# **Chapter 6 Nanomaterials for Monitoring and Remediation of Water Pollution**

Xing-yan Xue, Rong Cheng, Lei Shi, Zhong Ma, and Xiang Zheng

**Abstract** Water shortage and pollution are now serious challenges for many countries. Nanomaterials are promising new tools for water quality management due to their unique physicochemical properties, high economic benefit, high removal efficiency and environmental friendliness. Here we present four types of nanomaterials for water and wastewater treatment: nanofiltration membranes, nano-photocatalytic materials, nano-adsorption materials and nano-reducing materials. We discuss their properties, application scope and mechanism of pollutant removal. We also review nanomaterials used for water quality monitoring, especially for the detection of the extremely low concentration organic pollutants, inorganic pollutants and pathogens. Such nanomaterials include carbon nanotubes, magnetic nanoparticles, noble metal nanomaterials and quantum dots.

Keywords Nanomaterials • Water treatment • Wastewater treatment • Monitoring

# 6.1 Introduction

Water is the source of life. Rapid development of economy, heavy application of chemicals and imperfection of water management policy resulted in a series of water problems. Currently, Water shortage and pollution are the two major problems in both developing and developed countries. Water shortage and pollution are influenced by many factors such as human activities, population growth, users demand and global climate change (Savage and Diallo 2005). Polluted waters usually contain suspended matter, heavy metal, organic matter, bacteria, virus and many other complex compounds. Conventional water and wastewater treatment technologies such as adsorption, precipitation, coagulation and activated sludge process have many drawbacks such as low treatment efficiency, high cost and

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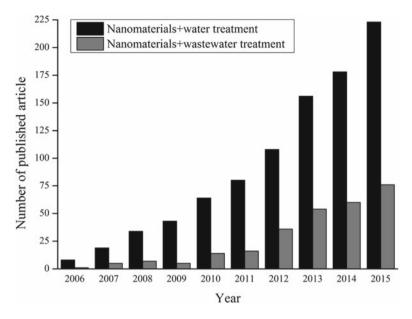


Fig. 6.1 Number of article published on the subjects of "nanomaterials+water treatment" and "nanomaterials+wastewater treatment" from 2006 to 2015

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. 6.1). Nanomaterials could remove many kinds of pollutants in water and wastewater treatment including refractory matters, organic matters and heavy metals.

Nanotechnology is related to the preparation of materials small than 100 nm in size. Several kinds of nanomaterials, such as iron-based nanomaterials, carbon-based nanomaterials and  $nTiO_2$ , have been widely studied in water quality management. These nanomaterials possess effective detection, adsorption and removal/degradation capacity to pollutants in water and wastewater. For example, nanoscale zero-valent iron has been proven to remove/degrade pollutants effectively including dyes (Fan et al. 2009), chlorinated solvents (Wang and Zhang 1997), pesticides (Elliott et al. 2009), lead (Ponder et al. 2001; Li and Zhang 2007) and cadmium (Li and Zhang 2007). Nano-Au can sensitively detected chlorpyrifos, malathion (Lisha et al. 2009), Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>+</sup> (Lin and Tseng 2010).

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; Liu et al. (2014) reviewed the application of nanomaterials for monitoring emerging chemical pollutants; 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. In this paper, an overview of recent advances in nanomaterials for water pollution remediation and monitoring were presented. Nanomaterials could be used in the treatment of surface water, ground water and wastewater. Nanofiltration membrane, nano-photocatalytic materials, nano-adsorption materials and nano-reducing materials could remove turbidity, hardness, heavy metal, organic matters and inorganic ions. Besides, nanomaterials including magnetic nanoparticles, carbon nanotubes and noble metal nanomaterials could be used in water quality monitoring. However, cost-effectiveness, technical hurdles and potential risk of nanomaterials are still challenges for their widespread application. Hence, more studies about nanomatrials in water pollution remediation and monitoring need to be done.

# 6.2 Application of Nanomaterials in Water and Wastewater Treatment

Nanomaterials are the materials which sized below 100 nm at least one dimension. Nanomaterials possess unique properties such as mechanical, electrical, optical, catalytic, magnetic and photonic properties in comparison to common materials. Based on the properties of nanomaterials and the removal principle of pollutants, nanomaterials in water and wastewater treatment can be classified as nanofiltration membrane, nano-photocatalytic materials, nano-adsorption materials and nano-reducing materials. Considering the kinds of pollutants, increasing production and usage of nanomaterials offer opportunities for the removal of various pollutants, which was listed in Table 6.1.

### 6.2.1 Nanofiltration Membranes

A nanofiltration membrane is a type of semipermeable membrane, which allows solvent molecules or some low molecular weight solutes or low ion permeation. Nanofiltration membranes possess pore size generally of 1-2 nm, molecular weight cut-off of 300–500 Da, water permeability of 5-50 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> and Operating pressure typically of 2-10 bar. Recently, the application of nanofiltration membrane has received wide attention due to its high flux, low investment, low operation pressure and cost. Cellulose acetate, polyamide, polyvinyl alcohol and sulfonated polysulfone can be used to form nanofiltration membrane (Savage and Diallo 2005; Cheng et al. 2011). Nanofiltration membrane could be used in the treatment of surface water, ground water and wastewater. 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 (Table 6.2) (Mohammad et al. 2015). However, studies on the removal of the

| Pollutants           | Examples                                                                                                                                                                                                                            | References                                                                                        |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| Heavy metal ions     | Pb <sup>2+</sup> ; Hg <sup>2+</sup> ; Ni <sup>2+</sup> ; Ag <sup>+</sup> ; Cd <sup>2+</sup> ; Cu <sup>2+</sup> ; Ni <sup>2+</sup> ; Zn <sup>2+</sup> ;<br>Ca <sup>2+</sup> ; Mg <sup>2+</sup> ; As <sup>3+</sup> ; As <sup>5+</sup> | Chang et al. (2014),<br>Maher et al. (2014),<br>Aarthi and Madras<br>(2008)                       |
| Organic dyes         | Orange II; Chrysoidine; Tropaeolin O; Acid<br>Orange; Acid Red                                                                                                                                                                      | Shu et al. (2010),<br>Chen et al. (2011),<br>Frost et al. (2010),<br>Lin et al. (2008)            |
| Chlorinated benzenes | Hexachlorobenzene; Pentachlorobenzene;<br>Tetrachlorobenzenes; Trichlorobenzenes;<br>Dichlorobenzenes; Chlorobenzene                                                                                                                | Shih et al. (2011),<br>Fan et al. (2011)                                                          |
| Trihalomethanes      | Bromoform; Dibromochloromethane;<br>Dichlorobromomethane                                                                                                                                                                            | Lien (2005)                                                                                       |
| Chlorinated ethenes  | Tetrachloroethene; Trichloroethene; <i>cis</i> -<br>Dichloroethene; <i>trans</i> -Dichloroethene;<br>1,1-Dichloroethene; Vinyl chloride                                                                                             | Lien and Zhang (2001)                                                                             |
| Inorganic anions     | Dichromate; Arsenic; Perchlorate; Nitrate                                                                                                                                                                                           | Jiang et al. (2011),<br>Zhang et al. (2011),<br>Harisha et al.<br>(2010)                          |
| Pesticides           | Dichlorodiphenyltrichloroethane; Lindane; chlorpyriphos; pyrethroid; malathion                                                                                                                                                      | Joo and Zhao<br>(2008), Shih et al.<br>(2011), El-Sheikh<br>et al. (2008), Parra<br>et al. (2002) |
| Microorganism        | Escherichia coli; Pseudomonas fluorescens;<br>Aspergillus versicolor; poliovirus 1; hepatitis B<br>virus; Herpes simplex virus; MS2 bacteriophage                                                                                   | Lee et al. (2008),<br>Liga et al. (2011)                                                          |
| Others               | Polychlorinated biphenyls; 2,4,6-Trinitrotoluene;<br>Hormones                                                                                                                                                                       | Mohammad et al. (2015)                                                                            |

 Table 6.1 Common pollutants that can be removed by nanomaterials

pharmaceutical active compounds from drinking water and surface water by nanofiltration membranes are relatively scarce so far (Radjenović et al. 2008; Verliefde et al. 2007).

The most common application field of nanofiltration membrane is the softening of water. Fang et al. (2013) developed new composite nanofiltration hollow fiber membranes for surface water softening, the results showed that the new hollow fiber membranes rejections for  $Ca^{2+}$  and  $Mg^{2+}$  were 90% while test for 3000 ppm total dissolved salt feed stream at 2 bar pressure, suggesting that the composite nanofiltration hollow fiber membranes could be effectively applied to surface water softening.

Numerous researches have proved that nanofiltration membrane showed an excellent performance on the remove of pesticides (Van der Bruggen et al. 2001; Van der Bruggen and Vandecasteele 2003). The removal efficiencies of pesticides with nanofiltration membrane were affected by pesticides, types of nanofiltration

|                  |                                                 | Transmembrane                       |       |                                                                                                                                                                                                   |                            |
|------------------|-------------------------------------------------|-------------------------------------|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| Pollutants       | Initial concentration                           | pressures                           | рН    | Removal efficiency                                                                                                                                                                                | References                 |
| $AS^{3+}$        | $100 \ \mu g \ L^{-1}$                          | 0.55 MPa                            | 9-10  | 40 %                                                                                                                                                                                              | Chang et al. (2014)        |
| $Ni^{2+}$        | 1 ppm                                           | 6 bar                               | 5.5   | 93 %                                                                                                                                                                                              | Maher et al. (2014)        |
| $Pb^{2+}$        | 1 ppm                                           | 5.8 bar                             | 5.5   | 86%                                                                                                                                                                                               | Maher et al. (2014)        |
| $Mg^{2+}$        | 200 ppm                                         | 5 bar                               | /     | 95.20 %                                                                                                                                                                                           | Zhong et al. (2012)        |
| $Mg^{2+}$        | 51-128 ppm                                      | 2 bar                               | 11    | More than 90%                                                                                                                                                                                     | Fang et al. (2013)         |
| $Ca^{2+}$        | 128 ppm                                         | 2 bar                               | 11    | 88%                                                                                                                                                                                               | Fang et al. (2013)         |
| Arsenic          | 0.0005 M                                        | 50 bar                              | 8     | 98.98%                                                                                                                                                                                            | Harisha et al. (2010)      |
| Fluoride         | 20 ppm                                          | $14 \text{ kgf cm}^{-2}$            | 10.01 | More than 98%                                                                                                                                                                                     | Chakrabortty et al. (2013) |
| Orange II        | 50 ppm                                          | 5 bar                               | /     | 86.76%                                                                                                                                                                                            | Zhong et al. (2012)        |
| Safranin O       | 50 ppm                                          | 5 bar                               | /     | 99.98 %                                                                                                                                                                                           | Zhong et al. (2012)        |
| Trichlorethylene | 400 μg/L                                        | 15 bar                              | /     | 92 %                                                                                                                                                                                              | Ducom and Cabassud (1999)  |
| Chlorpethylene   | 400 μg/L                                        | 15 bar                              | /     | 96 %                                                                                                                                                                                              | Ducom and Cabassud (1999)  |
| Chloroform       | 200 μg/L                                        | 10 bar                              | /     | 79 %                                                                                                                                                                                              | Ducom and Cabassud (1999)  |
| Phenol           | $50-200 \times 10^{-3} \times \text{kg m}^{-3}$ | $6*10^6 \mathrm{N} \mathrm{m}^{-2}$ | 2-11  | 80%                                                                                                                                                                                               | Bódalo et al. (2009)       |
| Imidacloprid     | $0.5-1.5 \text{ mg L}^{-1}$                     | 0.5; 1.0 MPa                        | ~     | <ul> <li>2.92% for nanofiltration membrane-4;</li> <li>3.70% for nanofiltration membrane-3;</li> <li>54.6% for nanofiltration membrane-2;</li> <li>97.6% for nanofiltration membrane-1</li> </ul> | Kiso et al. (2000)         |
| Dichlorvos       | $0.5-1.5 \text{ mg L}^{-1}$                     | 0.5; 1.0 MPa                        | ~     | <ul> <li>4.28% for nanofiltration membrane-4;</li> <li>13.0% for nanofiltration membrane-3;</li> <li>46.2% for nanofiltration membrane-2;</li> <li>86.7% for nanofiltration membrane-1</li> </ul> | Kiso et al. (2000)         |
| Simazine         | $0.5-1.5 \text{ mg L}^{-1}$                     | 0.5; 1.0 MPa                        | ~     | <ul> <li>6.40% for nanofiltration membrane-4;</li> <li>9.15% for nanofiltration membrane-3;</li> <li>59.8% for nanofiltration membrane-2;</li> <li>96.7% for nanofiltration membrane-1</li> </ul> | Kiso et al. (2000)         |
|                  |                                                 |                                     |       |                                                                                                                                                                                                   | (continued)                |

| Table 6.2 (continued) |                             |               |            |                                                                                                                                                                                                     |                      |
|-----------------------|-----------------------------|---------------|------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| Dallatonto            | Initial concentration       | Transmembrane | 11~        | Domand officiants                                                                                                                                                                                   | Defermence           |
| FUIIIIIIS             |                             | pressures     | pn<br>2 10 |                                                                                                                                                                                                     | Kelelices            |
| Simazine              | 100 µg L <sup>-1</sup>      | 15 bar        | 3-10       | More than 74%                                                                                                                                                                                       | Musbah et al. (2013) |
| Atrazine              | $100 \ \mu g \ L^{-1}$      | 15 bar        | 3-10       | 96 %                                                                                                                                                                                                | Musbah et al. (2013) |
| Diuron                | $100 \ \mu g \ L^{-1}$      | 15 bar        | 3-10       | More than 74%                                                                                                                                                                                       | Musbah et al. (2013) |
| Desethylatrazine      | $100 \ \mu g \ L^{-1}$      | 15 bar        | 3-10       | More than 74%                                                                                                                                                                                       | Musbah et al. (2013) |
| Simetryn              | 0.5–1.5 mg L <sup>-1</sup>  | 0.5; 1.0 MPa  | ~          | <ul> <li>6.69 % for nanofiltration membrane-4;</li> <li>6.95 % for nanofiltration membrane-3;</li> <li>57.6 % for nanofiltration membrane-2;</li> <li>98.6 for nanofiltration membrane-1</li> </ul> | Kiso et al. (2000)   |
| Atrazine              | 0.5–1.5 mg L <sup>-1</sup>  | 0.5; 1.0 MPa  | ~          | <ul> <li>10.9% for nanofiltration membrane-4;</li> <li>14.9% for nanofiltration membrane-3;</li> <li>68.4% for nanofiltration membrane-2;</li> <li>97.5% for nanofiltration membrane-1</li> </ul>   | Kiso et al. (2000)   |
| Thiram                | $0.5-1.5 \text{ mg L}^{-1}$ | 0.5; 1.0 MPa  | ~          | <ul> <li>8.42% for nanofiltration membrane-4;</li> <li>18.7% for nanofiltration membrane-3;</li> <li>56.4% for nanofiltration membrane-2;</li> <li>97.7% for nanofiltration membrane-1</li> </ul>   | Kiso et al. (2000)   |
| Malathion             | 0.5-1.5 mg L <sup>-1</sup>  | 0.5; 1.0 MPa  | ~          | <ul> <li>41.4% for nanofiltration membrane-4;</li> <li>42.0% for nanofiltration membrane-3;</li> <li>88.1% for nanofiltration membrane-2;</li> <li>99.64% for nanofiltration membrane-1</li> </ul>  | Kiso et al. (2000)   |
| Molinate              | 0.5–1.5 mg L <sup>-1</sup>  | 0.5; 1.0 MPa  | 1          | 20.0% for nanofiltration membrane-4;<br>20.4% for nanofiltration membrane-3;<br>60.7% for nanofiltration membrane-2;<br>98.5% for nanofiltration membrane-1                                         | Kiso et al. (2000)   |
| Isoprothiolane        | 0.5-1.5 mg L <sup>-1</sup>  | 0.5; 1.0 MPa  | ~          | <ul><li>28.1 % for nanofiltration membrane-4;</li><li>36.3 % for nanofiltration membrane-3;</li><li>93.7 % for nanofiltration membrane-2;</li><li>99.76 % for nanofiltration membrane-1</li></ul>   | Kiso et al. (2000)   |

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| Kiso et al. (2000)                                                                                                                                                                                    | Kiso et al. (2000)                                                                                                                                                                            | Kiso et al. (2000)                                                                                                                                                                                       | Kiso et al. (2000)                                                        | Kiso et al. (2000)                                                                                                                                    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul> <li>44.6% for nanofiltration membrane-4; Ki</li> <li>44.8% for nanofiltration membrane-3;</li> <li>95.1% for nanofiltration membrane-2;</li> <li>99.52% for nanofiltration membrane-1</li> </ul> | 99.51 % for nanofiltration membrane-4; Ki<br>99.32 % for nanofiltration membrane-3;<br>More than 99.95 % for nanofiltration<br>membrane-2; More than 99.95 % for<br>nanofiltration membrane-1 | <ul> <li>21.8 % for nanofiltration membrane-4; Ki</li> <li>29.3 % for nanofiltration membrane-3;</li> <li>72.8 % for nanofiltration membrane-2;</li> <li>99.3 % for nanofiltration membrane-1</li> </ul> | 5.52% for nanofiltration membrane-2;Ki18.5% for nanofiltration membrane-1 | 95.6 % for nanofiltration membrane-4;Ki96.5 % for nanofiltration membrane-3;88.9 % for nanofiltration membrane-2;96.8 % for nanofiltration membrane-1 |
| /<br>4 4 5 22                                                                                                                                                                                         | 7<br>25<br>29<br>29<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20<br>20                                                                                             | / 21<br>25<br>72<br>99                                                                                                                                                                                   | / 5.                                                                      | / 95<br>88<br>88<br>96                                                                                                                                |
| 0.5; 1.0 MPa                                                                                                                                                                                          | 0.5; 1.0 MPa                                                                                                                                                                                  | 0.5; 1.0 MPa                                                                                                                                                                                             | 0.5; 1.0 MPa                                                              | 0.5; 1.0 MPa                                                                                                                                          |
| 0.5–1.5 mg L <sup>-1</sup>                                                                                                                                                                            | $0.5-1.5 \text{ mg L}^{-1}$                                                                                                                                                                   | 0.5–1.5 mg L <sup>-1</sup>                                                                                                                                                                               | $0.5-1.5 \text{ mg L}^{-1}$                                               | $0.5-1.5 \text{ mg L}^{-1}$                                                                                                                           |
| Dizinon                                                                                                                                                                                               | Chlorpyrifos                                                                                                                                                                                  | Anilazine                                                                                                                                                                                                | Pyridine                                                                  | 2,3,5-trichloro-<br>pyridine                                                                                                                          |

membrane, transmembrane pressures and solution pH value. Van der Bruggen et al. (2001) found the rejections for simazine, atrazine, diuron and isoproturon were all in the 90–95% range with nanofiltration membrane. Kiso et al. (2000) studied the removal of 12 pesticides including imidacloprid, simetryn and dichlorvos with four nanofiltration membrane, the results show that the rejections of 12 pesticides decreased in an order from nanofiltration membrane-1 to nanofiltration membrane-4. The removal efficiencies of the pesticides except chlorpyrifos for each nanofiltration membrane were 86.7–99.95% for nanofiltration membrane-1, 46.2–99.95% for nanofiltration membrane-2, 3.7-99.32% for nanofiltration membrane-3, and 2.9-99.51% for nanofiltration membrane-4, respectively. The rejection of chlorpyrifos was more than 99% for four types of nanofiltration membrane. Moreover, pesticides might transform and produce new transformation products during transporting to groundwater. The pesticide transformation products (PTPs) have been found in groundwater in recent years, which are different from pesticides (Mohammad et al. 2015). Madsen et al. (Madsen and Søgaard 2014) compared the performance of nanofiltration/low pressure reverse osmosis/reverse osmosis membrane for treatment of pesticides and pesticide transformation products in groundwater, the results show that low pressure reverse osmosis membrane could effectively reject the pesticides and pesticide transformation products, but nanofiltration membrane could not effectively reject pesticide transformation products. Therefore, some measures should be taken to reject pesticide transformation products, such as low pressure reverse osmosis membrane.

Sentana et al. (2010) studied the remove of the disinfection by-products by three commercial nanofiltration (nanofiltration 27, nanofiltration 90 and Desal-HL-51) membranes, the results show that the nanofiltration 90 membrane performed better in reducing in the formation of trihalomethane and haloacetic acid formation potential compared with nanofiltration 90 and Desal-HL-51 membranes.

The problem of arsenic (As) has received wide attention. Nanofiltration membrane was capable of converting As<sup>3+</sup> into As<sup>5+</sup> and removing As (Sen et al. 2010). However, most studies of the removal of arsenic from groundwater by nanofiltration membrane still at the laboratorial scale.

Hormones stem from agricultural, industrial, medical and domestic activities, which could enter aquatic environment and cause adverse effects to human health. Different studies investigated the feasibility of using nanofiltration to remove hormones, demonstrating that these compounds could be largely rejected according to the adsorption effect (Semião and Schäfer 2011; Schäfer et al. 2011; Sanches et al. 2012).

Although nanofiltration membrane has some great advantages such as high membrane flux, low investment and low operation cost, membrane fouling is still a great limitation. Membrane fouling is occurred when a particle or solute molecule is deposited on a membrane surface or in membrane pores, and then the membrane's performance is degraded. And it is determined by some factors including concentration polarization, membrane pore blocking and surface deposition. Membrane fouling can lead to some adverse effects such as flux decline, cost increase and membrane degradation. Hence, some measures should be taken to control membrane fouling such as feed pretreatment, membrane surface modification, physical cleaning and chemical cleaning (Mohammad et al. 2015; Hilal et al. 2004). Generally, physical cleaning such as washing, backwashing and immerse, gasliquid mixing flushing is carried out regularly during the membrane operation. The water permeability of the membrane can achieve a certain degree of recovery in the short time, but the membrane flux will fall again. So physical cleaning can only be used to inhibit the growth of membrane fouling, and can't make the membrane flux completely recovered. The fouled materials can be washed with chemical agents such as acid, alkali. Acid could make insoluble substances convert into soluble substances. Alkali mainly remove protein, algae and other biological pollutants, colloid pollutants and organic pollutants (Lim and Bai 2003; Madaeni et al. 2001).

### 6.2.2 Nanophotocatalytic Materials

Photocatalysis is a promising process for the removal of trace contaminants and microbial pathogens (Aarthi and Madras 2007). But the limited photocatalytic activity limits its wide application. Compared to common photocatalytic materials, nano-photocatalytic materials have attracted more attention (Han and Ba 2009; Gupta and Tripathi 2011). Because of their large specific surfaces, nano-photocatalytic materials can enhance photocatalytic activity effectively (Lan et al. 2013). Up to now, nTiO<sub>2</sub>, nZnO, nWO<sub>3</sub>, nBiVO<sub>4</sub> and nAl<sub>2</sub>O<sub>3</sub> are widely used nano-photocatalytic materials. Among them, nTiO<sub>2</sub> is the most commonly used nanomaterial in water and wastewater treatment due to its high reactivity, low toxicity, thermal stability, and abundance as raw material (Table 6.3) (Gupta and Tripathi 2011; Chen and Mao 2007).

In aqueous environment, nTiO<sub>2</sub> photocatalyst can generate an electron/hole pair when it is irradiated with energy greater than the band gap. Then, electron/hole pair can migrate to the surface of  $nTiO_2$  and form reactive oxygen species ( $\cdot OH$ ,  $H_2O_2$ , etc.). The positive holes react with H<sub>2</sub>O and form hydroxyl radical, which promote the oxidation of organics (Kwon et al. 2008). nTiO<sub>2</sub> has been successfully applied for the organic wastewater treatment, including dye wastewater (Aarthi and Madras 2007; 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; García et al. 2012). Although nTiO<sub>2</sub> has some great advantages in the field of water and wastewater treatment, especially for dye wastewater and paper mill wastewater, it has some drawbacks such as low absorb efficiency of visible light, low recycle rate and high cost. In order to overcome above-mentioned drawbacks, several approaches have been studied including dye sensitization, doping, coupling and capping of  $nTiO_2$  (Gupta and Tripathi 2011). In particular, ion doping has received wide attention due to easy operation, high efficiency and more rapid reaction rate. Choi et al. (1994) reported that nTiO<sub>2</sub> doped with Fe<sup>3+</sup>, Mo<sup>5+</sup>, Ru<sup>3+</sup>, Os<sup>3+</sup>, Re<sup>5+</sup>, V<sup>4+</sup> and Rh<sup>3+</sup> significantly increased the photochemical reactivity of nTiO<sub>2</sub> for the oxidation of trichloromethane and reduction of

| <b>Table 6.3</b> Pollutants that can be removed by $nTiO_2$ | n be removed by nT               | 102                             |         |                                                                                                                                                                                                                      |                             |
|-------------------------------------------------------------|----------------------------------|---------------------------------|---------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
|                                                             | Initial                          |                                 |         |                                                                                                                                                                                                                      |                             |
| Pollutants                                                  | concentration                    | nTiO <sub>2</sub> dose          | рН      | Removal efficiency                                                                                                                                                                                                   | References                  |
| $Cu^{2+}$                                                   | 145 μM                           | $1{ m g~L^{-1}}$                | 10.8    | 100%                                                                                                                                                                                                                 | Aarthi and Madras (2008)    |
| Cr <sup>6+</sup>                                            | 215 μM                           | $1 \mathrm{g} \mathrm{L}^{-1}$  | 7       | 63 %                                                                                                                                                                                                                 | Aarthi and Madras (2008)    |
| Cu <sup>2+</sup>                                            | 250–515 μM                       | $1 \mathrm{g} \mathrm{L}^{-1}$  | /       | About 16%–40% in 120 min                                                                                                                                                                                             | Vinu and Madras (2007)      |
| Cr <sup>6+</sup>                                            | 120-250 mM                       | $1 \mathrm{g}  \mathrm{L}^{-1}$ | _       | 100 % in 5 min                                                                                                                                                                                                       | Vinu and Madras (2007)      |
| $\mathrm{Hg}^{2+}$                                          | 150 ppm                          | $5.0 \times 10^{-3} \text{ M}$  | natural | 100% in 130 min (253.7 nm light)                                                                                                                                                                                     | Skubal and Meshkov (2002)   |
| Methylene blue                                              | 25-75 ppm                        | $0.25-2 \text{ kg m}^{-3}$      | /       | Nearly 100 % in 150 min (The average solar intensity in a day between 10 a.m. and 2.30 p.m. was $0.753$ kW m <sup>-2</sup> )                                                                                         | Nagaveni et al. (2004)      |
| Orange G                                                    | 25 ppm                           | $1 \text{ kg m}^{-3}$           | _       | More than 90 % in 100 min                                                                                                                                                                                            | Nagaveni et al. (2004)      |
| Orange G                                                    | 40 <sup>-1</sup>                 | $1 \mathrm{g  L^{-1}}$          | /       | Nearly 100 % in 90 min (US + UV power intensity of 1.6 W cm <sup>-2</sup> )                                                                                                                                          | Vinu and Madras (2008)      |
| Remazol brill blue R                                        | 100 ppm                          | $1 \text{ kg m}^{-3}$           | /       | About 70% in 150 min                                                                                                                                                                                                 | Nagaveni et al. (2004)      |
| Remazol Brilliant Blue R                                    | $50 \text{ mg } \mathrm{L}^{-1}$ | $1~{ m g~L^{-1}}$               | /       | About 80% in 90 min                                                                                                                                                                                                  | Vinu and Madras (2008)      |
| Alizarin Red S                                              | $50 \text{ mg L}^{-1}$           | $1 \mathrm{g} \mathrm{L}^{-1}$  | /       | the complete degradation in 60 min                                                                                                                                                                                   | Vinu and Madras (2008)      |
| Indigo Carmine                                              | $50 \text{ mg L}^{-1}$           | $1 \mathrm{g} \mathrm{L}^{-1}$  | /       | the complete degradation in 30 min                                                                                                                                                                                   | Vinu and Madras (2008)      |
| 4-chlorophenol                                              | 250 mg L <sup>-1</sup>           | 2 g L-1                         | S       | The photocatalytic activity in the degradation of 4-chlorophenol was found to be higher for $Mg^{24}$ and $Ba^{24}$ doped nano TiO <sub>2</sub> than both pure nano TiO <sub>2</sub> and commercial TiO <sub>2</sub> | Venkatachalam et al. (2007) |
| 4-nitrophenol                                               | $30 \text{ mg L}^{-1}$           | $1 \mathrm{g} \mathrm{L}^{-1}$  | /       | 100% in 30 min                                                                                                                                                                                                       | Vinu and Madras (2007)      |
| Phenol                                                      | $30 \text{ mg L}^{-1}$           | $1 { m g L}^{-1}$               | /       | 100% in 30 min                                                                                                                                                                                                       | Vinu and Madras (2007)      |
| Cinosulfuron                                                | 15.5 μmol L <sup>-1</sup>        | $2.5 \text{ g L}^{-1}$          | /       | More than 90 % in 60 min (The irradiation spectrum was cut-off below 340 nm)                                                                                                                                         | Vulliet et al. (2002)       |
| Triasulfuron                                                | $16 \mu mol L^{-1}$              | $2.5 {\rm ~g~L^{-1}}$           | /       | Nearly 100% in 30 min                                                                                                                                                                                                | Vulliet et al. (2002)       |
|                                                             |                                  |                                 |         |                                                                                                                                                                                                                      |                             |

**Table 6.3** Pollutants that can be removed by nTiO<sub>3</sub>

| Methamidophos     | 100 pm                              | $0.5 \text{ g L}^{-1}$ | 10  | 100% in 5 h (UV irradiation with light energy greater than 3.2 eV)                           | Dai et al. (2008)   |
|-------------------|-------------------------------------|------------------------|-----|----------------------------------------------------------------------------------------------|---------------------|
| Chlorbromuron     | 0.1 mmol L <sup>-1</sup>            | $1 \mathrm{g  L^{-1}}$ | 5-6 | Nearly 100% photodegradation in 2 h (UV40 mW cm <sup>-2</sup> )                              | Parra et al. (2002) |
| Chlortoluron      | $0.1 \text{ mmol } \text{L}^{-1}$   | $1 { m g L}^{-1}$      | 5-6 | 100% in 1.5 h (UV40 mW cm <sup>-2</sup> )                                                    | Parra et al. (2002) |
| Metobromuron      | $0.1 \text{ mmol } \mathrm{L}^{-1}$ | $1 g L^{-1}$           | 5-6 | Nearly 100% in 2 h (UV40 mW cm <sup>-2</sup> )                                               | Parra et al. (2002) |
| Isoproturon       | $0.1 \text{ mmol } \mathrm{L}^{-1}$ | $1 {\rm ~g~L^{-1}}$    | 5-6 | 100% in 1.5 h (UV 40 mW cm <sup>-2</sup> )                                                   | Parra et al. (2002) |
| Malathion         | $10 \text{ mg L}^{-1}$              | $10 \text{ mg L}^{-1}$ | ~   | 98.2 % (the UV luminous intensity was 0.4 $\rm mW~cm^{-2})$                                  | Yu et al. (2010)    |
| MS2 bacteriophage | $\sim 7*10^9$ PFU mL <sup>-1</sup>  | 100 mg L <sup>-1</sup> | _   | 1.6 log inactivation of MS2 in 2 min (The total light intensity was 2.5 mW/cm <sup>2</sup> ) | Liga et al. (2011)  |
|                   |                                     |                        |     |                                                                                              |                     |

carbon tetrachloride. The dopant content influences the rate of electron/hole recombination and photocatalytic activity. As the dopant content increases, the electron/hole pairs within the space-charge region are separated by the large electric field before recombination. However, when the dopant content is high, the rate of electron/hole pairs recombination in the nTiO<sub>2</sub> increases. Therefore, there is an optimum content of dopant ion. Xin et al. (2007) studied the effect of the different doping ratio Fe<sup>3+</sup>–nTiO<sub>2</sub>, the results revealed that the nTiO<sub>2</sub> with a low doping concentration of Fe<sup>3+</sup> (Fe/Ti lower than 0.03 mol) enhanced the photocatalytic activity of nTiO<sub>2</sub>. However, the nTiO<sub>2</sub> containing a high doping concentration of Fe<sup>3+</sup> (Fe/Ti higher than 0.03 mol) is unfavorable to photocatalytic reactions.

## 6.2.3 Nanoadsorption Materials

Adsorption is commonly employed as pretreatment or advanced treatment to remove organic pollutants, heavy metals and residual chlorine in water and wastewater. The efficiency of nano-adsorption materials is higher than that of conventional absorbents due to high specific surface area, associated sorption sites and surface chemistry.

#### 6.2.3.1 Carbon Based Nanoadsorbents

Carbon nanotubes, a new type of nanomaterials, have received wide attention due to their unique properties, such as large specific surface area, high thermal stability and high chemical stability. Carbon nanotubes can be divided into single-walled carbon nanotubes and multi-walled carbon nanotubes. Carbon nanotubes are good adsorption materials for the remove of organic matter, heavy metal (Table 6.4).

Numerous studies have shown that carbon nanotubes were effective adsorbents and their efficiency was superior to activated carbon on adsorption of organic chemicals in water and wastewater treatment (Pan and Xing 2008; Su and Lu 2007; Wang et al. 2007). Su and Lu (2007) reported that the adsorption capacities of carbon nanotubes on natural dissolved organic matter (11.61 mg g<sup>-1</sup>) is higher than that of granular activated carbon  $(3.55 \text{ mg g}^{-1})$ , and the average weight losses of the carbon nanotubes (2.65%) is lower than that of granular activated carbon (6.40%). El-Sheikh et al. (2008) reported that the absorption capacity of multi-walled carbon nanotubes is three times that of activated carbon towards the pesticides. Long and Yang (2001) found that carbon nanotubes were better than activated carbon for dioxin removal. Its high adsorption capacity is mainly because of the large specific surface area and the pollutants-carbon nanotube interactions. In aqueous environment, carbon nanotubes strongly adsorb low molecular weight polar organic compounds due to the organic compounds-carbon nanotube interactions including hydrophobic effect,  $\pi$ - $\pi$  interactions, hydrogen bonding, and electrostatic interactions (Pan and Xing 2008; Qu et al. 2013). Different adsorption mechanisms might

|                      |                                      | -                           |      |                                                                                            |                                          |
|----------------------|--------------------------------------|-----------------------------|------|--------------------------------------------------------------------------------------------|------------------------------------------|
| Pollutants           | Initial concentration                | Carbon<br>nanotubes<br>dose | pН   | Removal<br>efficiency                                                                      | References                               |
| Pb <sup>2+</sup>     | 10-80 mg L <sup>-1</sup>             | 0.5g L <sup>-1</sup>        | 5    | 97.08 mg g <sup>-1</sup>                                                                   | Li et al. (2003a)                        |
| Pb <sup>2+</sup>     | $2-14 \text{ mg } \text{L}^{-1}$     | 0.5 g L <sup>-1</sup>       | 7    | 1 mg g <sup>-1</sup>                                                                       | Li et al. (2002)                         |
| Cu <sup>2+</sup>     | 10 mg L <sup>-1</sup>                | 5 g L <sup>-1</sup>         | 9    | Nearly 100%                                                                                | Pyrzyńska and<br>Bystrzejewski<br>(2010) |
| Cu <sup>2+</sup>     | 5-30 mg L-1                          | 0.5 g L <sup>-1</sup>       | 5    | 28.49 mg g <sup>-1</sup>                                                                   | Li et al. (2003a)                        |
| Cd <sup>2+</sup>     | 2-15 mg L <sup>-1</sup>              | 0.5g L <sup>-1</sup>        | 5    | 10.86 mg g <sup>-1</sup>                                                                   | Li et al. (2003a)                        |
| Cd <sup>2+</sup>     | 9.5 mg L <sup>-1</sup>               | 0.5 g L <sup>-1</sup>       | 7    | 1.1 mg g <sup>-1</sup>                                                                     | Li et al. (2003b)                        |
| Zn <sup>2+</sup>     | 10-80 mg L <sup>-1</sup>             | 0.5 g L <sup>-1</sup>       | 7    | 10.21–<br>11.23 mg g <sup>-1</sup>                                                         | Lu et al. (2006)                         |
| Zn <sup>2+</sup>     | 60 mg L <sup>-1</sup>                | 0.5 g L <sup>-1</sup>       | 1–5  | 37.03–46.94 mg<br>g <sup>-1</sup> and 30.3–<br>34.36 mg g <sup>-1</sup><br>from 5 to 45 °C | Lu and Chiu<br>(2006)                    |
| Co <sup>2+</sup>     | 10 mg L <sup>-1</sup>                | 5 g L <sup>-1</sup>         | 9    | More than 90%                                                                              | Pyrzyńska and<br>Bystrzejewski<br>(2010) |
| Ni <sup>2+</sup>     | 6–20 mg L <sup>-1</sup>              | 0.3 g L <sup>-1</sup>       | 6.55 | 9.8 mg g <sup>-1</sup>                                                                     | Chen and Wang<br>(2006)                  |
| U(VI)                | 10 <sup>-7</sup> -10 <sup>-4</sup> M | 1 g L <sup>-1</sup>         | 4    | 5.0 mmol g <sup>-1</sup>                                                                   | Schierz and<br>Zänker (2009)             |
| Th(IV)               | 32.32 μmol L <sup>-1</sup>           | 0.2 g L <sup>-1</sup>       | 1.9  | 65.8 μmol g <sup>-1</sup>                                                                  | Chen et al. (2007)                       |
| Fluoride             | 12 mg L <sup>-1</sup>                | 2 g L <sup>-1</sup>         | 5–9  | 14.4 mg g <sup>-1</sup>                                                                    | Li et al. (2001)                         |
| CHCl <sub>3</sub>    | 2 mg L <sup>-1</sup>                 | 0.33 g L <sup>-1</sup>      | 3-11 | 2.41 mg g <sup>-1</sup>                                                                    | Lu et al. (2005)                         |
| CHCl <sub>2</sub> Br | 2 mg L <sup>-1</sup>                 | 0.33 g L <sup>-1</sup>      | 3-11 | 1.23 mg g <sup>-1</sup>                                                                    | Lu et al. (2005)                         |
| CHClBr <sub>2</sub>  | 2 mg L <sup>-1</sup>                 | 0.33 g L <sup>-1</sup>      | 3-11 | 1.08 mg g <sup>-1</sup>                                                                    | Lu et al. (2005)                         |
| CHBr <sub>3</sub>    | 2 mg L <sup>-1</sup>                 | 0.33 g L <sup>-1</sup>      | 3-11 | 0.92 mg g <sup>-1</sup>                                                                    | Lu et al. (2005)                         |
| Phenol               | 0.1–100,000 mg<br>L <sup>-1</sup>    | /                           | 7    | 64.6 mg g <sup>-1</sup>                                                                    | Yang et al. (2008)                       |
| Aniline              | 0.1–100,000 mg<br>L <sup>-1</sup>    | /                           | 7    | 114.8 mg g <sup>-1</sup>                                                                   | Yang et al. (2008)                       |
| 1,2-dichlorobenzene  | 20 mg L <sup>-1</sup>                | 0.5 g L <sup>-1</sup>       | 3-10 | 30.8 and<br>28.7 mg g <sup>-1</sup> for<br>as grown and<br>graphitized CNT<br>in 40 min    | Peng et al. (2003)                       |
| Atrazine             | 5 mg L <sup>-1</sup>                 | 4 g L-1                     | 5    | 0.956 mg g <sup>-1</sup>                                                                   | El-Sheikh et al. (2008)                  |
| Propoxur             | 5 mg L <sup>-1</sup>                 | 4 g L-1                     | 5    | 0.625 mg g <sup>-1</sup>                                                                   | El-Sheikh et al. (2008)                  |
| Methidathion         | 5 mg L <sup>-1</sup>                 | 4 g L <sup>-1</sup>         | 5    | 1.11 mg g <sup>-1</sup>                                                                    | El-Sheikh et al. (2008)                  |

 Table 6.4
 Pollutants that can be removed by carbon nanotubes

act simultaneously. The dominant adsorption mechanism might be affected by carbon nanotubes, organic chemicals and environmental conditions (Pan and Xing 2008).

Carbon nanotubes could adsorb heavy metals including Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> effectively (Rao et al. 2007; Pyrzyńska and Bystrzejewski 2010; Li et al. 2005). Pyrzyńska and Bystrzejewski (2010) reported that carbon nanotubes have higher adsorption efficiency towards Co<sup>2+</sup> and Cu<sup>2+</sup> compared with activated carbons.

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

#### 6.2.3.2 Metal Based Nanoadsorbents

Iron oxide nanomaterials as adsorbent has received wide attention due to its high surface area, low toxicity and easy synthesis (Deliyanni et al. 2004; Huang et al. 2007; Xu et al. 2012). Iron oxide nanomaterials Iron oxide is a general designation of a large class of substance including many types.  $nFe_3O_4$ ,  $n-\gamma Fe_2O_3$  and  $n-\alpha Fe_2O_3$  are the most common three kinds of iron oxides nanomaterials in water and wastewater treatment.

Iron oxide nanomaterials could adsorb a variety of heavy metals including Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, As<sup>3+</sup> and Zn<sup>2+</sup> (Li and Zhang 2006; 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. 2010a) and radionuclides (Qu et al. 2013) (Table 6.5). Nassar (2010) reported that the maximum adsorption capacity of Pb<sup>2+</sup> onto nFe<sub>3</sub>O<sub>4</sub> was much higher than that of reported adsorbents. However, the adsorption of heavy metal onto iron oxide nanomaterials is still at the lab scale (Xu et al. 2012). Practical application is limited.

Other than iron oxide nanoparticle, nTiO<sub>2</sub>, nZnO and nAl<sub>2</sub>O<sub>3</sub> 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<sup>5+</sup> 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 regenerations.

| Pollutants               | Initial concentration     | Nanomaterial<br>Dose     | pН      | Removal efficiency       | Reference                         |
|--------------------------|---------------------------|--------------------------|---------|--------------------------|-----------------------------------|
| Cu <sup>2+</sup>         | 0–20 mmol L <sup>-1</sup> | 5 g L <sup>-1</sup>      | 4       | 0.5 mmol g <sup>-1</sup> | Kim et al. (2003)                 |
| Cu <sup>2+</sup>         | 200 mg L <sup>-1</sup>    | 5 g L <sup>-1</sup>      | 2–5.1   | 38.5 mg g <sup>-1</sup>  | Banerjee and<br>Chen (2007)       |
| Co <sup>2+</sup>         | 0–100mg L <sup>-1</sup>   | 20 g L <sup>-1</sup>     | 5.5     | 27.5 mg g <sup>-1</sup>  | Chang et al. (2006)               |
| Cu(II)                   | 18 ppm                    | 100 g L <sup>-1</sup>    | 8       | 30 mg g <sup>-1</sup>    | Mahdavian and<br>Mirrahimi (2010) |
| Cu(II)                   | 100 mg L <sup>-1</sup>    | 20 g L <sup>-1</sup>     | 2 and 5 | 12.43 mg g <sup>-1</sup> | Huang and Chen (2009)             |
| Cr(VI)                   | 10-50 mg L-1              | 3 or 6 g L <sup>-1</sup> | 5       | 30 mg g <sup>-1</sup>    | Wei et al. (2009)                 |
| Cr(VI)                   | 0-140 mg L <sup>-1</sup>  | 5 g L <sup>-1</sup>      | 2.5     | 15.3 mg g <sup>-1</sup>  | Yuan et al. (2009)                |
| Cr(VI)                   | 10-200 mg L-1             | 1 g L <sup>-1</sup>      | 2.5     | 25.8 mg g <sup>-1</sup>  | Hu et al. (2007)                  |
| Cr(VI)                   | 100 mg L <sup>-1</sup>    | 20 g L <sup>-1</sup>     | 2 and 5 | 11.24 mg g <sup>-1</sup> | Huang and Chen (2009)             |
| Pb(II)                   | 18 ppm                    | 100 g L <sup>-1</sup>    | 8       | 40 mg g <sup>-1</sup>    | Mahdavian and<br>Mirrahimi (2010) |
| Pb(II)                   | 100 mg L <sup>-1</sup>    | 10 g L <sup>-1</sup>     | 7       | 97.34%                   | Ahmad et al. (2009)               |
| Hg(II)                   | 100 mg L <sup>-1</sup>    | 10 g L <sup>-1</sup>     | 7       | 90 %                     | Ahmad et al. (2009)               |
| Cd(II)                   | 1.8 ppm                   | 100 g L <sup>-1</sup>    | 8       | 5 mg g <sup>-1</sup>     | Mahdavian and<br>Mirrahimi (2010) |
| Red dye                  | 200 mg L-1                | 1 g L <sup>-1</sup>      | 6       | 90 %                     | Iram et al. (2010)                |
| Fluoride                 | 20 mg L <sup>-1</sup>     | 1 g L <sup>-1</sup>      | 6.5     | 91.74 mg g <sup>-1</sup> | Zhao et al. (2010)                |
| Phosphate                | 50 mg P L-1               | 1 g L <sup>-1</sup>      | 4       | 13.65 mg g <sup>-1</sup> | Long et al. (2011)                |
| 1-naphthylamine          | 60 mg L <sup>-1</sup>     | 0.4 g L <sup>-1</sup>    | 6.5     | 200 mg g <sup>-1</sup>   | Hu et al. (2011)                  |
| Phenanthrene             | 0.4 ng mL <sup>-1</sup>   | 0.2 g L <sup>-1</sup>    | 3–10    | more than 90 %           | Zhang et al. (2010a)              |
| Fluoranthene             | 0.4 ng mL <sup>-1</sup>   | 0.2 g L <sup>-1</sup>    | 3-10    | more than 90 %           | Zhang et al.<br>(2010a)           |
| Pyrene                   | 0.4 ng mL <sup>-1</sup>   | 0.2 g L <sup>-1</sup>    | 3–10    | more than 90 %           | Zhang et al.<br>(2010a)           |
| Benzo(a)<br>anthracene   | 0.4 ng mL <sup>-1</sup>   | 0.2 g L <sup>-1</sup>    | 3–10    | more than 90 %           | Zhang et al.<br>(2010a)           |
| Benzo[b]<br>fluoranthene | 0.4 ng mL <sup>-1</sup>   | 0.2 g L <sup>-1</sup>    | 3–10    | more than 90 %           | Zhang et al.<br>(2010a)           |

 Table 6.5
 Pollutants that can be removed by iron oxide nanomaterials

### 6.2.3.3 Polymeric Nanoadsorbents

Recently, polymeric nano-adsorbents have emerged as a novel type of adsorbent materials for the removal of heavy metals and organic pollutants in water and wastewater. Regarding the environmental concerns, these adsorbents are typically made up of polystyrene or polyacrylic ester matrix (Ray and Shipley 2015). Although

polymeric nano-adsorbents have excellent properties such as pore size distribution, large surface area, tunable surface chemistry and excellent mechanical rigidity, they have some drawbacks such as low adsorption capacities and high cost (Ray and Shipley 2015; Pan et al. 2009).

### 6.2.4 Nanoreducing Materials

As a kind of effective reductant for pollutants removal in water, nano zero-valent metals have attracted much attention science 1980s. Iron is a metal with standard redox potential ( $E^0 = -0.44$  V). It is thus an effective reductant when reacting with oxidized contaminants in water. Nanoscale zero-valent iron is the particle size of zero-valent iron between 1 and 100 nm. The use of nanoscale zero-valent iron for the removal of contaminants in water and wastewater has received wide attention due to its high reduction performance, large specific surface area and high reactivity. Other types of nano-reducing materials have also been tested for water and wastewater treatment, such as nZn and nNi. In particular, nanoscale zero-valent iron is the most commonly used nanomaterial for groundwater remediation (Mueller et al. 2012). Nanoscale zero-valent iron has been successfully applied for the treatment of water and wastewater contaminated with chlorinated organic compounds (Arnold et al. 2002), arsenic (Kanel et al. 2005), heavy metals, including chromium (Scott et al. 2011), cadmium (Scott et al. 2011), copper (Li and Zhang 2007; Karabelli et al. 2008), silver (Li and Zhang 2007), zinc (Li and Zhang 2007; Klimkova et al. 2011), dves (Lin et al. 2008; Fan et al. 2009) and phenol (Liu et al. 2005; Elliott et al. 2009; Crane and Scott TB 2012) (Table 6.6). 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.

The pollutants removal by nanoscale zero-valent iron is affected by many factors such as type of pollutants, nanoscale zero-valent iron concentration, temperature and solution pH value. Lin et al. (2008) reported that the removal of AB24 dye by nanoscale zero-valent iron, the results showed that the degradation efficiency of AB24 dye increased with increasing nanoscale zero-valent iron concentration (0-4 g L<sup>-1</sup>) and temperature (10–50 °C). The reaction rate is highly pH-dependent, the rate constants decreased as the pH increased from 3 to 6 or above 9 and the rate increased as pH increased from 6 to pH 9. The reduction of AB24 dye by ZVI dominated the surface reaction at pH lower than 6; whereas at pH higher than 6, the removal of AB24 dye was mainly due to an adsorption reaction. Li and Zhang (2007) reported that the removal efficiency of eight metal ions including Cd<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>6+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> with nanoscale zero-valent iron is 36.5%, 71.0%, 92.5%, 97.5%, 99.7%, 99.7% and 99.8%. In the study performed by Li and Zhang (2007), as for metals with standard potential E0 very close to or more negative than that of iron (E<sup>0</sup>, -0.41 V), such as Zn<sup>2+</sup> and Cd<sup>2+</sup>, the removal mechanism is sorption and surface complexation. As for metals with  $E^0$  greatly more positive than iron

| Pollutants         concentration         Nanomaterial dose         pH         Removal efficiency $As^{*+}$ 5 mg L <sup>-1</sup> 0.50 and 1.04 g L <sup>-1</sup> 6.5         121 mg r <sup>-1</sup> $As^{*+}$ 1 mg L <sup>-1</sup> 1 g L <sup>-1</sup> 0.50 and 1.04 g L <sup>-1</sup> 6.5         125 mg r <sup>-1</sup> $As^{*+}$ 5 mg L <sup>-1</sup> 0.50 and 1.04 g L <sup>-1</sup> 6.5         125 mg r <sup>-1</sup> 0.50 mg r <sup>-1</sup> $As^{*+}$ 1 mg L <sup>-1</sup> 1 g L <sup>-1</sup> 0.50 mg r <sup>-1</sup> 1 g L <sup>-1</sup> 0.50 mg r <sup>-1</sup> $As^{*+}$ 1 mg L <sup>-1</sup> 1 g L <sup>-1</sup> 0.5         182.mg r <sup>-1</sup> 0.6 $As^{*+}$ 100 mg L <sup>-1</sup> 1 g L <sup>-1</sup> 10.7         9.6% after 7 days $Cu^{++}$ 10 mg L <sup>-1</sup> 10 g L <sup>-1</sup> 5.7         99% after 7 days $Cu(V1)$ 10 mg L <sup>-1</sup> 10 g L <sup>-1</sup> 5.7         99% after 7 days $Cu(V1)$ 10 mg L <sup>-1</sup> 10 g L <sup>-1</sup> 5.7         99% after 7 days $Cu(V1)$ 10 mg L <sup>-1</sup> 10 g L <sup>-1</sup> 5.7         99% after 7 days $Cu(V1)$ 10 mg L <sup>-1</sup> 10 g L <sup>-1</sup> 5.7         99% after 7 days | ic |                                | PH<br>6.5<br>4-10<br>6.5<br>7<br>6.5 | Removal efficiency<br>121 mg g <sup>-1</sup>                      | References<br>Du et al. (2013) |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|--------------------------------|--------------------------------------|-------------------------------------------------------------------|--------------------------------|
| Smg L^1 $0.50$ and $1.04$ g L^1 $6.5$ Img L^1 $1 g L^{-1}$ $1 g L^{-1}$ $4-10$ Smg L^1 $0.50$ and $1.04$ g L^1 $6.5$ Img L^1 $1 g L^{-1}$ $1 g L^{-1}$ $7$ icc $2 mg L^{-1}$ $1 g L^{-1}$ $7$ $1 mg L^{-1}$ $1 g L^{-1}$ $1 g L^{-1}$ $6.5$ $1 mg L^{-1}$ $1 g L^{-1}$ $1 g L^{-1}$ $6.5$ $1 000 mg L^{-1}$ $1 g L^{-1}$ $1 4.67$ $1 00 mg L^{-1}$ $1 0 g L^{-1}$ $2.5 T$ $1 0 mg L^{-1}$ $1 0 g L^{-1}$ $2.5 T$ $1 0 mg L^{-1}$ $1 0 g L^{-1}$ $2.5 T$ $0 0 0 mg L^{-1}$ $1 0 g L^{-1}$ $2.5 T$ $0 0 0 mg L^{-1}$ $1 0 g L^{-1}$ $2.5 T$ $0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 $                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | .j | 7                              | 6.5<br>4-10<br>6.5<br>7<br>6.5       | 121 mg g <sup>-1</sup>                                            | Du et al. (2013)               |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | į. |                                | 4-10<br>6.5<br>7<br>6.5              | 00 / 00 00 : 10 F                                                 |                                |
| Smg L <sup>-1</sup> $0.50$ and $1.04$ g L <sup>-1</sup> $6.5$ ling L <sup>-1</sup> $1 g L^{-1}$ $6.5$ licc $2 mg L^{-1}$ $1 g L^{-1}$ $6.5$ lic $2 mg L^{-1}$ $1 g L^{-1}$ $6.5$ loon mg L <sup>-1</sup> $2.5 g L^{-1}$ $100$ $6.5$ $1000 mg L^{-1}$ $1.2 g L^{-1}$ $4.67$ $0 mg L^{-1}$ $10 g L^{-1}$ $10 g L^{-1}$ $2.57$ $0 mg L^{-1}$ $10 g L^{-1}$ $10 g L^{-1}$ $2.57$ $0 mg L^{-1}$ $10 g L^{-1}$ $2.57$ $2.7$ $0 mg L^{-1}$ $10 g L^{-1}$ $2.57$ $2.7$ $0 mg L^{-1}$ $10 g L^{-1}$ $2.57$ $2.7$ $0 mg L^{-1}$ $2.0 g L^{-1}$ $2.57$ $2.0 g L^{-1}$ $0 mg L^{-1}$ $2.0 g L^{-1}$ $2.7$ $2.7$ $0 mg L^{-1}$ $2.0 g L^{-1}$ $2.7$ $2.0 g L^{-1}$ $0 mg L^{-1}$ $2.0 g L^{-1}$ $2.0 g L^{-1}$ $2.6$ $0 mate         2.0 mg L^{-1} 2.6 g L^{-1} 2.6 $                                                                                                                                                                                                                                                                                                                                                                                                                      |    |                                | 6.5<br>7<br>6.5                      | 00.0-99.9 % III 12 II                                             | Kanel et al. (2005)            |
| ing $L^{-1}$ I g $L^{-1}$ I g $L^{-1}$ $I^{-1}$                                                                                                                                                                                                                                                                                                                                                                                                                                     | .2 |                                | 7<br>6.5                             | $125 \text{ mg g}^{-1}$                                           | Du et al. (2013)               |
| ic $2 mg L^{-1}$ $1 g L^{-1}$ $6.5$ $1000 mg L^{-1}$ $2.5 g L^{-1}$ $10$ $500 mg L^{-1}$ $1.5 g L^{-1}$ $4.67$ $500 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $10 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $10 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $10 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $0$ $10 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $0$ $10 mg L^{-1}$ $10 g L^{-1}$ $8.57$ $0$ $20 mg L^{-1}$ $2.0 g L^{-1}$ $3.0$ $0$ $20 mg L^{-1}$ $2.0 g L^{-1}$ $9$ $0$ $20 mg L^{-1}$ $2.0 g L^{-1}$ $9$ $0$ $20 mg L^{-1}$ $2.0 g L^{-1}$ $9$ $0$ $0.5 g L^{-1}$ $0.5 g L^{-1}$ $7.0$ $0$ $0.0 mg L^{-1}$ $2.0 g L^{-1}$ $5.6$ $0$ $10 mg L^{-1}$ $2 g L^{-1}$ $5.6$ $0$ $10 mg L^{-1}$ $0.5 g L^{-1}$ $5.6$ $0$ $0.0 g L^{-1}$ $0.5 g L^{-1}$ $5.6$ $0$ $0.0 g L^{-1}$ $0.5 g L^{-1}$ $5.6$ $0$ $0.0 g L^{-1}$ $0.5 g L^{-1}$ $5.6$                                                                                                                                                                                                                                                      | .9 | -                              | 6.5                                  | Nearly 100% in 10 min                                             | Kanel et al. (2006)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    | -                              |                                      | $18.2 \text{ mg g}^{-1}$                                          | Zhu et al. (2009)              |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |                                | 10                                   | More than 99.9%                                                   | Üzüm et al. (2008)             |
| $\begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |    |                                | 4.67                                 | 43.3%-99.9%                                                       | Karabelli et al. (2008)        |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |                                | >5.7                                 | 96% after 7 days                                                  | Scott et al. (2011)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |                                | 4                                    | More than 96% in 140 min                                          | Kim et al. (2013)              |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    | 10 o I -1                      | >5.7                                 | 99% after 7 days                                                  | Scott et al. (2011)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    | 1001                           | >5.7                                 | 99% after 7 days                                                  | Scott et al. (2011)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    | $2.0 {\rm ~g~L^{-1}}$          | 3.0                                  | >90 %                                                             | Liu et al. (2012)              |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |    | $0.04-0.12~{ m g~L^{-1}}$      | 9                                    | 24 %-90 %                                                         | Xu and Zhao (2007)             |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    | $3 \text{ g L}^{-1}$           | 4.0                                  | Nearly 100% in 20 min                                             | Shi et al. (2011)              |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |    |                                | 5                                    | 97.2%                                                             | Jiang et al. (2011)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |                                | 7.0                                  | Nearly 100% in 120 min                                            | Zhang et al. (2011)            |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |                                | $10 {\rm ~g~L^{-1}}$                 | 90 %,54.58 %,19.79 %,3.27 % at 75 °C,60<br>°C,40 °C,25 °C in 24 h | Cao et al. (2005)              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |    | $2 \mathrm{g} \mathrm{L}^{-1}$ | natural                              | 100%                                                              | Luo et al. (2013)              |
| $ \begin{array}{ccccc} \mbox{mge} \mbox{dye} & 100\mbox{ mg} \mbox{L}^{-1} & 0.5\mbox{ g} \mbox{L}^{-1} & 6.5 \\ \mbox{blue} \mbox{dye} & 94\mbox{ mg} \mbox{L}^{-1} & 1\mbox{ g} \mbox{L}^{-1} & 5.9 \\ \mbox{50\mbox{ mg} \mbox{L}^{-1} & 0.3\mbox{ g} \mbox{L}^{-1} & 5.6 \\ \end{array} $                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |    |                                | 5.6                                  | Almost 100% after 30 min                                          | Shu et al. (2010)              |
| blue dye $94 \text{ mg } \text{L}^{-1}$ $1 \text{ g } \text{L}^{-1}$ $5.9$<br>$50 \text{ mg } \text{L}^{-1}$ $0.3 \text{ g } \text{L}^{-1}$ $5.6$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |    |                                | 6.5                                  | Nearly 100% after 30 min                                          | Chen et al. (2011)             |
| $50 \text{ mg } \text{L}^{-1}$ $0.3 \text{ g } \text{L}^{-1}$ $5.6$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |    | $1 \mathrm{g  L^{-1}}$         | 5.9                                  | 89.36% in 30–60 min                                               | Frost et al. (2010)            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |    | $0.3 \text{ g L}^{-1}$         | 5.6                                  | completely removed in 20 min                                      | Lin et al. (2008)              |
| Azo dye methyl orange $100 \text{ mg } \text{L}^{-1}$ $0.2-0.5 \text{ g } \text{L}^{-1}$ $6$ $70.3\%-100\%$ in 60 min                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |    |                                | 9                                    | 70.3 %-100 % in 60 min                                            | Fan et al. (2009)              |

Table 6.6 Pollutants that can be removed by nanoscale zero-valent iron

| Table 6.6 (continued)                             |                                                             |                                       |         |                                                                      |                       |
|---------------------------------------------------|-------------------------------------------------------------|---------------------------------------|---------|----------------------------------------------------------------------|-----------------------|
| Dollutouts                                        | Initial                                                     | Monomotoniol doco                     | I,      | Domorol officionary                                                  | Doforman              |
| Follutants                                        | concentration                                               |                                       | ц       |                                                                      |                       |
| Tetrachloroethene                                 | 20 mg L <sup>-1</sup>                                       | 5gL <sup>-1</sup>                     | /       | 100% in 90 min                                                       | Lien and Zhang (2001) |
| Trichloroethylene                                 | $10 \text{ mg L}^{-1}$                                      | $5~{ m g~L^{-1}}$                     | /       | 90 % in 30 min                                                       | Choe et al. (2001)    |
| Trichloroethene                                   | $20 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | 100% in 90 min                                                       | Lien and Zhang (2001) |
| Vinyl chloride                                    | $20 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | 100% in 80 min                                                       | Lien and Zhang (2001) |
| Chloroform                                        | $10 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | Completely dechlorinated within 5 min                                | Choe et al. (2001)    |
| Nitrobenzene                                      | $10 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | 100%                                                                 | Choe et al. (2001)    |
| Nitrotoluene                                      | $10 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | 85%                                                                  | Choe et al. (2001)    |
| Dinitrobenzene                                    | $10 \text{ mg L}^{-1}$                                      | $5 \mathrm{g \ L^{-1}}$               | /       | 80%                                                                  | Choe et al. (2001)    |
| Dinitrotoluene                                    | $10 \text{ mg L}^{-1}$                                      | $5 \mathrm{~g~L^{-1}}$                | /       | 70%                                                                  | Choe et al. (2001)    |
| 1,1-dichloroethene                                | $20 \text{ mg L}^{-1}$                                      | $5 \mathrm{~g~L^{-1}}$                | /       | 100% in 90 min                                                       | Lien and Zhang (2001) |
| cis-1,2-dichloroethene                            | $20 \text{ mg L}^{-1}$                                      | $5 \text{ g L}^{-1}$                  | /       | 100% in 80 min                                                       | Lien and Zhang (2001) |
| trans-1,2-dichloroethene                          | $20 \text{ mg L}_{-1}$                                      | $5 \mathrm{~g~L^{-1}}$                | /       | 100% in 90 min                                                       | Lien and Zhang (2001) |
| 2,2-bis(4-Chlorophenyl)-<br>1,1,1-trichloroethane | $1.09 \text{ mg L}^{-1}$                                    | $0.05 \text{ g L}^{-1}$               | 7       | over 90 % in 4 h                                                     | Tian et al. (2009)    |
| <i>p</i> -chlorophenol                            | 20-100  mg<br>$\mathrm{L}^{-1}$                             | $0.3~{ m g~L^{-1}}$                   | /       | 100% (4 days)                                                        | Cheng et al. (2007)   |
| 2,4,6-trinitrotoluene                             | 80 mg L <sup>-1</sup>                                       | $5 \text{ g L}^{-1}$                  | 4       | More than 99% in 3 h                                                 | Zhang et al. (2010b)  |
| Metronidazole                                     | $80 \text{ mg } \mathrm{L}^{-1}$                            | $0.1~{ m g~L^{-1}}$                   | 5.6     | Rapidly removed in 5 min                                             | Fang et al. (2011)    |
| Lindane                                           | $1 \text{ mg L}^{-1}$                                       | $0.02-0.5 \text{ g } \mathrm{L}^{-1}$ | 7.9-8.3 | 45% to nearly 100% within 300 min                                    | Joo and Zhao (2008)   |
| Atrazine                                          | $5 \mathrm{mg}\mathrm{L}^{-1}$                              | $0.1 { m ~g~L^{-1}}$                  | 7.0–8.2 | More than 95% under anaerobic condition: 35% under aerobic condition | Joo and Zhao (2008)   |
| Hexachlorobenzene                                 | $5 \text{ mg L}^{-1}$                                       | $2-20 \text{ g } \mathrm{L}^{-1}$     | /       | About 25–70% degradation in 24 h                                     | Shih et al. (2011)    |
| Escherichia coli                                  | $1 \times 10^{6} - 2 \times 10^{6}$<br>CFU mL <sup>-1</sup> | $1.2-110 \text{ mg L}^{-1}$           | 8       | 0.82 log inactivation/mg L <sup>-1</sup> nanoFe-h                    | Lee et al. (2008)     |

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such as  $Cu^{2+}$ ,  $Ag^+$ , and  $Hg^{2+}$ , the removal mechanism is predominantly reduction. As for metal ions with  $E^0$  slightly more positive than iron such as  $Ni^{2+}$  and  $Pb^{2+}$ , they can be immobilized at the nanomaterial surface by both sorption and reduction.

# 6.3 Applications of Nanomaterials for Water Quality Monitoring

Water quality monitoring is of importance to pollution sources control, water quality management and public health. With the development of water quality monitoring technology, some novel technologies were applied in microbial water quality monitoring including phylochips, quantitative real-time polymerase chain reaction and pyrosequencing (Aw and Rose 2012). Besides, previous studies showed that nanomaterials could be used in organic pollutants, inorganic pollutants and pathogen detection, including magnetic nanoparticles, carbon nanotubes, noble metal nanomaterials and quantum dots.

Pathogens detection in water is vital for human health. Many pathogens including bacteria such as Legionella, Escherichia coli and Helicobacter, viruses such as Enteroviruses, Hepatitis viruses and Rotaviruses, and protozoan such as Cryptosporidium and Giardia associated with drinking water are closely related to human diseases. Nanomaterial enabled pathogens sensors are consist of recognition agents, nanomaterials and a signal transduction mechanism. Among 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.

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.

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. Quantum dots can overcome the limitations of traditional fluorescence dyes and simultaneously detect multiple emission peaks from a single wavelength of light. For example, quantum dots can detect Escherichia coli O157: H7 and salmonella typhimurium simultaneously and expected to detect 3–4 species simultaneously in the near future (Yang and Li 2006). Taking advantage of the optical properties of quantum dots, they will help in pathogen detection certainly (Yang and Li 2006; Hahn et al. 2005). Quantum dots were capable of differentiating minute amounts of pathogenic bacterial cells among larger populations of innocuous cells due to their sensitivity and larger absorption cross sections (Hahn et al. 2005).

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 et al. 2009). Lysozyme Type VI-Stabilized Gold Nanoclusters was used to detect  $Hg^{2+}$  and  $CH_3Hg^+$  (Lin and Tseng 2010), the limits of detection for  $Hg^{2+}$  and  $CH_3Hg^+$  were estimated to be 3 pM and 4 nM. Lysozyme Type VI-Stabilized Gold Nanoclusters provided an about 330-fold improvement in the detection of  $Hg^{2+}$  in comparison to bovine serum albumin-stabilized gold Nanoclusters. More immortally, this probe was successfully used in seawater. Vega et al. (2007) reported the use of the carbon nanotube-modified glassy carbon electrode for the detection of phenolic estrogens.

# 6.4 Challenges of Applying Nanomaterials in Water Quality Management

Although nanomaterials enabled water and wastewater treatment and monitoring have shown great potentials in the future, cost-effectiveness and technical hurdles are still challenges for their development and commercialization. The cost of nanomaterials is relatively high. Studies on some nanomaterials such as nanoscale zerovalent iron are mostly carried out at the lab scale. Many laboratory studies have evaluated the performance of nanoscale zero-valent iron for removing various pollutants. However, the research on the treatment performance and the long-term performance of real water and waste water with nanomaterials is limited due to the short time of laboratory studies and complication of real water and wastewater.

In addition, potential risk of nanomaterials is another challenge for their widespread application. An increasing number of nanomaterials will be released to the environment due to the increasing application of nanomaterials in water and wastewater treatment and monitoring, which have attracted more and more concern. 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 nanoecotoxicology need to be done.

# 6.5 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 membrane could be used in the production of potable water and the removal of metals, disinfection by-products, pesticides and emerging contaminants from contaminated water. However membrane fouling is still a great limitation. nTiO<sub>2</sub> has some excellent performance in the field of water

and wastewater treatment, especially for dye wastewater and paper mill wastewater. The surface modification of  $nTiO_2$  is being studied for optimization. However, it has some drawbacks including narrow light response range and low recycle rate. Carbon nanotubes, iron oxides nanomaterials,  $nTiO_2$  and polymeric nano-adsorbents have shown high adsorption capacities. Enhancing the regeneration of absorbents must be explored to reduce the cost in water quality management. In addition, nanoscale zero-valent iron could be used to remove heavy metals and organic pollutants by reduction or oxidation and degree of removal could be enhanced through functionalization. However, the persistence of activity is limited. Nanomaterials-based sensors have the potential to detect heavy metals, organic pollutants and pathogen in water and wastewater. Nanomaterials are used to improve the detection sensitivity and response speed of pollutions. In a word, nanomaterials have received extensive research in water pollution remediation and monitoring. However, there are many problems for their practical application need to be study and solve including cost-effectiveness, technical hurdles and potential risk of nanomaterials.

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