Environ Chem Lett (2017) 15:23–27
DOI 10.1007/s10311-016-0595-x

REVIEW

Nanomaterials for water pollution monitoring and remediation

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Received: 31 October 2016 / Accepted: 2 November 2016 / Published online: 16 November 2016

Abstract Water shortage and pollution are serious challenges for many countries. Nanomaterials are promising new tools for water quality management due to unique physicochemical properties, high economic benefit, high removal efficiency and environmental friendliness. Here we describe four types of nanomaterials used for water treatment: nanofiltration membranes, photocatalytic nanomaterials, adsorption nanomaterials and reducing nanomaterials. We discuss their properties, applications and mechanisms for pollutant removal. We also review nanomaterials used for water quality monitoring, notably nanomaterials used for the detection of trace pollutants and pathogens. These nanomaterials include carbon nanotubes, magnetic nanoparticles, noble metal nanomaterials and quantum dots.

Keywords Nanomaterials · Water treatment · Wastewater treatment · Monitoring

Introduction

Rapid development of economy, heavy application of chemicals and imperfection of water management policies resulted in a series of water problems including water shortage and pollution (Savage and Diallo 2005). Conventional water and wastewater treatment technologies such as adsorption, precipitation, coagulation and activated sludge processes have many drawbacks including low treatment efficiency, high cost and secondary pollution. Due to their unique physicochemical properties, economic benefit, efficiency and environmental friendliness, much attention has been paid to nanomaterials in water quality management recently (Fig. 1).

So far, many relative reviews on nanomaterials in water monitoring and treatment have been reported. Andreescu et al. (2009) reviewed the application of advanced nanomaterials in environmental monitoring; Qu et al. (2013) reviewed the performance of nanomaterials in water and wastewater treatment; Bystrzejewska-Piotrowska et al. (2009) reviewed the application of nanoparticles in environmental management. However, a comprehensive view on nanomaterials in water quality management is still lacking.

Here we present four types of nanomaterials for water and wastewater treatment: nanofiltration membranes, nano-photocatalytic materials, nano-adsorption materials and nano-reducing materials. And the nanomaterials used for water quality monitoring are also discussed, including carbon nanotubes, magnetic nanoparticles, noble metal nanomaterials and quantum dots. They are widely used in the detection of the extremely low concentration organic pollutants, inorganic pollutants and pathogens. This review is an abridged version of the chapter published by Xue et al. (2016).

Application of nanomaterials in water and wastewater treatment

Nanofiltration membranes

The nanofiltration membrane is a type of semipermeable membrane, which allows solvent molecules or some low

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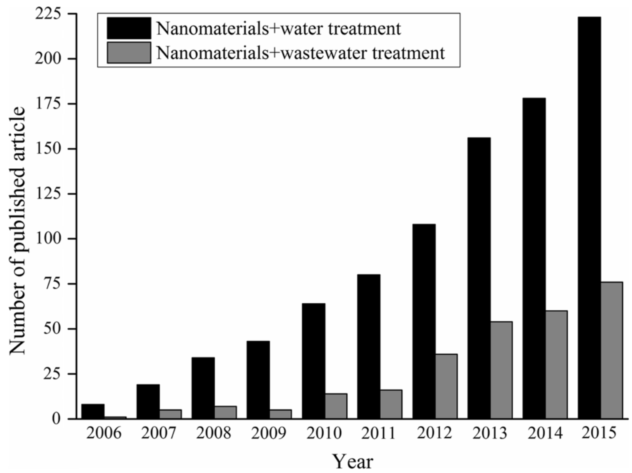

Fig. 1 Number of articles published on the subjects of "nanomaterials + water treatment" and "nanomaterials + wastewater treatment" from 2006 to 2015

molecular weight solutes or low ion permeation. Nanofiltration membranes could be used in the treatment of surface water, ground water and wastewater. The most common application field of nanofiltration membranes is the softening of water (Fang et al. 2013). Apart from the purpose to remove turbidity, hardness, fluorides, disinfection by-products and pesticides, recent studies have reported that nanofiltration has also being used for the removal of arsenic and emerging contaminants such as pharmaceuticals, hormones and personal care products (Mohammad et al. 2015; Schäfer et al. 2011; Sen et al. 2010). However, studies on the removal of the pharmaceutical active compounds from drinking water and surface water by nanofiltration membranes are relatively scarce so far (Verliefde et al. 2007).

Membrane fouling is still a great limitation in the application of nanofiltration membranes. Membrane fouling can lead to some adverse effects such as flux decline, cost increase and membrane degradation. Currently, some measures could be taken to control membrane fouling such as feed pretreatment, membrane surface modification, physical cleaning and chemical cleaning (Mohammad et al. 2015).

Photocatalytic nanomaterials

Up to now, $nTiO_2$, nZnO, nWO_3, $nBiVO_4$ and nAl_2O_3 are widely used nanomaterials in photocatalysis. Among them, $nTiO_2$ is the most commonly used nanomaterial in water and wastewater treatment due to its high reactivity, thermal stability and abundance as the raw material (Gupta and Tripathi 2011).

As reported, $nTiO_2$ has been successfully applied for the organic wastewater treatment, including dye wastewater (Nagaveni et al. 2004), chemical industry wastewater, pesticide wastewater, oily wastewater (Yang et al. 2012); inorganic wastewater treatment and microbial control (Kwon et al. 2008; Qu et al. 2013). However, $nTiO_2$ still has some drawbacks including low absorb efficiency of visible light and low recycle rate. In order to overcome above-mentioned drawbacks, several approaches have been studied to modify $nTiO_2$, including dye sensitization, doping, coupling and capping (Gupta and Tripathi 2011).

Adsorption nanomaterials

Carbon-based nano-adsorbents

Carbon nanotubes including single-walled carbon nanotubes and multi-walled carbon nanotubes are good adsorption materials for the remove of organics and heavy metals including Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} (Rao et al. 2007; Pyrzyńska and Bystrzejewski 2010). Su and Lu (2007) reported that the adsorption capacity of carbon nanotubes on natural dissolved organic matters (11.61 $mg \cdot g^{-1}$) was higher than that of granular activated carbon (3.55 $mg \cdot g^{-1}$), and the average weight loss of the carbon nanotubes (2.65%) was lower than that of granular activated carbon (6.40%). In aqueous environment, carbon nanotubes strongly adsorb low molecular weight polar organic compounds due to the organic compounds–carbon nanotubes interactions including hydrophobic effect, π–π interactions, hydrogen bonding and electrostatic interactions (Pan and Xing 2008; Qu et al. 2013).

Regeneration is a key factor determining the cost-effectiveness of carbon nanotubes. Lu et al. (2006) reported that the adsorbed Zn^{2+} on single-walled carbon nanotubes and multi-walled carbon nanotubes can be reversed by 0.1 $mol \cdot L^{-1}$ nitric acid solutions and the adsorption capacity was maintained after ten cycles of regeneration and reuse. It suggested that carbon nanotubes could be regenerated by reducing the solution pH value. And the adsorption capacity of carbon nanotubes was not much fluctuant after several cycles of adsorption/desorption reaction.

Metal-based nano-adsorbents

nFe_3O_4, n-γFe_2O_3 and n-αFe_2O_3 are the most common three kinds of iron oxide nanomaterials in water and wastewater treatment. Iron oxide nanomaterials could adsorb a variety of heavy metals (e.g., Pb^{2+}, Cu^{2+} and Zn^{2+}) (Huang and Chen 2009; White et al. 2009); organic pollutants (e.g., red dye, 1-naphthylamine, polycyclic aromatic hydrocarbons) (Iram et al. 2010; Hu et al. 2011; Zhang et al. 2010) and radionuclides (Qu et al. 2013). However, the adsorption of heavy metal onto iron oxide nanomaterials is still at the laboratory scale (Xu et al. 2012).

Other than iron oxide nanoparticle, $nTiO_2$, nZnO and nAl_2O_3 were also effective adsorbents for the removal of heavy metals, metallic pollutants and radionuclides (Hua et al. 2012). Similar to carbon nanotubes, metal oxide nano-adsorbents could also be regenerated by changing solution pH (Sharma et al. 2009), and then the adsorption capacity remained relatively stable (Hu et al. 2006). However, opposite results were also reported. Deliyanni et al. (2003) reported that adsorption of As^{5+} on akaganéite-type nanocrystals can be reversed, but the adsorption capacity would reduce about 25 ~ 30% after each cycles of the regeneration and reuse. So akaganéite-type nanocrystals must be replaced after 2 ~ 4 cycles of regenerations.

Reducing nanomaterials

As a kind of effective reductant for pollutants removal in water, nanoscale zero-valent metals have attracted much attention science 1980s. Iron is a metal with standard redox potential of −0.44 V ($E^0 = -0.44$ V). It is thus an effective reductant when reacting with oxidized contaminants in water. Now nanoscale zero-valent iron (nZVI) has been successfully applied for the treatment of water and wastewater contaminated with chlorinated organic compounds (Arnold et al. 2002), heavy metals, including chromium (Scott et al. 2011), cadmium (Scott et al. 2011), copper (Li and Zhang 2007), silver (Li and Zhang 2007), zinc (Li and Zhang 2007; Klimkova et al. 2011), dyes (Lin et al. 2008) and phenol (Liu et al. 2005). Li and Zhang (2007) reported that the removal efficiency of eight metal ions including Cd^{2+}, Ni^{2+}, Zn^{2+}, Cr^{6+}, Cu^{2+}, Pb^{2+} and Ag^{+} with nZVI is 36.5, 71.0, 92.5, 97.5, 99.7, 99.7 and 99.8%. Due to the significant variation in contaminant chemistry, numerous possible contaminant removal pathways have been performed, including sorption, complexation, (co)precipitation and surface-mediated chemical reduction. In the study performed by Li and Zhang (2007), as for metals whose standard potential E^0 are very close to or more negative than that of iron, such as Zn^{2+} and Cd^{2+}, the removal mechanism for metals is sorption and surface complexation. As for metals whose E^0 are greatly more positive than that of iron, such as Cu^{2+}, Ag^{+} and Hg^{2+}, the removal mechanism is predominantly reduction. As for metals whose E^0 are slightly more positive than that of iron, such as Ni^{2+} and Pb^{2+}, they can be immobilized at the surface of nZVI by both of sorption and reduction.

Applications of nanomaterials for water quality monitoring

Water quality monitoring is of importance to pollution sources control, water quality management and public health. Previous studies showed that nanomaterials could be used in the detection of organic pollutants, inorganic pollutants and pathogen, including magnetic nanoparticles, carbon nanotubes, noble metal nanomaterials and quantum dots.

Pathogens detection in water is vital for human health. Nanomaterial-enabled pathogens sensors consist of recognition agents, nanomaterials and a signal transduction mechanism. Among the three components, nanomaterials are used to improve the detection sensitivity and response of pathogens due to their unique properties such as optical, electrochemical and magnetic properties. Hahn et al. (2005) used functionalized quantum dots to detect single cells of Escherichia coli O157: H7 serotype, the results showed that quantum dots were superior to traditional fluorescent dyes in terms of sensitivity and stability.

Nanomaterials can also be used in the detection of organic and inorganic pollutants. Nano-Au could detect chlorpyrifos and malathion at per billion levels from surface water (Lisha and Anshup 2009a, b). Lysozyme type VI-stabilized gold nanoclusters was used to detect Hg^{2+} and CH_3Hg^{+} (Lin and Tseng 2010), and the limits of detection for Hg^{2+} and CH_3Hg^{+} were estimated to be 3 pM and 4 nM.

Magnetic nanomaterials and carbon nanotubes have been applied for sample concentration and purification. Magnetic nanocomposite can be used to develop pathogen detection kits. Although carbon nanotubes performed the excellent sensitivity, heterogeneity is a great challenge. The carbon nanotubes production and purification processes often introduce contaminants and impurities, and even the carbon nanotubes structure degradation. Hence, it is necessary to produce homogeneous carbon nanotubes.

Challenges of applying nanomaterials in water quality management

Although nanomaterials have shown great potentials in water and wastewater treatment and monitoring cost-effectiveness and technical obstacles are still challenges for their development and commercialization. The cost of nanomaterials is relatively high. Many laboratory studies have evaluated the performance of nanoscale zero-valent iron for removing various pollutants. However, the research on the long-term performance of nanomaterials for real water and wastewater treatment is still limited. In addition, potential risk of nanomaterials is another challenge for their widespread application. The environmental behavior and possible environmental effects of nanomaterials are still unknown. Human health risk assessment and ecological risk assessment of nanomaterials are limited (Moore 2006). Relevant laws and regulations were still lacking. Hence, more studies about nanotoxicology and nano-ecotoxicology need to be done.

Conclusion

The application of nanomaterials in water quality management has received wide attention due to their unique electrical, mechanical, catalytic, optical, magnetic and photonic properties. Nanofiltration membranes could be used in the production of potable water and the removal of metals, disinfection by-products, pesticides and emerging contaminants from contaminated water. As a classic photocatalyst, $nTiO_2$ shows excellent performance in the treatment of water and wastewater, especially dye wastewater and paper mill wastewater. Carbon nanotubes, iron oxides nanomaterials and $nTiO_2$ have shown high adsorption capacities. And nZVI could be used to remove heavy metals and organic pollutants by reduction or oxidation. However, there are still some drawbacks in the application of nanomaterials, including membrane fouling of nanofiltration membranes, low absorption efficiency of visible light of $nTiO_2$, regeneration of carbon nanotubes and the dispersity of nZVI. In addition, nanomaterials, such as carbon nanotubes, magnetic nanoparticles, noble metal nanomaterials and quantum dots, could be used for water quality monitoring, especially for the detection of the extremely low concentration organic pollutants, inorganic pollutants and pathogens. In a word, nanomaterials have received extensive attention in water pollution remediation and monitoring. However, there are still some problems to be studied and solved, including cost-effectiveness, technical obstacles and potential risk of nanomaterials.

Acknowledgements This work was supported by the Fundamental Research Funds for the Central Universities, and the Research Funds of Renmin University of China (Grant No. 11XNK016), which are greatly acknowledged.

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