issue in the 21st century. Water, being a universal solvent
dissolves all kinds of contaminants like, metal ions, inorganic anions, organic dyes, pesticides and insecticides, radioactive elements, etc. Therefore, great challenges lie in the removal of contaminants from drinking water at ultra-trace levels at affordable cost.

Different techniques such as, adsorption, membrane filtration, ion exchange, capacitive deionization, etc. have evolved in the recent past. Among these technologies, adsorption has proved to be economical and efficient in removing targeted pollution from water in large scale. Nanomaterials due to large surface area, easy surface modification and selective catalytic activity turned out to be an effective adsorbent for water purification.

In this article, authors focus on the use of noble metal nanoparticles and graphene for the purification of water. From published literature of our group, we have chosen several areas of activity such as, 1) Removal of toxic metal ions by physical adsorption, 2) Removal or degradation of organic pollutants either to less toxic or non-toxic end products and 3) Detection/sensing of toxic contaminants.

2. Results and Discussion

According to the recent regulations by several bodies such as Environmental Protection Agency (EPA), World Health Organization (WHO) and European Union (EU), various toxic materials are regulated in drinking water\(^1\). It can be seen that most of the hazardous materials are halogenated compounds and next in the list are metals as shown in Fig. 1. Concentrations at which these materials become hazardous are very small and there is a need to create new technologies to remove them efficiently at room temperature.
Fig. 1 Contaminants regulated and likely to be regulated by US EPA. 

- Halogenated organics
- Metals
- Organochlorine pesticides
- Inorganic salts
- Biological contaminants
- Nuclear
- Benzo derivatives
- Carbamate pesticides
- Unclassified
- Triazine derivative pesticides
- Organophosphorus pesticides
- Organobromine pesticide
- Non-metals
- Nitrophenol derivatives
- Dioxin
- Benzo and halogenated organics
- Organometallics

Adapted with permission from Reference 1.

2.1 Removal of Toxic Metal ions by Noble Metal Nanoparticles

Nanomaterials due to their large surface area (generally attributed due to its large surface to volume ratio) and easy chemical modification of their surfaces turned out to be excellent adsorbents for diverse contaminants. They can also undergo chemical processes such as catalysis or alloying. Here, we are going to discuss noble metal nanoparticles and graphene for uptake of different metal ions from drinking water. Metal ions such as arsenic, mercury and lead are very toxic for human health even at ultra-low concentrations. According to WHO, the minimum contaminant level for arsenic, mercury and lead are 10, 2 and 15 ppb, respectively. Lisha et.al. in 2009 reported that gold nanoparticles (AuNPs) supported over alumina can effectively
remove Hg$^{2+}$ from drinking water$^2$. The adsorption capacity was about 10 times more than the previously reported adsorbents. Bhootaraju and Pradeep in 2010 reported the uptake of toxic metals like mercury, lead and cadmium from drinking water using naked or monolayer protected silver nanoparticles (AgNPs)$^3$. Sumesh et.al. immobilized AgNPs over alumina and used the material as a potent adsorbent for mercury ions, showing an adsorption capacity of 0.8 g/g of silver$^4$. Later, Shankar et. al. in 2013, developed a novel strategy to synthesize silver nanoparticles based aluminium oxyhydroxide-chitosan composite and used it in the form of a water purifier$^5$. Variations of this composite can remove toxic metal ions like arsenic and lead from water. Another composite structure can have a continuous supply of silver ions into water which promises to provide microbially safe drinking water at affordable cost. Fig. 2 shows the mechanistic pathway for

**Fig. 2** a Mechanism showing the strategy used for the preparation of nano-composites. The process of preparing aluminium oxyhydroxide with a biological template is shown, b Photographs showing the stability of aluminium hydroxide-based gel at pH 6 but settles down at pH 7 and 8, c Photographs of the composite granules showing that the material is stable in water and d TEM image showing a network-like structure of the composite along with silver nanoparticles. Reprinted with permission from Reference 5.
the preparation of the composite and its detailed characterization. One of the important aspects of the synthesis of this composite is that it is made in water at room temperature, but the composite is as stable as sand. Sreeprasad et al. in 2011, first showed a strategy to immobilize graphene over river sand which effectively removes metal ions like mercury from drinking water at low cost.

2.2 Removal or Degradation of Organic Pollutants

Removal of organic contaminants like pesticides and dyes is necessary due to their toxic effects on human body. Pesticides due to their toxicity can affect human nervous, cardiovascular, respiratory and reproductive systems even in low concentrations. Nair and Pradeep discovered noble metal nanoparticle-based halocarbon degradation and pesticide destruction in 2003 and developed the world’s first nanochemistry-based water filter in 2007 which can effectively remove pesticides like malathion and chlorpyrifos from drinking water. The chemistry involved is reductive dehalogenation in the case of halocarbon pesticides. Jain and Pradeep in 2005 reported the antibacterial property of supported AgNps and used it as an potential water filter. Bhootaraju and Pradeep in 2012 studied the mechanistic pathway for the degradation of pesticides (chlorpyrifos) to less toxic by-products using AgNps, shown in Fig. 3. The application of AgNps for the degradation of other chlorocarbons like CCl₄, C₆H₅CH₂Cl and CHCl₃ was also reported in 2013. In the recent past, graphene has emerged as a potent adsorbent for organic moieties. Sreeprasad et al. in 2011 reported the antibacterial property of graphene and graphene oxide which hints at the applicability of RGO/GO towards water purification. Shihabudheen et al. in 2012 showed that graphene can remove pesticides like chlorpyrifos, malathion and endosulphan from water. The adsorption capacity was very high, even more than the self weight of graphene. Recently, Sen Gupta and Sreeprasad et al. developed a cost effective and green methodologies for the preparation of graphene...
from sugar and asphalt\textsuperscript{14,15}. They immobilized graphene over river sand without any binder and applied the material for water purification. The material showed high adsorption capacity for Rhodamine 6G (R6G), a rhodamine dye and chlorpyrifos. The strong adsorption capacity of the material is clear from the fact that it can even decolorize commercial soft drinks like coca-cola. Fig. 4 shows the photographs of removal of R6G and coca-cola using graphene sand composite (GSC).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Mechanistic pathway showing the degradation of chlorpyrifos by silver nanoparticles to less toxic 3,5,6-trichloro-2-pyridinol (TCP) and diethyl thiophosphate (DETP). Reprinted with permission from Reference 9.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Photographs of GSC column bed for removal of (A) R6G and (B) coca cola. Adapted with permission from Reference 13.}
\end{figure}
2.3 Detection of Toxic Contaminants

Besides removal, detection of particular contaminants in drinking water is also necessary. There is a need for selective sensors for the detection of specific contaminants in water. Sensitivity of metal ions to clusters was shown in 2007 by Muhammed et. al. Again in 2010, Muhammed and Pradeep detected copper ion from water with luminescent Au quantum clusters. This quantum cluster showed a turn-off luminescence for \( \text{Cu}^{2+} \) and turn-on luminescence for glutathione \(^{17}\). Chakraborty et. al in 2012 sensed 5d block metal ions such as, \( \text{Pt}^{2+}, \text{Au}^{3+} \) and \( \text{Hg}^{2+} \) with \( \text{Ag}_{25} \) clusters at a low concentration of 1 ppb \(^{18}\). George et. al. in 2012 reported luminescent, freestanding \( \text{Au}_{15} \) film which can detect toxic metal ions such as \( \text{Hg}^{2+}, \text{As}^{3+}, \text{As}^{5+} \) and \( \text{Cu}^{2+} \). Mathew et. al. in the same year made a breakthrough by detecting trinitrotoluene (TNT) at sub-zeptomolar level by the hybrid structures, \( \text{Au}@\text{SiO}_2@\text{Ag}_{15} \). They anchored \( \text{Ag}_{15} \) cluster protected with bovine serum albumin (BSA) over silica coated Au mesoflower and termed the composite as \( \text{Au}@\text{SiO}_2@\text{Ag}_{15} \) MF. This composite was effective in detecting TNT in very low concentrations; metal enhanced luminescence from one mesoflower is quenched by just 9 molecules of TNT and a few ions of mercury.

3. Conclusion

Authors have introduced noble metal nanoparticles and graphene based composites for the purification of water. This article summarizes some of our recent efforts in understanding the chemistry of nanoscale materials for the purification of drinking water at affordable cost. The application of metal/metal oxide nanoparticles/graphene-based chemistry for drinking water purification can be summarized for three major types of contaminants: halogenated organics including pesticides, heavy metals like arsenic and microorganisms. There are several
materials emerging in the recent past and their chemistry may also be utilized for this application at affordable cost.

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**References**


