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Removal of arsenic, nitrate, persistent organic pollutants and pathogenic microbes from water using redox-reactive minerals

ANNA A. BOGUSH, JONG KYU KIM and LUIZA C. CAMPOS

Civil, Environmental and Geomatic Engineering Department, University College London, Chadwick Building, Gower Street, London WC1E 6BT, UK,
e-mail: a.bogush@ucl.ac.uk (annakhol@gmail.com), j.k.kim@ucl.ac.uk, l.campos@ucl.ac.uk

Water pollution is a major global problem at present, involving inorganic and organic contaminants such as heavy metals, pesticides and pharmaceutical compounds, as well as pathogens. Therefore, the development of water-management strategies and appropriate water-treatment technologies has been the subject of intense research for decades. This chapter reviews the potential use of redox-reactive minerals as reactive media in environmental cleanup technologies especially in the removal of arsenic, nitrate, persistent organic pollutants and pathogenic microbes. The properties and applications of five classes of redox-reactive materials are summarized: zero-valent metals, mixed-valence iron oxyhydroxides, Fe-bearing clays, mixed-valence manganese oxides and titanium and zinc oxides. Examples and case studies that demonstrate the significant role of these reactive materials in water-treatment processes are also provided.

1. Introduction

Rapid industrial development, urban growth and domestic and agricultural activities are the main contributors to the quality deterioration of water bodies (*i.e.* surface and ground waters) and soils. Pollution of aquatic and terrestrial environments is the contamination of streams, lakes, groundwater, rivers and soils by substances harmful to the entire ecosystem. The major soil and water pollutants are chemical, biological or physical materials. These pollutants are the major threat to human health, especially in densely populated countries such as China and India.

Inorganic pollutants include heavy metals (*e.g.* Cd, Pb, Cr, Cu, V and Hg) and metalloids (*e.g.* As, Se and Sb) and these are regarded collectively as the most serious environmental contaminants globally due to their high toxicity and links to many forms of cancer (Riley *et al.*, 1992; Smedley and Kinniburgh, 2002; Mishra *et al.*, 2010; Tchounwou *et al.*, 2012). The treatment of heavy metals and metalloids is essential due to their persistence in the environment (Dangerous Substances Directive, 1976; Bradl, 2005). Organic pollutants include petroleum and its derivatives, polycyclic aromatic

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hydrocarbons (PAHs), and chlorinated hydrocarbons. These contaminants affect the aquatic ecosystem by depletion of dissolved oxygen (LENNTECH (a)). They are also known to have direct health effects including cancer, damage to the nervous system and reproductive disorders (Rao and Rao, 1997; Mosharraf Hossain *et al.*, 2012). Biological pollution is another major concern caused by invasive biological species including viruses, bacteriophage and bacteria. Millions of people die of illnesses contracted through infectious microorganisms, and most cases are caused by microbiological contamination of water supplies (Inamori and Fujimota, 2007). The major sources of biological contamination are domestic and agricultural activities.

Various water-treatment processes utilize chemical, physical and/or biological solutions to remove pollutants from water (Cheremisinoff, 2002; Bradl, 2005). Biological slow sand filtration was the sole method used to treat water until the advent of rapid gravity filters at the end of 19th century, followed by the introduction of chlorination and chemical coagulation (Bowles *et al.*, 1983). The appearance of organic and inorganic compounds and emergent pathogens in water led to the development of many other processes. Water-treatment processes currently available include, among others, adsorption, membrane filtration, oxidation, ion exchange and photocatalysis. Oxidants employed in water treatment include chlorine, ozone and hydroxyl radicals ($^{\bullet}OH$). However, some of these oxidants have been found to produce by-products as a result of either reactions with compounds in water or as a natural decay of the product itself (Legube *et al.*, 1989; McGuire *et al.*, 1990). Some of these by-products are caused by the application, in particular, of chlorine, including halogenated organics such as thrihalomethanes, which are said to be carcinogenic. As result, there is a need for the development and application of chemicals that are efficient but non-toxic or harmful to human health.

There is increasing interest in employing reduction-oxidation (redox) reactions using redox-reactive minerals in environmental remediation technologies due to their cost effectiveness and potential for the development of sustainable remediation technologies. Redox reactions transform the valence states of toxic contaminates (*e.g.* dissolved Cr^{VI}) to less reactive and less toxic forms (*e.g.* less soluble Cr^{III}) (Borch *et al.*, 2010). Redox-reactive materials have been evaluated to break down chlorinated solvents (*e.g.* trichloroethane, trichloroethylene, dichloroethene, tetrachloroethylene, vinyl chloride) in groundwater of permeable reactive zones (Sivavec *et al.*, 1997; USEPA, 2008c; Karn *et al.*, 2009; Bardos *et al.*, 2011) and the removal of redox-active elements such as U and Cr (see Fig. 1 from Ahmed *et al.*, 2010b; Dickinson and Scott, 2010; Crane *et al.*, 2011), and Cr (Schrick *et al.*, 2004; Cao and Zhang, 2006).

Amongst the redox-reactive minerals used in water treatment are iron-bearing phases (magnetite, green rust, zero-valent iron (ZVI), *etc.*), iron-bearing clay phases, sulfides, manganese oxide (MnO_2) and titanium oxide (TiO_2). Besides their redox properties, these materials have unique surface characteristics that lead to exceptional sorption and ion exchange properties. These redox-reactive media can be very useful in water-cleanup processes and environmental protection technologies. This chapter provides a review with examples of promising water-treatment processes involving redox-

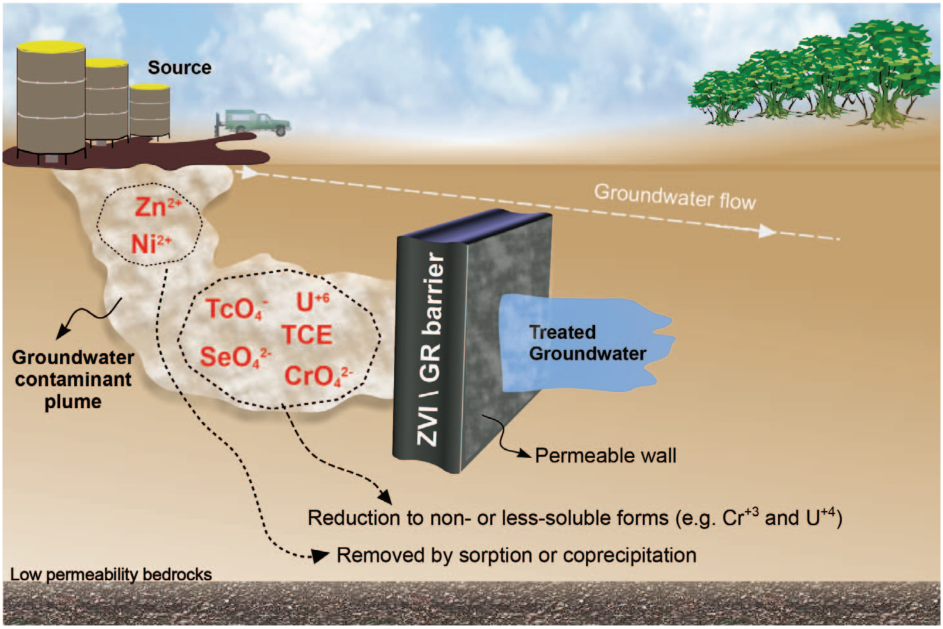

Figure 1. Permeable reactive barrier system: Zero-valent iron/ green rust (ZVI/GR) to remove inorganic and organic contaminants from groundwater. (Reproduced with the permission of the Environmental Chemistry Group of the Royal Society of Chemistry from Ahmed *et al*., 2010)

reactive minerals for the removal of arsenic, nitrate, persistent organic pollutants and pathogenic microbes.

1.1 Properties of some redox-reactive minerals

In this section, we will discuss the properties of five groups of redox-reactive minerals: zero-valent metals, mixed-valence iron oxyhydroxides, Fe-bearing clays, mixed-valence manganese oxides and titanium and zinc oxides. The main properties of these redox-reactive minerals are summarized in Table 1.

Zero-valent metals (*e.g.* Fe^0, Zn^0, Ni^0, *etc*.) are used as strong reducing agents in water treatment. For example, the corrosion of zero-valent iron (ZVI) in water under the aerobic or anaerobic condition can be described by the following reactions:

$$2Fe^0_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} \text{ (aerobic, fast process)} \quad (1)$$

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \text{ (anaerobic, slow process)} \quad (2)$$

In the first reaction, zero-valent iron reduces the oxygen present in water, leading to a decrease in redox potential (often < −0.5 V) and an increase in pH. In equation 2, ZVI reduces water to hydrogen and hydroxide, and an increase in pH occurs. Products of ZVI corrosion such as Fe^{2+} and H_2 are also reducing agents (Tratnyek *et al*., 2003). However, the condition, media and nature of the contaminants can influence

Table 1. Properties of the redox-reactive minerals.

Redox-reactive mineral		Redox property	Redox processes	Parameters	Application
Zero-valent metals (ZVM)	Zero-valent iron (ZVI)	$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$, $E = -0.44$ V; $\Delta G = +42.5$ kJ/electron; formation of oxidizing intermediates (O_2^-, H_2O_2, $^{\bullet}OH$, Fe(IV)) under oxic conditions	Direct reduction at the metal surface; reduction by ferrous iron and hydrogen (with catalyst); oxidation by oxidizing intermediates	mZVI (>0.1 nm) with SSA $\leqslant 1$ m^2/g; nZVI (20−100 nm) with SSA $\approx$ 10−40 m^2/g; Fe(0) content 20−90%; bcc Fe(0) and Fe_3O_4 were identified in nZVI	Reductive and oxidative treatment of polluted waters containing inorganic (Cr, As, U, Th, Cl, N) and organic (chlorinated hydrocarbons, pesticides, viruses, pathogenic microbes) contaminants
	Zero-valent zinc (ZVZ)	$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$, $E = -0.76$V, $\Delta G = +73.6$ kJ/electron	Reduction at the metal surface	–	Catalyst, reductive treatment of polluted waters
Mixed Fe(II)-Fe(III) minerals	Magnetite ($Fe^{2+}Fe_2^{3+}O_4$)	E varies by almost 1 V	Reduction and adsorption at the mineral surface	Spinel group; $pH_{PZC} \approx 6$; SSA varies from ~2 to 257 m^2/g	Reductive and adsorptive treatment of polluted waters from inorganic contaminants
	Green rusts ($[Fe^{II}_{6-x}Fe^{III}{}_{x}\text{-}OH_{12}]_x^{+}$) with interlayers of anions (Cl^-, SO_4^{2-} and CO_3^{2-}) and water molecules	E varies, because of the variable composition (Fe^{2+}/Fe^{3+} ratio)	Reduction and adsorption at the surface of green rust	Structure of a pyroaurite type; PZC of $GRSO_4$ = 8.3±0.1 and PZC of $GRCO_3$ = 8.35±0.05; GR particle size $\approx$ 50−200 nm	Reductive and adsorptive treatment of polluted waters from inorganic contaminants

Fe-bearing clay minerals	Fe^{3+}/Fe^{2+} clay minerals (*e.g.* smectite – Fe content < 30 wt.%)	*E* varies considerably, because of the Fe oxidation state, the clay mineral structure, the total Fe content, and the ordering of structural cations	Redaction and adsorption processes at the active site of the Fe-bearing clay mineral	Reducing agents: bacteria, dithionite, hydrazine, hydrogen gas, hydrogen sulfide; Structural Fe^{2+} content changed from 10% to 90%	Reductive treatment of polluted waters containing inorganic and organic contaminants
Manganese oxides	Pyrolusite	E varies	oxidation and absorption	single-chain structure	Oxidative treatment of polluted waters containing inorganic and organic contaminants
	Birnessite	E varies	surface-mediated oxidation and absorption	layer structures	Oxidative treatment of polluted waters containing inorganic and organic contaminants
ZnO	Hexagonal wurtzite, cubic zincblende	$ZnO+h\nu \rightarrow e^{-}+h^{+}$, E_g=3.3 eV; $e^{-}+O_2 \rightarrow O_2^{-}$; $H_2O+h^{+} \rightarrow {}^{\bullet}OH+H^{+}$; ${}^{\bullet}OH$+orgaric pollutants→Intermediates→CO_2+H_2O	Photocatalysis and oxidation processes	Wurtzite crystal structure; SSA of ZnO ≈ 2.5–12 m^2/g	Photocatalytic oxidative degradation of organic pollutants (herbicides, insecticides and pesticides)
TiO_2	Anatase, brookite and rutile	$TiO_2+h\nu \rightarrow e^{-}+h^{+}$, E_g=3.2 eV; $H_2O+h^{+} \rightarrow {}^{\bullet}OH+H^{+}$; $O_2+e^{-} \rightarrow O_2^{-}$; $O_2^{-}+H^{+} \rightarrow HO_2^{\bullet}$; $h^{+}+O_2^{-} \rightarrow 2O^{\bullet}$	Photocatalysis and oxidation processes	Tetragonal crystal; TiO_2 particle size ≈ 6–104 nm with SSA ≈ 14–254 m^2/g	Photocatalytic oxidative degradation of organic pollutants (herbicides, insecticides and pesticides)

E – Standard reduction potential and ΔG – Gibbs free energy changes at 25C and pH 7.

significantly the mechanism of reactions of Fe^0, with contaminants involving multiple competing pathways (see Fig. 2 from Matheson and Tratnyek, 1994; Dickinson and Scott, 2010). Under oxic conditions, Fe(II) oxidation leads to the formation of intermediates (O_2^-, H_2O_2, $^{\bullet}OH$ and Fe(IV)), which are able to oxidize pollutants such as As (Leupin and Hug, 2005).

Matheson and Tratnyek (1994) described a model of possible pathways for the reduction of chlorinated solvents by ZVI. The model proposed three reaction pathways: (1) direct electron transfer from ZVI to the adsorbed halocarbon occurs, resulting in dechlorination and production of Fe^{2+}; (2) Fe^{2+} dechlorinates the halocarbon, producing Fe^{3+}; (3) H_2 from the anaerobic reduction of water can dechlorinate halocarbon if a catalyst is present. Understanding the relative importance of these reaction pathways is essential for the development and performance assessment of ZVI-based remediation technologies.

Micro- and nanoscale zero-valent iron (mZVI>0.1 μm and nZVI<0.1 μm) has been investigated widely in water-treatment applications (Sayles *et al.*, 1997; Li *et al.*, 2006; Fu *et al.*, 2014). ZVI is used to treat the following types of contaminants (Yan *et al.*, 2013): organic pollutants (chlorinated solvents, pesticides, azo-dyes, flame retardants, and antibiotics); inorganic contaminants (nitrate, arsenic, hexavalent chromium, heavy metals and radionuclides). The characteristics of nZVI are summarized in the comprehensive reviews by Nurmi *et al.* (2005) and Yan *et al.* (2013). The key advantage of nZVI is its large surface area which provides more reactive sites with

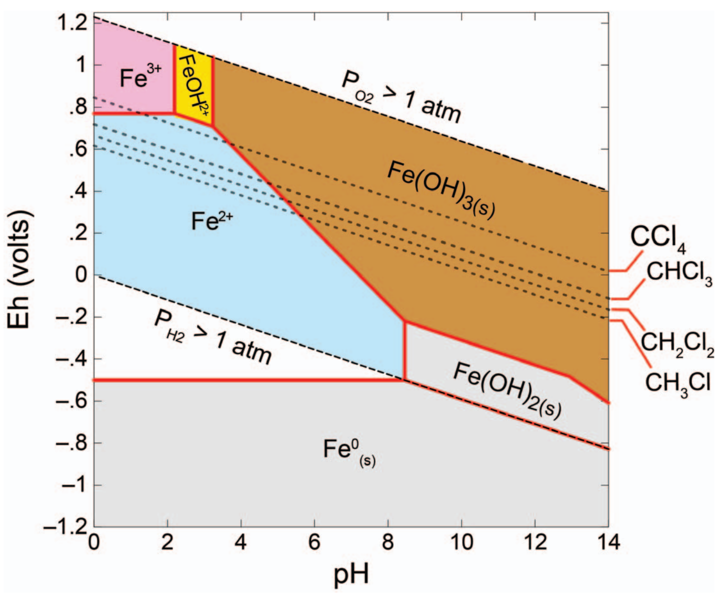

Figure 2. Pourbaix diagram for the Fe^0–H_2O system constructed with the suppression of hematite, magnetite, goethite and FeO. Modified, with the permission of the Royal Society of Chemistry, using *Geochemist's Workbench*, from Matheson and Tratnyek (1994).

more rapid degradation of contaminants compared to mZVI (USEPA, 2008b). For example, the average specific surface area (SSA) of the nZVI is in the range of 10–40 m^2/g and SSA of conventional microscale iron powder is typically $\leqslant 1\ m^2/g$ (Cao and Zhang, 2006). The disadvantages of nZVI are: difficulty in preparing stable and well dispersed nZVI; limited life of nZVI particles; the agglomeration or clumping of particles to each other or to the soil surface (USEPA, 2008a; Yan *et al.*, 2013). Agglomeration may be caused by groundwater conditions, surface properties of the particles, the age of the materials or shipping conditions (USEPA, 2008a). Using surface coating of nZVI with polyelectrolytes or non-ionic surfactant can improve the particle stability (Yan *et al.*, 2013).

Mixed Fe(II)-Fe(III) minerals (*e.g.* magnetite (Fe_3O_4) and green rusts) contain the ferrous (Fe^{2+})–ferric (Fe^{3+}) iron redox couple, and can control several environmental processes (reduction of several chemicals, redox mediating reactions, biological nutrient cycling, *etc.*). Thus, these minerals play important roles in the reductive treatment of polluted waters containing different contaminants. Magnetite is a common, naturally occurring mineral and a member of the spinel group. Magnetite can form during biotic and abiotic reduction of Fe(III) oxides and as a result of the oxidation of Fe(II) and Fe(0) (Anthony *et al.*, 1997; Cornell and Schwertmann, 2003; Gorski, 2009; Gorski *et al.*, 2010). At room temperature, Fe_3O_4 has a spinel face-centred cubic unit cell with the chemical formula often written as $Fe^{3+}_A[Fe^{2+}Fe^{3+}]_BO_4$, where A and B represent the tetrahedral and octahedral sites, respectively (Santos-Carballal *et al.*, 2014). Magnetite stoichiometry ($x = Fe^{2+}/Fe^{3+}$) can range from 0 to 0.5, where 0.5 corresponds to the most reduced form (stoichiometric magnetite), and 0 is the completely oxidized form (maghemite: γ-Fe_2O_3) (Gorski *et al.*, 2010). The specific surface areas for synthetic magnetite, synthetic nano-scale mesoporous magnetite, mechanically activated magnetite and three commercial magnetite chemicals (two ALFA chemicals with 97% and 99.999% purity and one Sigma Aldrich (<50 nm; $\geqslant$98% purity)) are 95.2-95.3, 247-257, 0.5-6.1, 5.59, 2.76 and 52.5 m^2/g (Sun *et al.*, 1998; Illés and Tombácz, 2004; Balâž *et al.*, 2010; Crane *et al.*, 2011). Gorski *et al.* (2010) investigated the factors controlling rates of contaminant (particularly for nitrobenzene) reduction by magnetite (Fe_3O_4) which are still poorly understood. They showed that rates of nitrobenzene ($ArNO_2$) reduction became almost five orders of magnitude faster as the particle stoichiometry increased from 0.31 to 0.50. They also proposed that both redox and Fe^{2+} diffusion processes plays important role in contaminant reduction by magnetite. The pH value of the point of zero charge (PZC) of magnetite in the absence of multivalent cations is about 6 (Sun *et al.*, 1998; Pang *et al.*, 2007; Ficai *et al.*, 2012). The presence of excess cations such as Fe^{2+} or Fe^{3+} in magnetite can greatly influence the zeta potential (Sun *et al.*, 1998; Marmier *et al.*, 1999; Illés and Tombácz, 2004; Pang *et al.*, 2007). Magnetite particles are positively and negatively charged at the dispersion pH values below and above the PZC, respectively (Sun *et al.*, 1998; Pang *et al.*, 2007). Sun *et al.* (1998) explained that at pH $< pH_{PZC}$ the protonation may be significant, at pH $\approx pH_{PZC}$ coagulation occurs, and at pH $> pH_{PZC}$ deprotonation and surface metal ion hydrolysis dominate.

Green rusts (GRs) are layered double hydroxide compounds and are intermediate phases in the formation of Fe oxides and oxyhydroxides such as goethite, lepidocrocite and magnetite (Schwertmann and Fechter, 1994). GRs are products of abiotic and microbially induced corrosion of iron and steel (Génin *et al.*, 1998; Kumar *et al.*, 1999; O'Loughlin *et al.*, 2003). The general formula of green rust is $[Fe^{II}_{(1-x)}Fe^{III}_{x}(OH)_2]^{x+}$ $\cdot[(x/n)A^{n-})\cdot mH_2O]^{x-1.2}$ where $x = Fe^{III}/Fe_{total}$, A^{n-} denotes interlayer anions with charge *n*, and *m* is moles of water molecules (Ahmed *et al.*, 2010a,b). Green rusts have a structure of a pyroaurite type consisting of positively charged trioctahedral iron hydroxide layers of variable composition ($[Fe^{II}_{6-x}Fe^{III}{}_{x}OH_{12}]^{x+}$) with interlayers of anions such as carbonate, sulfate and chloride and water molecules (Bernal *et al.*, 1959; Brindley and Bish, 1976; Hansen *et al.*, 1994; Schwertmann and Fechter, 1994). Fougerite ($[Fe^{2+}_4Fe^{3+}_2(OH)_{12}][CO_3]\cdot 3H_2O$) is the natural analogue of green rust (Genin *et al.*, 2001). There is an analytical challenge to handling, sampling and characterizing green rusts due to its quick transformation into ferric phases (*e.g.* goethite and magnetite) under oxidizing conditions (Ahmed *et al.*, 2010b). Ahmed *et al.* (2010a,b) developed a chemostat reactor combined with *in situ* time-resolved X-ray scattering measurements in order to characterize accurately GR and understand its formation and further transformation. Synthesized GR particle sizes vary from 50 to 200 nm (Ruby *et al.*, 2003, 2006; Bocher *et al.*, 2004; Guilbaud *et al.*, 2013). Guilbaud *et al.* (2013) determined that the point of zero charge (PZC) values are 8.3±0.1 and 8.35±0.05 for GR containing SO_4^{2-} ($GRSO_4$) and GR containing CO_3^{2-} ($GRCO_3$), respectively.

Fe-bearing clay minerals, such as rectorite (RAr-1 (illite:smectite = 50:50), 4.9 wt.% Fe, SSA – 144 m^2/g); illite (IMt-1, 12.3 wt.% Fe, SSA – 5 m^2/g); nontronite (NAu-2, 23.4 wt.% Fe, SSA – 271 m^2/g)) are important redox-reactive phases in subsurface soils and sediments, and play an important role in contaminant reduction (White and Peterson, 1996; Ernstsen *et al.*, 1998; Hofstetter *et al.*, 2003, 2006; Schwarzenbach *et al.*, 2010; Neumann *et al.*, 2011; Liu *et al.*, 2012). Gorski *et al.* (2012a) quantified the electron-accepting and -donating capacities (Q_{EAC} and Q_{EDC}) at applied potentials (Eh) of –0.60 V and +0.61 V, respectively, for four natural Fe-bearing smectites (SWa-1, 12.6 wt.% Fe), Na-rich montmorillonite (SWy-2, 2.3 wt.% Fe), and two nontronites (NAu-1, 21.2 wt.% Fe and NAu-2, 19.2 wt.% Fe). They showed that for SWa-1 and SWy-2 sample, all the structural Fe was redox-active over the tested Eh range but for NAu-1 and NAu-2, a significant fraction (~18%) of the structural Fe was redox-inactive. Iron may be distributed randomly or clustered in the octahedral sheet. Khaled and Stuki (1991) showed that the total layer charge of unaltered (oxidized) Fe-bearing smectites (SWa-1) measured by K^+, Ca^{2+}, Zn^{2+} or Cu^{2+} varies from 66.3 to 77.3 $cmol_c/kg$. Structural iron (*e.g.* Fe^{3+}) in clay minerals can be reduced to Fe^{2+} by different reducing agents (*e.g.* hydrazine, hydrogen gas, hydrogen sulfide) but the two most commonly used agents are dithionite and metal-reducing bacteria (Stucki *et al.*, 1984, 1987; Neumann *et al.*, 2011). Bacteria including *Shewanella*, *Geobacter*, *Pseudomonas* and *Bacillus* may reduce structural iron in clay (Stucki and Getty, 1986; Stucki *et al.*, 1987; Kostka *et al.*, 1999; Stucki, 2005). Fe^{2+} released can reduce organic and inorganic pollutants. Neumann *et al.*, (2011) showed that the redox properties of structural Fe are affected by its bonding environment in the clay's lattice, the total Fe content, the ordering of structural cations and the Fe oxidation state. Gorski *et al.* (2012b) investigated the redox properties of structural Fe in an iron-bearing clay mineral (ferruginous smectite, SWa-1), including the distribution of apparent reduction potentials of Fe^{3+}/Fe^{2+} pairs, the reversibility and pH dependence of electron transfer to and from structural Fe. Large changes in the standard reduction potential were observed for ferruginous smectite (−0.28 V to −0.54 V) as the structural Fe^{2+} content changed from 10% to 90% (Gorski *et al.*, 2012b). Lear and Stucki (1989) showed that specific surface area (SSA) of swelling SWa-1 (SSA $\approx$ 720 m^2/g) decreased with increasing Fe^{2+} in the octahedral sheet and about 20% of the layers collapsed completely in Fe-bearing smectite. Reduction of Fe^{3+} to Fe^{2+} in the dioctahedral structure of clay minerals is reflected in an increase in the negative surface charge and in cation fixation (Stucki, 2005). Kostka *et al.* (1999) added that SSA decreased by 170 m^2/g and the cation exchange capacity increased from 0.81 to 1.05 mEq/g in SWa-1 upon reduction of structural Fe by bacteria. In addition, Khaled and Stucki, (1991) showed that the total layer charge of chemically reduced Fe-bearing smectites (SWa-1) measured by K^+, Ca^{2+}, Zn^{2+} or Cu^{2+} varies from 77.9 to 99.7 $cmol_c/kg$.

Manganese-bearing minerals such as manganese oxides play an important role in removal of inorganic and organic pollutants (Moore *et al.*, 1990; Tournassat *et al.*, 2002; Tebo *et al.*, 2004; Mohan and Pittman, 2007; Con *et al.*, 2013). Manganese can form oxides with main oxidation states of +2 and +3 (*e.g.* MnO_2, Mn_2O_3, Mn_3O_4). Therefore, Mn oxides are capable of acting either as reducing agents ($Mn^{2+} - e^- = Mn^{3+} - e^- = Mn^{4+}$) or oxidizing agents ($Mn^{4+} + e^- = Mn^{3+} + e^- = Mn^{2+}$) (Fierro, 2006). Manganese oxides are used for many different applications in water treatment, soil and sediment remediation, metal removal and recovery, and they are also used as catalysts, sorbents and electrical conductors (Tebo *et al.*, 2004). Pyrolusite is manganese dioxide (MnO_2, single chain structure) formed under oxidizing conditions in manganese-bearing hydrothermal deposits, bogs, lakes and oceanic systems (Anthony *et al.*, 1997). Birnessite, with an empirical formula of $(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$, is a major manganese-bearing mineral occurring in soil, aquifers and oceanic and aquatic systems (Anthony *et al.*, 1997; Tournassat *et al.*, 2002). Lanson *et al.* (2000) determined the structural formula of hexagonal birnessite to be $H^+_{0.33}Mn^{3+}_{0.111}Mn^{2+}_{0.055}(Mn^{4+}_{0.722}Mn^{3+}_{0.111}\square_{0.167})O_2 \cdot (H_2O)_{0.50}$, where $\square$ is a Mn vacancy in the octahedral layer. These vacancies, in turn, can be reactive sorption sites for pollutants (Tournassat *et al.*, 2002). The presence of Mn(III), Mn(II) and vacant sites within Mn oxide minerals cause negative surface charges, which can be compensated by cation sorption.

Titanium dioxide (TiO_2: anatase, brookite and rutile) is a widely used semiconductor photocatalyst (Fujishima *et al.*, 2000; Hashimoto *et al.*, 2005). Titanium dioxide (TiO_2) is chemically stable in acidic and basic conditions and costs relatively little (Castellote and Bengtsson, 2011). When aqueous TiO_2 suspensions are irradiated with light energy greater than the band-gap energy (E_g), TiO_2 is activated and can combine with water or dissolved oxygen (or both) to form highly reactive species, including O_2^-, $^\bullet OH$, $HO_2^\bullet$ and $O^\bullet$, which can oxidize and degrade a range of contaminants (Table 1; USEPA, 2008a; Hashimoto *et al.*, 2005). The band-gap energy of TiO_2 (anatase) is 3.2 eV, which corresponds to photons with a wavelength of 388 nm (Castellote and Bengtsson, 2011). Rutile has a 3.0 eV band-gap energy. In general, anatase gives better reaction results than rutile for hydrogen production in photocatalysis. There are several reasons why anatase is more efficient in photocatalysis. It is probably because of the higher reduction potential of photogenerated electrons in anatase than in rutile, *i.e.* the bottom of the conduction band of anatase is located at a point 0.1 V more negative than that of rutile (Hashimoto *et al.*, 2005), and the recombination of electron-hole pairs is slower in anatase than in rutile. Suttiponparnit *et al.* (2011) showed that nanoscale titanium oxide particles have different specific surface areas: (a) TiO_2 (P25) nanoparticles (27 nm) with SSA = 57.4 m^2/g; (b) anatase TiO_2 nanoparticles of 6, 16, 26, 38, 53 and 104 nm with SSA of 253.9, 102.1, 61.5, 41.2, 29.7 and 15 m^2/g, respectively; (c) rutile TiO_2 particle of 102 nm with SSA of 13.8 m^2/g. Nanoscale TiO_2 has been shown to mineralize a variety of herbicides, insecticides and pesticides *via* photocatalysis and can convert other contaminants to less toxic compounds (Konstantinou and Albanis, 2003).

Zinc oxide, a II-VI compound semiconductor, has been used as a pigment in rubber, sun-blocking ointments and paint, as well as a food supplement. Recently its application in water treatment has been acknowledged increasingly as a suitable alternative for TiO_2 due to its comparable band-gap energy (3.37 eV) and lower cost of production (Yu and Yu 2008; Sapkota *et al.*, 2011; Doria *et al.*, 2013; Hoseinzadeha *et al.*, 2014). ZnO has a large excitation binding energy (60 meV) at room temperature (Yu and Yu, 2008). ZnO nanoparticles with excitation wavelengths of 300 nm and 350 nm exhibited a strong and wide photoluminescence signal in the range 400 to 550 nm, with the energy of the excitation light being greater than the band-gap energy, having two obvious photoluminescence peaks at ~420 and 480 nm, respectively (Liqiang *et al.*, 2006). These photoluminescence signals are attributed to excitonic photoluminescence, which results mainly from surface-oxygen vacancies and defects of ZnO nanoparticles (Liqiang *et al.*, 2003).

2. Removal of arsenic

Arsenic in drinking-water is a hazard to human health, potentially causing arsenicosis, a chronic disease with a significant latency period for non-cancer (skin lesions, hyperkeratosis, melanosis, blackfoot disease, diabetes and neurological dysfunction) and cancer effects including those of bladder, skin and lung cancers (National Research Council, 1999; WHO, 2001, 2003a; Roberts *et al.*, 2004; Hopenhayn, 2006). Arsenic enters drinking water supplies from natural deposits or from agricultural, mining or industrial practices. Arsenic is present at various concentrations (<10−5300 μg/L) in the groundwater of several countries, including Bangladesh, India, Mongolia, Thailand, China, Vietnam, Nepal, Myanmar, Cambodia, Pakistan, Mexico, Argentina, Chile, Hungary, Romania, Germany, USA and Canada (Kinniburgh and Smedley, 2001; Smedley and Kinniburgh, 2002; Welch and Stollenwerk, 2003; Sun, 2004; Vaughan, 2006; Hopenhayn, 2006; Edmunds *et al.*, 2015). The WHO guideline for arsenic in drinking water is 10 μg/L.

Arsenic can occur in the environment in different oxidation states (−3, 0, +3 and +5), and in natural waters is mostly found in inorganic form as trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Redox potential and pH are the most important factors controlling arsenic speciation (Masscheleyn *et al.*, 1991). Arsenic(V) is generally the main As species in oxygen-rich surface waters and As(III) usually predominates in groundwater (Smedley and Kinniburgh, 2002). The common pentavalent (+5) species in natural waters are AsO_4^{3-}, $HAsO_4^{2-}$ and H_2AsO_4, and trivalent (+3) species are $As(OH)_3$, $As(OH)_4^-$, $AsO_2OH_2^-$ and AsO_3^{3-} (Mohan and Pittman, 2007). Toxicity depends upon the chemical species and, in general, As(III) is 20 to 60 times more toxic than As(V) (Korte and Fernando, 1991). The toxicity of arsenic for aquatic organisms decreases in the order: arsenite (As^{3+}) > arsenate (As^{5+}) > monomethylarsonic acid (CH_5AsO_3) > dimethylarsinic acid ($C_2H_7AsO_2$) > arsenobetaine ($C_5H_{11}AsO_2$) (Hindmarsh and McCurdy, 1986; Shiomi, 1994; CCME, 1999).

The most common treatment processes for arsenic removal from water include chemical precipitation, oxidation, biological oxidation, co-precipitation, adsorption, ion exchange, filtration and membrane technology (reverse osmosis, electrodialysis and nanofiltration) (NSF, 2001; Bissen and Frimmel, 2003; Holm and Wilson, 2006; Mondal *et al*., 2006; Mohan and Pittman 2007; Jain and Singh, 2012). Table 2 shows the efficiency of the main treatment process for arsenic removal. Redox-reactive minerals play a significant role in arsenic removal and can be used in several water-treatment technologies. Sometimes a combination of processes can be used, *e.g.* oxidation by filtration through zero-valent ions (Leupin and Hug, 2005).

2.1. Chemical precipitation

Chemical precipitation is an effective process used for arsenic removal and is usually applied in water treatment plants by coagulation-flocculation (Fig. 3). Four precipitation processes using redox compounds can be used: iron coagulation, iron/manganese precipitation and lime softening (Table 3).

Table 2. Main treatment processes for arsenic removal from water.

Technology	Efficiency removal	Reference
Chemical precipitation	95%	Vu *et al*. (2003)
Adsorption on different media	up to 99%	Mohan and Pittman (2007)
Chemical oxidation and filtration	80−95%	Jain and Singh (2012)
Reverse osmosis	99%	NSF (2001)
Ion exchange	>90%	Mondal *et al*. (2006)
Aeration	20−25%	Holm and Wilson (2006)

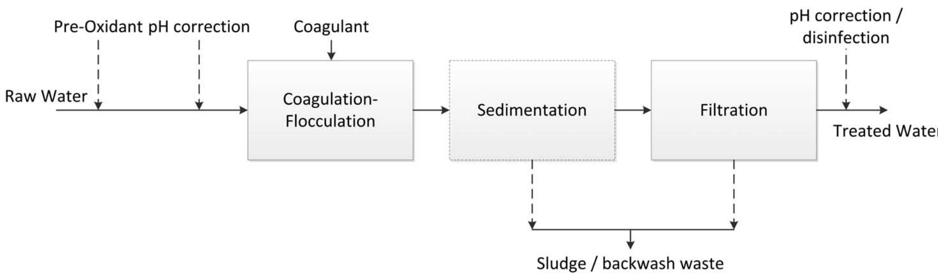

Figure 3. Schematic representation of a chemical precipitation process for water treatment. Dashed lines indicate optional processes.

Arsenic in drinking water can be removed effectively with alum if a pre-oxidant such as chlorine, potassium permanganate, ozone or hydrogen peroxide is used (Table 4). For precipitation with iron metals, ferric chloride or ferric sulfate can be used. Iron-based coagulants are usually more effective at removing As(V) than aluminium salts. This is because iron hydroxides are more stable than aluminium hydroxides in the pH range 5.5−8.5 (Jain and Singh 2012). Lakshmanan *et al.* (2008) found that the efficiency of removal of As(V) was significantly greater than As(III) when iron, titanium and zirconium coagulants (in decreasing order of efficiency) were used at pH values of 6.5, 7.5 and 8.5. Therefore, depending on the raw water characteristics, pH adjustment prior to coagulant addition may be required to achieve the optimum coagulation/precipitation. A final pH correction after disinfection is usually required to ensure acceptable pH levels in the distribution system.

When raw water (*e.g.* groundwater) contains both iron and arsenic, the best method is to oxidize Fe(II) by an aeration/oxidation process (Fig. 4) and the resulting Fe(III)

Table 3. Chemical precipitation processes for arsenic removal (modified from Mondal *et al*., 2006).

Process	Efficiency of removal (%)	Advantages	Disadvantages
Precipitation with iron	60−90	Proven and reliable	Use of chemical; high-As contaminated sludge; dose of oxidizing chemicals influences the removal efficiency.
Precipitation with Fe/Mn	40−90	Proven and reliable	Higher and lower pH reduces efficiency; use of chemical; high-As contaminated sludge; dose of oxidizing chemicals influence the removal efficiency.
Lime softening	80−90	Proven and reliable; reduces corrosion	Sulfate ions influence efficiency; secondary treatment is required; use of chemicals.

Table 4. Main oxidants used in water treatment.

Oxidant	Advantages	Disadvantages
Chlorine	Well established technology Low cost	Highly corrosive and toxic. Reacts with some organic compounds to create disinfection by-product.
Ozone	No harmful by-products Generated onsite so few problems with transport/handling Increase dissolved oxygen (DO) content in water	Complex technology Highly reactive and corrosive. Provides no residual in drinking water. Relatively high implementation cost.
Potassium permanganate	Controls taste and odour Oxidizes iron and manganese Control of DBP formation Oxidizes As(III) very quickly	Higher relative cost. No primary disinfection capability. Possibly pink colour in water. Difficulty in handling.
Hydrogen peroxide	Does not produce residuals	Reacts with various compounds.

precipitates the arsenic. Leupin and Hug (2005) found that during the oxidation of Fe(II) by dissolved oxygen, As(III) was partially oxidized and As(V) adsorbed on the hydrous ferric oxides (HFO) that formed. To improve arsenic removal, in this case, it is necessary to use an oxidant to oxidize both Fe(II) and As(III). Arsenic(V) then adsorbs onto the iron hydroxide precipitates that are ultimately filtered out of solution.

Roberts *et al.* (2004) investigated arsenic removal with Fe(II) and Fe(III) by passive treatment. They showed that application of Fe(II) was more advantageous than the Fe(III) applied usually because oxidation of Fe(II) by dissolved oxygen caused partial oxidation of As(III) and formation of Fe(III) (hydr)oxides with greater sorption capacities. Roberts *et al.* (2004) showed that five hourly additions of 5 mg of Fe(II)/L or

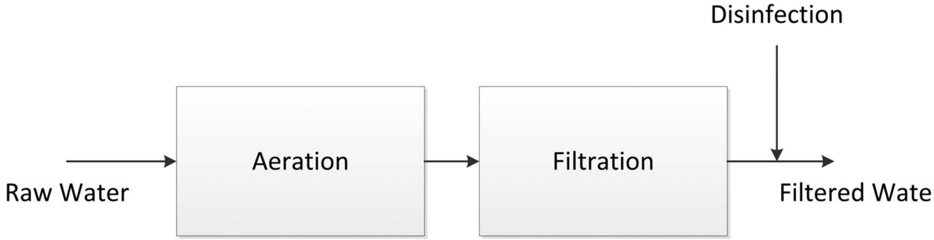

Figure 4. Schematic representation of aeration process for water treatment.

eight additions of 2.5 mg/L every 30 min to water containing 500 mg/L As(III), 3 mg/L P and 30 mg/L Si would suffice to attain the 50 ppb limit without an added oxidant. The removal efficiency of arsenic depends heavily on the initial iron and arsenic concentrations; where the Fe:As mass ratio should be at least 20:1 (Jain and Singh, 2012). Arsenic removal also depends on the anion composition of arsenic-contaminated waters. Groundwater in Bangladesh, for instance (Kinniburgh and Smedley, 2001), has high concentrations of silicate and phosphate which can influence negatively the rate of arsenic removal (Meng *et al.*, 2000, 2002).

2.2 Oxidation and adsorption

Oxidation and adsorption technologies have been used widely to treat As-polluted groundwater, reducing arsenic concentrations to <10 μg/L. Amongst the redox-based adsorbents for the removal of arsenic are iron-based sorbents (*e.g.* granular ferric hydroxide, zero-valent iron (ZVI), iron coated sand, *etc.*), red mud, activated carbon, biochar, lignite and peat (Sun *et al.*, 2006; Mohan and Pittman, 2007; Jain and Singh, 2012). Natural hematite, goethite and magnetite, for example, were also found to be suitable adsorbents to remove both As(III) and As(V) from solutions, with hematite having the highest sorption capacity, especially at acidic pH (Gimenez *et al.*, 2007). Raven *et al.* (1998) investigated arsenic adsorption on ferrihydrite. They concluded that the adsorption reaction was relatively fast and almost complete within the first few hours. They also showed that adsorption maxima arsenite and arsenate were ~0.6 and 0.25 mol As/mol Fe, respectively. Magnetite is effective in arsenic remediation (Yean *et al.*, 2005; Yavuz *et al.*, 2010). Yavuz *et al.* (2010) showed that percentage of As removal increases with decrease of magnetite particle size: (1) the magnetite particle size (MPS) was 300 nm and the As percentage removal (AsPR) was ~25–29%; (2) MPS = 20 nm and AsPR = ~91–97%; and (3) MPS = 12 nm and AsPR = ~98–99%. Joshi and Chaudhuri (1996) showed that iron oxide-coated sand might be a good material for use in small systems or home-treatment units for removing As(III) and As(V) from groundwater. Iron oxide-coated sand has more pores and a large surface area (Lo *et al.*, 1997). The system temperature has a significant influence on iron-phase formation, *i.e.* at low temperature (60ºC) only an amorphous iron phase is produced; at 150ºC goethite and hematite are produced; and at 300–500ºC only hematite forms (Lo *et al.*, 1997). Guo and Chen (2005) used bead cellulose loaded with iron oxyhydroxides (BCF) for the removal of arsenate and arsenite from aqueous systems. They determined that the adsorption capacity for arsenite and arsenate was 99.6 and 33.2 mg/g BCF at pH 7.0 with Fe content of 220 g/L. They also showed that arsenate removal is better at acidic pH but arsenite – in a wide pH range of 5–11.

Using ZVI to remove arsenic from polluted waters is quite promising, but it is still difficult to predict the mechanism and efficiency of this process due to variations in aqueous parameters (pH, water composition, oxic or anoxic conditions). For example, under oxic conditions; Fe(0) corrodes, forming various amorphous and crystalline iron-bearing phases (hematite, maghemite, lepidocrocite, magnetite, green rust) which can adsorb As(III) and As(V) (Su and Puls, 2001a, 2003; Manning *et al.*, 2002; Bang *et al.*, 2005; Leupin and Hug, 2005; Lien and Wilkin, 2005). By contrast, under anoxic conditions arsenic is adsorbed on the surface of iron in an unspecified form (Leupin and Hug, 2005). Leupin and Hug (2005) investigated the fate of arsenic and iron in a filter containing a mixture of iron filings and sand with synthetic groundwater similar to groundwater in Bangladesh. They proposed the following reactions that can occur in this system under oxic conditions:

$$Fe(0) + 2H_2O + 1/2O_2 \rightarrow Fe(II) + H_2O + 2OH^- \quad (3)$$

$$Fe(II) + 1/4O_2 + H_2O \rightarrow Fe(III) + 1/2H_2O + OH^- \quad (4)$$

$$Fep(III) + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (5)$$

$$Asp(III) + \text{intermediates } (^{\cdot}OH;\ Fe(IV)) \rightarrow As(IV) \quad (6)$$

$$As(IV) + O_2 \rightarrow As(V) + {}^{\cdot}O_2^- \quad (7)$$

It was found that Fe(II) existed partly as a dissolved compound and partly as an adsorbed complex on the surfaces of iron filings and sand. Iron(II) oxidation led to the formation of intermediate complexes (O_2^-, H_2O_2, OH and Fe(IV)), some of which are able to oxidize As(III) (Leupin and Hug, 2005). Those authors concluded that the hydrous ferric oxides formed in this system were excellent substrates for the adsorption of As(V). They found that 15−18 mg of Fe(III) are needed to remove 90% of 500 mg/L As(V) (with 3 mg/L of P and 20 mg/L of Si). Subsequently, the USEPA (2008a) showed that nanoscale zero-valent iron (nZVI) may be more effective than hydrous ferric oxide because nZVI has a high reactive surface area and can degrade contaminants more rapidly and completely than macroscale ZVI under similar environmental conditions (USEPA, 2008a). Du *et al.* (2013) developed a bifunctional resin-supported nanosized ZVI (N-S-ZVI) composite by combining the oxidation properties of $nZVI/O_2$ with adsorption features of iron oxides and anion-exchange resin N-S (as a supporter, a dispersant of nZVI and an adsorbent of anions). The maximum adsorption capacities of N-S-ZVI for As(III) and As(V) were 121 and 125 mg/g, respectively (Du *et al.*, 2013).

Manganese minerals such as manganese oxides (pyrolusite and birnessite) also play an important role in arsenic removal. The main reactions occurring in this process are: (1) reductive dissolution of MnO_2 surface; (2) oxidation of As(III) by MnO_2; and (3) adsorption of As(V) on the MnO_2 surface (Moore *et al.*, 1990; Tournassat *et al.*, 2002; Mohan and Pittman, 2007). Nesbitt *et al.* (1998) showed that the oxidation of As(III) results in the release of As(V) and Mn(II) according to the reactions:

$$2MnO_2 + H_3AsO_3 + H_2O \rightarrow 2MnOOH^* + H_3AsO_4 \quad (8)$$

$$2MnOOH^* + H_3AsO_3 + 4H+ \rightarrow 2Mn^{2+} + H_3AsO_4 + 3H_2O \quad (9)$$

where MnOOH* is a Mn(III) intermediate.

Con *et al.* (2013) investigated the properties of nano-dimensional MnO_2 (30−50 nm) prepared by redox reaction between $MnSO_4$ and $KMnO_4$ in a water–ethanol solution. The separate MnO_2 nano particles were coated on already-existing MnO_2 (pyrolusite) grains to create adsorption material for treatment of arsenic in a water environment

(Con *et al.*, 2013). The maximum adsorption capacity (84 mg/g) of arsenic on nano-MnO_2 coated on pyrolusite was about ten times greater than the maximum adsorption (8.67 mg/g) of MnO_2 produced by electrolysis oxidation coating on the same substrate (Con *et al.*, 2013).

Chakravarty *et al.* (2002) studied a low-cost ferruginous manganese ore (FMO), which consisted mainly of pyrolusite (MnO_2) and goethite (FeOOH), for the removal of arsenic from groundwater. Those authors showed that FMO can remove both As(III) and As(V) in the pH range 2.0−8.0 without any pre-treatment. They used FMO for the purification of six groundwater samples containing arsenic concentrations in the range 0.04−0.18 ppm and concluded that arsenic removals are almost 100% in all cases. The cost of the FMO is ~50−56 US$ per metric tonne (Chakravarty *et al.*, 2002).

'Greensand' is a green iron-rich clay-like mineral (*e.g.* glauconite) that has ion-exchange properties. The greensand is treated with $KMnO_4$ until the sand grains are coated with a layer of manganese oxides of various Mn valence states. Arsenic-removal processes by greensand comprise oxidation, ion exchange and adsorption. Arsenic complexes displace species from the manganese oxide (presumably OH^- and H_2O) to become bound to the greensand surface (in effect, an exchange of ions occurs). The manganese oxide surface oxidizes As(III) to As(V), which is then adsorbed onto the surface. As a result of the electron transfer and adsorption of As(V), reduced manganese (Mn(II)) is released from the surface. Subramanian *et al.* (1997) investigated the effectiveness of manganese greensand filtration (MGSF) in batch and column experiments. Batch experiments showed that the removal efficiency of arsenic by MGSF up to the interim maximum acceptable concentration (IMAC = 25 μg/L) was 60% for 24 h equilibration. In a column experiment, the removal efficiency was 41%. However, in the presence of Fe(II), especially at an Fe/As concentration ratio of 20, manganese greensand gave an overall efficiency of 83% and a throughput volume of 1440 L (Subramanian *et al.*, 1997).

Red mud, a by-product of the alumina production process, is also a promising material for the remediation of arsenic-contaminated waters (Altundogan *et al.*, 2000, 2002; Mohan and Pittman, 2007). The capacities were 4.3 μmol/g at a pH of 9.5 for As(III) and 5.1 μmol/g at a pH of 3.2 for As(V) (Altundogan *et al.*, 2002). Untreated red mud can contain high concentrations of hazardous elements including As, Pb, Hg, Cd and Cr (Ruyters *et al.*, 2011; Wang and Liu, 2012) and, therefore, requires purification before use. Seawater-neutralized red mud (Bauxol) has a higher sorption capacity with respect to arsenic (14.4 μmol/g) than unmodified red muds (Genc-Fuhrman *et al.*, 2003, 2004a,b, 2005). Furthermore, Bauxol activated by acid and heat treatment increased arsenic adsorption (Genc-Fuhrman *et al.*, 2004a,b).

In general, arsenic adsorption depends on the arsenic oxidation state, pH and property of the adsorbent surface. Usually the adsorption media is packed into a column. During the adsorption process contaminated water enters at the top of the column and flows downward through the bed and leaves through the underdrain system. The media may become clogged with suspended solids present in the feed water, resulting in increased head loss across the bed. When the maximum head loss is achieved, the media must be backwashed to remove clogging. In order to minimize an increase in head loss, it is recommended that the influent water to the column has less than 5 mg/L of suspended solids (Reynolds and Richards, 1996), otherwise a pre-filter will be necessary (Fig. 5). When the adsorbent is exhausted, the column media must be regenerated or disposed of, and replaced with new media.

2.3. *In situ* treatment technologies

Conventional engineering technologies for the treatment of groundwater, such as pump and treat, are expensive. Therefore, *in situ* technologies, like Permeable Reactive Barriers (effective passive remediation technology combining subsurface fluid-flow management with chemical and biological treatment), have received increased attention in recent years (USEPA, 1998; Blowes *et al.*, 2000; Wilkin *et al.*, 2009). For example, Blowes and Ptacek (1994) proposed the use of iron as a reactive barrier material and subsequently this technology has been developed and improved (USEPA, 1998). Lackovic *et al.* (2000) investigated ZVI as a main material for permeable reactive barriers (PRBs) to remove arsenic from groundwater. A mechanism of arsenic removal by ZVI using a combination of abiotic surface precipitation and adsorption was proposed. Those authors also demonstrated that both As(III) and As(V) could be removed effectively from aqueous solution under anoxic conditions without the use of a preoxidation step.

Zero-valent iron, used for As removal, can be corroded under the influence of dissolved oxygen (DO), forming various iron-bearing phases such as ferric oxide, oxyhydroxide and hydroxide. Several studies have shown that arsenic precipitated, co-precipitated and adsorbed onto ZVI corrosion products, including iron hydroxides, oxyhydroxides and mixed-valence Fe(II)–Fe(III) green rusts (Farrell *et al.*, 2001; Manning *et al.*, 2002; Su and Puls, 2003; Bang *et al.*, 2005; Leupin and Hug, 2005; Lien and Wilkin, 2005). Beaulieu and Ramirez (2013) applied a commercially available product containing ZVI, organic carbon substrate and sulfate to an aquifer contaminated by dissolved arsenic and iron. The PRB was capable of removing 97% of the arsenic, achieving 5 μg/L of total arsenic for ~2 y.

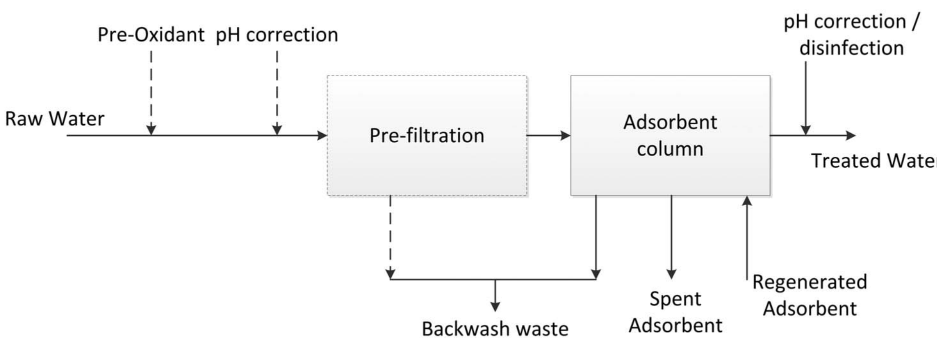

Figure 5. Schematic representation of adsorption process for water treatment. Dashed lines indicate optional processes.

It was shown that sodium-sulfate-type groundwater is better suited for arsenic treatment by ZVI than calcium-bicarbonate-type groundwater (Beak and Wilkin, 2009). This is because carbonate minerals (calcite, aragonite, *etc.*) can form in PRBs due to pH increase during the corrosion of the metallic iron (Beak and Wilkin, 2009). Precipitation of carbonate minerals can cause decreases in porosity, permeability and ZVI reactivity because iron surfaces become coated, blocking pores and cementing materials (USEPA, 2003; Beak and Wilkin, 2009). Deeper in the aquifer, sulfate from groundwater can be reduced to sulfides (usually iron sulfides) which provide additional surfaces for arsenic removal. Beak and Wilkin (2009) investigated the PRB core samples using XANES analysis and concluded that As is probably present in three forms in the PRB (*i.e.* As(V) and As(III) sorbed to Fe (oxy)hydroxides and As(III) sorbed to Fe sulfide phases. Rao *et al.* (2009) investigated the effects of humic acid on arsenic(V) removal by ZVI from groundwater. They concluded that the removal rate of arsenic by Fe(0) was inhibited in the presence of humic acid due to the formation of soluble Fe-humates in groundwater. Humic acid can also block adsorption sites (Gu *et al.*, 1994). The binding capacity of humic acid for dissolved Fe is estimated to be ~0.75 mg Fe/mg of humic acid (Rao *et al.*, 2009). Inorganic anions in groundwater, such as bicarbonate, sulfate, nitrate, silicate, phosphate and chromate, can also inhibit arsenic removal due to competition for adsorption sites on corrosion products (Su and Puls, 2001a,b, 2003; Tyrovola *et al.*, 2006). Therefore, the effect of inorganic and organic compounds on the removal of arsenic from different groundwaters should be taken into account in the design of ZVI PRBs.

Other materials such as iron-bearing minerals (*e.g.* goethite, magnetite, akaganeite, ferrihydrite, *etc.*), granular ferric hydroxide, granular ferric oxide, furnace slag, hydrous ferric oxide loaded into activated carbon or furnace slag, and composite materials (iron oxides with calcium oxides and limestone; compost with zero-valent iron, *etc.*) have also been proposed for permeable reactive barriers (USEPA, 1998; Sasaki *et al.*, 2008; Gibert *et al.*, 2010).

Zero-valent iron-based permeable reactive barrier technologies are very suitable, effective and reliable for arsenic remediation and potentially cost-effective options (they require minimal operation and maintenance expenditure), but there is still a need for more investigation of the chemistry, geochemistry, hydrogeology and microbiology involved for long-term field applications. Direct injection of nZVI into contaminated aquifers could be less costly than traditional pump-and-treat methods and using PRBs (USEPA, 2008a). To use this direct injection technology, the geological and hydrological conditions, geochemical properties of aquifer, concentration and type of contaminant must be investigated in detail in order to optimize the effectiveness of the nZVI (USEPA, 2008a). Gavaskar *et al.* (2005) indicated that the price for nZVI varied from \$20 to \$77 per pound depending on the quantity purchased. They explained that the price of nZVI has decreased in more recent years because of a decrease in the price of raw materials and increase in manufacturing capacity and number of suppliers (Gavaskar *et al.*, 2005). Information on the cost of nZVI direct injection is limited. The USEPA (2008a), for example, provided total remediation costs for three sites which varied from \$255,500 to \$4,000,000. USEPA (2008a) and Gavaskar *et al.* (2005) estimated the total nZVI injection implementation cost ranged from \$250,000 to \$1,400,000. The total nZVI injection implementation cost is quite variable and depends on many factors including: site type, environmental conditions and the geology of areas to be treated, type of contaminants, concentrations and speciation of contaminants, volume of contaminated water, installation of a monitoring well, sampling, extent of the plume, nZVI injection, post-injection sampling, reporting and any challenges that may have occurred during remediation (USEPA, 2008a; Gavaskar *et al.*, 2005).

3. Removal of nitrate

Nitrate (NO_3^-) is an essential nutrient for animals and plants (nitrogen is part of DNA and proteins) but in large concentrations may cause some health problems. Nitrate is a tasteless, colourless and odourless compound that cannot be detected unless the water is analysed chemically (Self and Waskom, 2008). The maximum recommended contaminant concentration in drinking water, according to the US Environmental Protection Agency and the World Health Organization, is: (1) 45 ppm as nitrate (NO_3^-) and 10 ppm as nitrogen in nitrate (NO_3-N) (EPA, 2009); and (2) 50 ppm as nitrate and 11 ppm as nitrogen in nitrate (WHO, 2011).

Nitrates occur naturally in soil, rocks and surface and ground waters but become potentially more hazardous because they are applied as agricultural fertilizers. The common sources of nitrite include animal waste, manure, septic systems, industrial processes, municipal wastewater and sludge (Self and Waskom, 2008). Nitrates are very soluble and dissolve easily in natural waters, causing widespread contamination. Elevated concentrations of nitrate in surface waters promote excessive growth of plankton (mainly algae) and plants causing eutrophication, as well as death of aquatic living organisms (insects, invertebrates, fish, *etc.*) due to anoxia. High concentrations of nitrate in drinking water may cause chronic diseases, birth defects, gastric problems due to the formations of nitrosamines, as well as methemoglobinemia (blue baby syndrome) which can result in brain damage and death (Camargo and Alonso, 2006; Self and Waskom, 2008).

Drinking water treatments such as conventional purification (*e.g.* coagulation, flocculation, sedimentation and filtration) are not suitable for nitrate removal. The common technologies used to remove nitrate from drinking water are chemical denitrification, distillation, ion exchange, reverse osmosis and electrodialysis (Follett and Hatfield, 2001). These methods have some limitations and difficulties when applied in small communities (Huang *et al.*, 1998; Jeong *et al.*, 2012).

3.1. Application of iron-bearing minerals

Redox-reactive minerals such as Fe(II)-bearing minerals can, potentially, remove nitrate from drinking water. It was proposed that Fe(II) can reduce nitrate to nitrite, which converts to N_2 and/or might react with dissolved organic matter (Postma *et al.*, 1991; Davidson *et al.*, 2003; Burgin and Hamilton, 2007). For example, green rusts

A pilot-scale PRB at a lead-smelting facility operated by ASARCO, East Helena, Montana, USA.

The ASARCO East Helena lead smelter is located near East Helena in Montana (USA). The plant operated from 1888 to 2001. Wilkin *et al*. (2009) showed that groundwater underneath the site is contaminated with arsenic, selenium, lead, cadmium and zinc. Plumes of arsenic and selenium have migrated offsite whereas the occurrence of other dissolved metals is restricted within site boundaries. In June 2005, a 9.1 m long (perpendicular to groundwater flow), 13.7 m deep, and 1.8 to 2.4 m wide (in the direction of groundwater flow) pilot-scale permeable reactive barrier was installed at that area. The reactive barrier was designed to treat groundwater contaminated with moderately high concentrations of both As(III) and As(V), as well as other elements. The reactive barrier was installed over three days using bio-polymer slurry methods and modified excavating equipment for deep trenching (Wilkin *et al*., 2009). The reactive medium was composed entirely of granular iron which was selected based on long-term laboratory column experiments. The trench was backfilled with a 7.6 m-thick layer of granular iron (from 6.1 to 13.7 m below ground surface) and a 6.1 m-thick layer of sand (from 0 to 6.1 m below ground surface). The top of the granular iron zone was located >2 m above the maximum groundwater level observed during site characterization studies. The base of the granular iron zone is located ~1 m above the confining ash tuff deposit. The PRB contains ~174 t of granular iron with an estimated initial porosity of ~50% (Wilkin *et al*., 2009).

A monitoring network consisting of 40 multilevel wells was installed in 2005 within and around the PRB. Wilkin *et al*. (2009) collected and analysed groundwater samples within 1, 4, 12, 15 and 25 months of operation. Arsenic concentrations were >25 ppm in wells located hydraulically upgradient of the PRB; within the PRB, arsenic concentrations were reduced to 0.01 ppm after 2 y of monitoring.

Wilkin *et al*. (2009) concluded that ZVI can be used effectively to treat groundwater contaminated with arsenic, given appropriate groundwater geochemistry and hydrology.

Source : Wilkin *et al*. (2009)

(GRs) are excellent reductants for nitrate (Hansen *et al.*, 1996; Hansen and Koch, 1998). Hansen *et al.* (1996) suggested that sulfate green rust [$Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4{\cdot}yH_2O$] should be considered as a possible important reductant for the reduction of nitrate to ammonium in subsoils, sediments or aquifers where microbially mediated reduction rates are small. Hansen *et al.* (1994) estimated the free energy of sulfate GRs formation, and indicated that GRs were stable in strongly reducible and non-acidic condition at equilibrium state. They also demonstrated that sulfate green rust reacts with nitrate producing ammonia and magnetite according to the following reaction (Hansen *et al.*, 1996):

$$[Fe_4^{II}Fe_2^{III}(OH)_{12}]SO_4(s) + 1/4NO_3^- + 3/2OH^- \leftrightarrow SO_4^{2-} + 1/4NH_4^+ + 2Fe_2O_4(s) + 6{\cdot}1/4H_2O \quad (10)$$

Hansen and Koch (1998) determined that active nitrate reducing sites were located at the green rust surface and that the accessibility of nitrate to these sites controls the reaction rate.

Redox-reactive iron-bearing clay phases (Stucki *et al.*, 1984) can also play a significant role in nitrate reduction according to Day (2010) who determined a clear relationship between the amount of Fe(II) present in the clay structure and the amount of nitrate removed from a dilute solution. The reactive sites were located on the edge surfaces of the clay layers. The reduced form of Na^+-SWa-1 smectite took up a small amount of nitrate due to coulombic repulsion between the negatively charged smectite surface and nitrate anions. This process can inhibit significantly nitrate reduction by Fe(II)-bearing smectite (Day, 2010). In order to solve this problem, Su *et al.* (2012) proposed the modification of smectite with polydiallyldimethylammonium chloride (poly-DADMAC) which resulted in the creation of a positively charged surface on the smectite where nitrate could be adsorbed easily. Then nitrate can be reduced to nitrite by the structural Fe(II) in the redox-modified smectite (Su *et al.*, 2012). Those authors demonstrated extensive nitrate reduction by the positively charged, cationic polymer-modified, reduced-Fe ferruginous smectite and concluded that these novel redox-reactivated organoclays have important adsorption and reduction properties. However, there are still many questions concerning the mechanisms and kinetics of nitrate reduction by redox-reactive iron-bearing clay.

Micro- and nano-scale zero-valent iron can also reduce nitrate (Young *et al.*, 1964; Huang *et al.*, 1998; Till *et al.*, 1998; Alowitz and Scherer, 2002; Westerhoff, 2003) through the following equation:

$$4Fe^0 + NO_3^- + 7H_2O \leftrightarrow 4Fe^{2+} + NH_4^+ + 10OH^- \quad (11)$$

Alkalinity is produced in this process and, therefore, pH is an important parameter which can influence the reaction kinetics (Huang *et al.*, 1998; Huang and Zhang; 2002; Choe *et al.*, 2004; Miehr *et al.*, 2004). Choe *et al.* (2004) investigated nitrate reduction by ZVI under anaerobic and various pH conditions. The pH rise was neutralized by the addition of acids (HCl and CH_3COOH), and NO_3^- reduction occurred continuously and completely with the appearance of green rusts at pH 6.5. Thus, the formation of green rust leads to nitrate reduction in this process.

3.2. Electrochemical methods

Electrochemical methods for nitrate removal show high potential as effective and low cost technologies which do not require the addition of chemicals before or after treatment, and which produce small amounts of sludge (Koparal and Ogutveren, 2002). The latter authors investigated the feasibility of the nitrate removal from water by an electrocoagulation method with a bipolar, packed-bed reactor filled with iron Raschig rings. The following reactions occurred in this system:

$$2H_2O + 2e \leftrightarrow H_2 + 2OH^- \text{ at the cathode} \tag{12}$$

$$Fe^0 \leftrightarrow Fe^{2+} + 2e \text{ at the anode} \tag{13}$$

$$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2 \leftrightarrow Fe(OH)_3 \text{ in the solution} \tag{14}$$

Koparal and Ogutveren (2002) found that the concentration of nitrate decreased from 300 mg/L to 50 mg/L in ~10 min with an energy consumption of about 0.7×10^{-4} kWh/g at 80 V. They also showed that electrocoagulation is more cost effective than electroreduction (energy consumption of 1×10^{-3} kWh/g).

Jeong *et al*. (2012) investigated the performance of a ZVI packed-bed bipolar electrolytic cell for nitrate removal (Fig. 6). They used ZVI not only as conductive particles but also as electron donors. In their experiment pH increased slightly due to the consumption of hydrogen ions during nitrate reduction, with iron corrosion as a product, according to the following equations:

$$NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O \tag{15}$$

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \tag{16}$$

$$2NO_3^- \; 5Fe^0 + 12H^+ \rightarrow 5Fe^{2+} + N_{2(g)} + 6H_2O \tag{17}$$

$$NO_2^- + 3Fe^0 + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O \tag{18}$$

$$2NO_2^- + 3Fe^0 + 8H^+ \rightarrow 3Fe^{2+} + N_{2(g)} + 4H_2O \tag{19}$$

$$6NO_3^- + 10Fe^0 + H_2O \rightarrow 5Fe_2O_{3(s)} + 6OH^- + 3N_{2(g)} \tag{20}$$

$$NO_3^- + 2.82Fe^0 + 0.75Fe^{2+} + 2.25H_2O \rightarrow NH_4^+ + 1.19Fe_3O_{4(s)} + 0.5OH^- \tag{21}$$

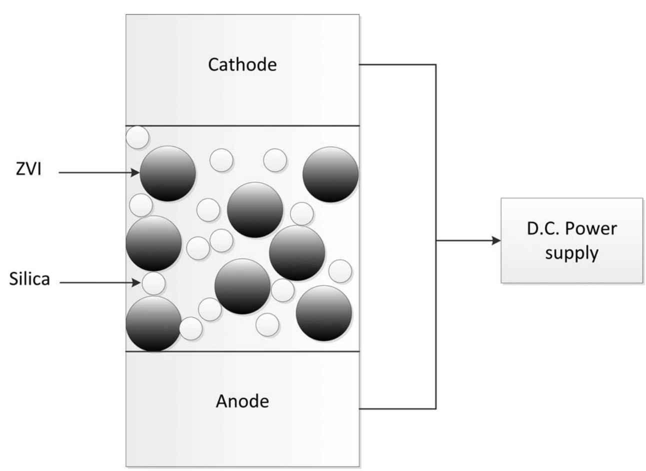

Figure 6. Schematic representation of a ZVI packed-bed bipolar electrolytic cell.

As a result of these redox reactions, ZVI removed >99% of the nitrate and the influx nitrate was converted to ammonia (20% to a maximum of 60%) and nitrite (always less than 0.5 mg/L as N in the effluent). The mechanism of nitrate removal was nitrate reduction in the lower part of the reactor under acidic conditions, followed by adsorption in the upper part of the reactor under alkaline conditions (Jeong *et al.*, 2012).

4. Removal of persistent organic pollutants

Some organic pollutants are toxic and cannot be degraded by natural environmental degradation. These organic pollutants, termed 'persistent organic pollutants' (POPs), refer to a variety of chemical compounds which contain carbon and are resistant to environmental degradation by chemical, biological and photolysis processes (Ritter *et al.*, 2007). POPs have low water contents, high fat solubilities and low vapour pressure. It has been proven that some POPs cause death or illness including certain cancers (*e.g.* breast, prostate) and endometriosis, neurobehavioural disorders, and disruption of the endocrine system (Ritter *et al.*, 2007). As a result of major threats to human health, the United Nations Environment Programme Governing Council (UNEPGC) has short-listed an initial twelve POPs substances for elimination, including organochlorine pesticides, cancer-causing polychlorinated biphenyls (PCBs) and the super-toxic dioxins and furans (Ritter *et al.*, 2007). Tonnes of POPs are being developed and manufactured every day and used in various products, including pesticides, industrial chemicals, food additives, pharmaceutical and personal care products (PPCPs), endocrine disruptor, surfactants and fuel additives (Pal *et al.*, 2010).

4.1. Conventional treatment technologies for POPs

Conventional treatment technologies for POPs in water consist of coagulation/flocculation, biofiltration, filtration and disinfection. The efficiency of POPs removal using these conventional technologies may be a joint function of the pollutant's structure and the treatment process applied.

Coagulation/flocculation, which removes only hydrophobic compounds associated with particle or colloidal material with a large organic carbon content, is not regarded as an efficient way of removing most POPs because most of these compounds are polar and hydrophilic (Yu *et al.*, 2008). Activated sludge, which uses air and a biological floc composed of bacteria and protozoa, is commonly used in municipal sewage and industrial wastewater-treatment plants (Jones *et al.*, 2002). It is possible, therefore, that POPs are easily removed by this treatment process.

Adsorption processes using either powdered activated carbon (PAC) or granular activated carbon (GAC) could play an important role in the removal of POPs (Yu *et al.*, 2008). Hydrophobic interactions are the principal mechanism in activated carbon adsorption of organic compounds (Yoon *et al.*, 2003). Therefore, POPs with higher octanol/water partition coefficients (K_{ow}) could be removed by activated carbon.

Powdered activated carbon with microfiltration (PAC-MF) systems and PAC with ultrafiltration (PAC-UF) systems, which combine PAC adsorption with low-pressuredriven membrane filtration, have shown great potential to achieve the removal of POPs from water. They have been considered as an alternative process for the remove of low molar mass compounds, including nano-sized POPs such as phenol, clofibric acid (a pharmaceutical product), methaldehyde (pesticide), which could not be removed by the membrane alone. Figure 7 shows the PAC with membrane hybrid process, in which the membrane module is arranged in connection with the adsorption reactor and operated in cross-flow mode (Delgado *et al.*, 2012). However, the PAC with membrane filtration system carries a high capital cost and energy consumption compared with conventional activated carbon processes.

Some conventional technologies have been adapted with redox processes for degradation of POPs in water and wastewater treatment. These include the ZVI with absorbent process and semiconductor (photocatalyst) with membrane filtration process (Zhang *et al.*, 2005; Luo *et al.*, 2007; Madaeni and Ghaemi, 2007; Zhu *et al.*, 2009; Doria *et al.*, 2013; Khraisheh *et al.*, 2014). As redox processes are the main topic of this book, they will be discussed in more detail in the next section.

4.2. Reduction and oxidation process for POPs

Redox processes are used in a wide variety of POPs remediation schemes for water. Generally, ZVI has been applied widely as a reductive material for the dechlorination of chlorinated organic compounds such as carbon tetrachloride (CT), trichloroethylene (TCE) and dichloroethylene (PCE) in ground and surface waters. Gillham and O'Hannesin (1994), using the results of CT reduction by ZVI, concluded that the reductive dechlorination of CT occurred at the metal surface. Matheson and Tratnyek, (1994) and Muftikian *et al.* (1995) proposed that the dechlorination process is a consequence of direct oxidative corrosion of the iron by TCE according to the following equations:

$$Fe^0 \rightarrow Fe^{2+} + 2e \tag{22}$$

$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^- \text{ (on an iron phase surface)} \tag{23}$$

Semiconductor materials (such as TiO_2 anatase phase, TiO_2 rutile phase, ZnO, CdS, ZnS, WO_3, WSe_2, $SrTiO_3$, Si, GaAs, CdTe, SnO_2, Fe_2O_3, *etc.*), which can be regarded as photocatalysts, have also been applied to remove or degrade POPs in water. These materials can generate oxidation reactions from photo-generated holes, and reduction reactions from photo-generated electrons. Among those photocatalysts, TiO_2 has been used widely in water-treatment applications. Titanium dioxide (TiO_2) is the most industrially suitable photocatalyst because it has the most efficient photoactivity, the greatest stability and the lowest cost (Hashimoto *et al.*, 2005). Figure 8 shows redox

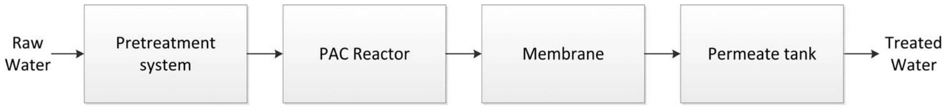

Figure 7. Schematic representation of the PAC with a membrane hybrid system.

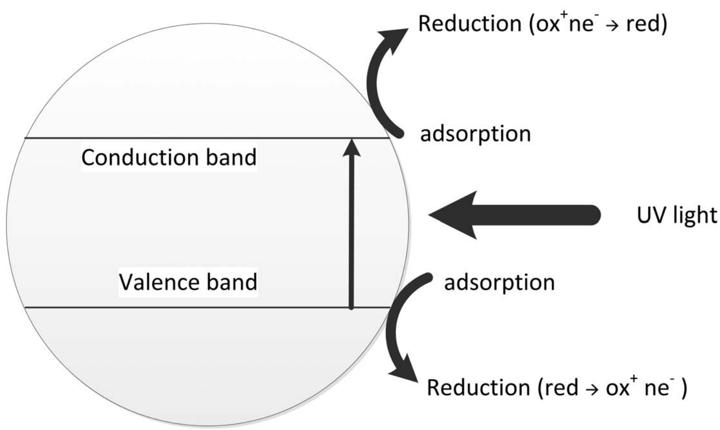

Figure 8. Redox reactions involved in the photocatalysis process.

reactions in the photocatalysis process. Khraisheh *et al*. (2014) researched the removal of pharmaceutical and personal care products, which are classified as emerging and persistent pollutants, from waters using novel TiO_2 with a coconut-shell powder composite. Three pharmaceutical and personal-care-products pollutants were removed with an efficiency of 99% from water. Doria *et al.* (2013) investigated the removal of metaldehyde (pesticide) using ZnO/Laponite composite using batch tests, and achieved greater removal efficiencies with combined redox and adsorption reactions than with an adsorption reaction only.

The photocatalyst membrane hybrid process has been investigated extensively because it has great potential for the development of efficient treatment systems compared with photocatalytic treatment or filtration system only. Membrane processes are well known in the chemical, medical, water and wastewater treatment and many other industries. Madaeni and Ghaemi (2007) investigated the effects of coating membrane surface with TiO_2 particles and UV radiation in creating self-cleaning to avoid the problem of fouling the membrane surface. Ma *et al.* (2009) invented a novel Ag-TiO_2/hydroxylapatite/Al_2O_3 bioceramic composite membrane which has anti-fouling properties and highly efficient bacterial adsorption properties. Ag-TiO_2 in this novel membrane acted as a powerful photocatalyst to attack bacteria in water.

Redox-reactive nanoparticles (NPs) have also been applied extensively to remove POPs in water. The nano-scale zero-valent iron (nZVI) technology, in which the advantages of the reductive potential of ZVI can be maintained, and the large surface area to volume can be exploited, gives rapid and high degradation efficiency for organic pollutants. Moreover, stable NPs with various chemical additives (*e.g.* polyelectrolytes, polymers, and surfactants) or NPs immobilized on inorganic or organic substrates have also been reported. Zhu *et al*. (2011) investigated the dechlorination of recalcitrant PCBs, which are one of the POPs, and a group of aromatic compounds notorious for their toxicity and persistence in the environment (UNEP, 2010). Nano-scale Ni/Fe particles were applied and compared to NZVI and nano-Ni^0. The

Chlorinated-solvent source-zone remediation *via* ZVI-Clay soil mixing at Marine Corps Base Camp Lejeune, North Carolina, USA.

ZVI-Clay was applied *in situ* with soil mixing to treat a chlorinated solvent, TeCA, TCE, and degradation products, consisting primarily of cDCE, tDCE, and VC at Site 89, Camp Lejeune, North Carolina. The dimensions of the treated zone include a surface footprint of 3010 m^2, a volume of 22,900 m^3 of soil was treated to an average depth of 7.6 m by mixing with 2% ZVI and 3% bentonite. Soil-mixing equipment (Fig. 9) included a crane, rotary table, and mixing auger were used in this field.

Figure 9. Soil mixing equipment (left) and mixing was completed using 3 m diameter augers (right) – Photos' credit: *Professor Charles Shackelford* (CSU).

In several of the soil- and groundwater-monitoring sites, the total concentration of CVOC decreased more than 99% within 1 y of completion of the mixing of ZVI-Clay with soil.

Source : Olson *et al*. (2012)

dechlorination products were more prevalent in the presence of nano-scale Ni/Fe than other redox-reactive particles, and biphenys, cyclohexyl-benzene and 1-alkyl-benzenes were detected as the main by-products. The conclusion is that the reactive nano-scale Ni/Fe can retain PCBs in subcritical water for rapid catalytic hydrodechlorination. Zhu *et al.* (2010) reported that nano-scale Cu/Fe bimetals have been used in the dechlorination of hexachlorobenzene (HBC), a representative polychlorinated additive in agricultural antiseptics. They found that HCB reduction was significantly increased by nano-scale Cu/Fe. HCB removal was nearly complete within 48 h of reaction with nano-scale Cu/Fe.

5. Removal of bacteria and other microorganisms

Bacteria and microorganisms that are not removed through filtration are usually inactivated/killed during disinfection, which is the last stage in conventional water treatment. Redox-reactive compounds commonly used for water disinfection include silver and/or copper, and these have been used for centuries due to their bactericidal and algaecidal properties. The advantage of silver and/or copper is that they do not produce by-products such as trihalomethanes during disinfection while maintaining an effective residual. Most modern silver-copper systems use electrolytic ions generated to control their concentration. The electrolytic ion generators consist of positive and negative electrodes made of the silver and/or copper contained in a vessel. To release the metal ions into the water, a DC power source is used to provide current with a potential of a few volts. The concentration of metal ions released in the water depends on the current and water flow passing the electrodes. Silver-copper systems have been used successfully in hospitals for *Legionella* control (Box 3) and ionization units range from US$40,000 to 80,000 with maintenance costs varying from US$1500 to 4000 for electrode replacement (Lin *et al.*, 2001). Silver ion systems have also been applied successfully to disinfect rainwater for human consumption in rural communities in Mexico (Adler *et al.*, 2011).

Silver-copper ionization system for Legionella's control in hospitals

A long-term study was carried out in 16 hospitals in Pennsylvania, USA, to determine the efficacy of silver-copper ionization as a disinfection method in controlling Legionella in water systems. Surveys were conducted during 1995 and 2000 to determine the hospitals' experience with the maintenance of the system, contamination of water with Legionella, and occurrence of hospital-acquired Legionnaires' Disease. Each hospital had an average of 435 beds. All 16 hospitals had cases of Legionnaires' Disease prior to installing the silver-copper disinfection system. Prior to this, most of the hospitals had other disinfection systems, including superheat and flush, ultraviolet light, and hyperchlorination. After installation, in 1995, 50% of the hospitals reported 0% positivity, and 43% still reported 0% in 2000, with respect to cases of Legionnaires' Disease. After 1995, no new cases of hospital-acquired Legionnaires' Disease were reported in any of these hospitals.

Source: Stout and Yu (2003)

TiO_2 and ZnO are redox-reactive compounds that have also been used for microbial disinfection of water by photocatalytic reaction. A recent study of the degradation of Methylene Blue found that TiO_2 nanoparticles generated more reactive oxygen species (ROS) and led to increased loss of cell viability than the ZnO nanoparticles for three of the four species of bacteria examined (*S. aureus*, *B. subtilis*, *E. coli* and *P. aeruginosa*)

(Barnes *et al*., 2013). The ZnO particles produced less ROS than the TiO_2 nanoparticles under ultraviolet light, and they were shown to be toxic to two of the bacterial species even under dark conditions. *P. aeruginosa* cells were resistant to all types of treatment indicating a potential limitation to the application of these nanoparticles for water disinfection with these redox-reactive compounds. Another study investigating inactivation of *E. coli* by TiO_2/Cu nanosurfaces (*i.e*. DC-magnetron sputtered thin films) in the dark and under low-intensity actinic light found TiO_2/Cu sputtered layers to be sensitive to actinic light (Baghriche et *al*., 2012). This work demonstrated the spectral characteristics of Cu/CuO indicating that Cu does not substitute for Ti^{4+} in the crystal lattice. The hybrid composite TiO_2/Cu sample produced fast bacterial inactivation times (<5 min) under diffuse actinic light (4 mW/cm^2). A direct relation between the film optical absorption obtained by diffuse reflectance spectroscopy and bacterial inactivation kinetics by the TiO_2/Cu samples was also demonstrated. Baghriche et *al.* (2012) suggested that the bacterial inactivation mechanism by TiO_2/Cu occurred *via* interfacial charge transfer involving charge transfer between TiO_2 and Cu.

Metallic gold is another redox-reactive compound that has been used successfully in microbial disinfection. Biodegradable Au nanocomposite hydrogels have been developed recently using acrylamide and wheat protein isolate (Jayaramudu *et al*., 2013). The gold nanoparticle composite hydrogels have been shown to be a potential candidate for antibacterial applications.

5.1. Effects of redox compounds on health and DBP production

Silver is not particularly toxic to human beings, and although large doses of this metal used for certain medical treatments have been found to cause discoloration of the skin, hair and nails (argirosis), no problems have been noted with the low concentrations needed to disinfect water. Treatment of drinking water with silver produces no by-products and the World Health Organization's (WHO) guidelines for drinking water quality indicate levels of silver of up to 0.1 mg/L can be tolerated without risk to health (WHO, 2003b). There is also insufficient evidence for negative health effects of silver ions (Lin *et al*., 2002) and copper-silver ionization (LENNTECH (b)) and their by-products.

Titanium dioxide is the most widely used photocatalyst because of its efficient photoactivity, high stability, low cost and negative toxicity for humans and animals. A study by Richardson *et al.* (1996) observed a single type of organic DBP (tentatively identified as 3-methyl-2,4-hexanedione) in ultra-filtered raw water treated with TiO_2/UV alone.

6. Conclusions

Redox-reactive minerals (green rusts, iron-bearing clay phases, ZVI, manganese oxides, TiO_2, ZnO, Ag, *etc.*) play a significant role in water-treatment processes. In this chapter we have demonstrated that proven treatment technologies using redox minerals are effective at reducing the levels of arsenic, nitrate, organic pollutants and pathogenic microbes to concentrations which are less than the recommended maximum contaminant concentrations in surface and ground water. Selection of an appropriate cost-effective treatment technology for pollutant removal from drinking water requires a detailed investigation of the quality and composition of the raw water as well as consideration of simplicity, sustainability, feasibility, reliability and costs of chosen technologies.

Knowledge is still limited on the fate, transport and toxicological effects of some redox-reactive minerals (particularly nano-scale materials such as nZVI) in the environment. For example, agglomeration of nanoscale redox-reactive minerals (nRAM) in surface and underground waters and their interaction with other compounds present in the system can impact the reactivity and mobility (transport) of nRAM. Studies related to surface modification (*e.g.* coating) of nanoparticles or addition of compounds which can inhibit nRAM agglomeration and improve water-treatment technologies with increasing mobility and activity of nRAM within aquifers are required. Further comprehensive investigations are needed to understand fully reaction mechanisms and redox-reactive mineral fates in contaminated waters, as well as to determine cost-effective and environmentally friendly waste-water management. Investigation of the kinetic and thermodynamic controls on the redox reactivity of RAM (particularly complex heterogeneous redox-reactive minerals) is very important for the future.

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