



Review

Remediation technologies for heavy metal contaminated groundwater

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ARTICLE INFO

Article history:

Received 6 January 2011

Received in revised form

17 May 2011

Accepted 3 June 2011

Available online 25 June 2011

Keywords:

Groundwater

Heavy metals

Remediation technology

Soil

Water treatment

ABSTRACT

The contamination of groundwater by heavy metal, originating either from natural soil sources or from anthropogenic sources is a matter of utmost concern to the public health. Remediation of contaminated groundwater is of highest priority since billions of people all over the world use it for drinking purpose. In this paper, thirty five approaches for groundwater treatment have been reviewed and classified under three large categories viz chemical, biochemical/biological/biosorption and physico-chemical treatment processes. Comparison tables have been provided at the end of each process for a better understanding of each category. Selection of a suitable technology for contamination remediation at a particular site is one of the most challenging job due to extremely complex soil chemistry and aquifer characteristics and no thumb-rule can be suggested regarding this issue. In the past decade, iron based technologies, microbial remediation, biological sulphate reduction and various adsorbents played versatile and efficient remediation roles. Keeping the sustainability issues and environmental ethics in mind, the technologies encompassing natural chemistry, bioremediation and biosorption are recommended to be adopted in appropriate cases. In many places, two or more techniques can work synergistically for better results. Processes such as chelate extraction and chemical soil washings are advisable only for recovery of valuable metals in highly contaminated industrial sites depending on economical feasibility.

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1. Introduction

“Heavy metal” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4000 kg m⁻³, or 5 times more than water (Garbarino et al., 1995) and they are natural components of the earth's crust. Although some of them act as essential micro nutrients for living beings, at higher concentrations they can lead to severe poisoning (Lenntech, 2004). The most toxic forms of these metals in their ionic species are the most stable oxidation states e.g. Cd²⁺, Pb²⁺, Hg²⁺, Ag⁺ and As³⁺ in which, they react with the body's bio-molecules to form extremely stable biotoxic compounds which are difficult to dissociate (Duruibe et al., 2007).

Abbreviations: AMD, acid mine drainage; BET, Brunauer, Emmett and Teller; BSR, biological sulphate reduction; EDTA, ethylenediaminetetraacetic acid; FMBO, ferric and manganese binary oxides; GAC, granular activated carbon; HA, humic acid; HFO, hydrous ferric oxides; HRT, hydraulic residence time; ISBP, in-situ bioprecipitation process; PHC, peanut husk carbon; PRB, permeable reactive barrier; SPLP, synthetic precipitation leaching procedure; SRB, sulphate reducing bacteria; TCLP, toxicity characteristics leaching procedure; UF/EUF, ultrafiltration/electro-ultrafiltration; USEPA, United States Environment Protection Agency; ZVI, zero valent iron.

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In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticides or petroleum byproducts. They can become mobile in soils depending on soil pH and their speciation. So a fraction of the total mass can leach to aquifer or can become bioavailable to living organisms (Alloway, 1990; Santona et al., 2006). Heavy metal poisoning can result from drinking-water contamination (e.g. Pb pipes, industrial and consumer wastes), intake via the food chain or high ambient air concentrations near emission sources (Lenntech, 2004). In the past decade, Love Canal tragedy in the City of Niagara, USA demonstrated the devastating effect of soil and groundwater contamination on human population (Fletcher, 2002). The diffusion phenomenon of contaminants through soil layers and the change in mobility of heavy metals in aquifers with intrusion of organic pollutants are being studied in more details in recent years (Cuevas et al., 2011; Satyawali et al., 2011).

Over the past few decades, many remediation technologies were applied all over the world to deal with the contaminated soil and aquifers. Many documents and reviews on these technologies for remediating organic and inorganic pollutants are available (Diels et al., 2005; Evanko and Dzombak, 1997; Khan et al., 2004; Mulligan et al., 2001; Scullion, 2006; USEPA, 1997; Yin and Allen, 1999). Review on heavy metal removal from waste waters is also published recently (Fu and Wang, 2011). Apart from the report by USEPA (1997), no document reviewing the heavy metal

remediation technologies for groundwater in the recent times is available. A technology functioning successfully under some operating conditions, inherently possess some limitation by virtue of which it may not function as effectively in other conditions. So, a document, summarizing all the applied and emerging technologies for heavy metal groundwater and soil remediation, along with their scopes, advantages and limitations will come handy for the scientific research community for designing newer technologies as well as in the decision making process of the heavy metal affected community trying to fish out a suitable solution for their problem.

So, in this review, we have focused on the removal of only heavy metals from groundwater, i.e. the water which is located in soil pore spaces and in the fractures of rock units. Groundwater is entirely related with the soil through which it flows. So, in the course of our review, we came across many soil remediation technologies, some of which were relevant to groundwater remediation as well have been discussed.

In the past, some technologies were applied for removing only petroleum products, some for inorganic solvent removal, while some were earmarked for heavy metal removal. Of late, this barrier has been diminishing as researchers around the world are combining various technologies to achieve desirable result. All the

reviewed technologies have been classified under three categories viz Chemical Technologies, Biological/Biochemical/Biosorptive Technologies and Physico-Chemical Technologies. In some cases, these technologies overlapped. However, this is the consequence of the changing face of the science and technology in the modern world where interdisciplinary studies are gaining ground over compartmentalized field of studies.

2. Heavy metals in ground water: sources, chemical property and speciation

Heavy metals occur in the earth's crust and may get solubilised in ground water through natural processes or by change in soil pH. Moreover, groundwater can get contaminated with heavy metals from landfill leachate, sewage, leachate from mine tailings, deep-well disposal of liquid wastes, seepage from industrial waste lagoons or from industrial spills and leaks (Evanko and Dzombak, 1997). A variety of reactions in soil environment e.g. acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange processes can influence the speciation and mobility of metal contaminants. The rate and extent of these reactions will depend on factors such as pH, Eh, complexation with other

Table 1
Speciation and chemistry of some heavy metals.

Heavy metal	Speciation and chemistry	Concentration limits	References
Lead	Pb occurs in 0 and +2 oxidation states. Pb(II) is the more common and reactive form of Pb. Low solubility compounds are formed by complexation with inorganic (Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids). The primary processes influencing the fate of Pb in soil include adsorption, ion exchange, precipitation and complexation with sorbed organic matter	Surface agricultural soil: 7–20 ppm Soil levels: up to 300 ppm USEPA, Maximum Contaminant Level (MCL) in drinking water: 0.015 ppm	(Bodek et al., 1988; Evanko and Dzombak, 1997; Hammer and Hammer, 2004; Smith et al., 1995; WHO, 2000)
Chromium	Cr occurs in 0, +6 and +3 oxidation states. Cr(VI) is the dominant and toxic form of Cr at shallow aquifers. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) (especially Ba^{2+} , Pb^{2+} and Ag^+). Cr (III) is the dominant form of Cr at low pH (<4). Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions. The leachability of Cr(VI) increases as soil pH increases	Normal groundwater concentration: < 0.001 ppm Lethal dose : 1–2 g MCL of USEPA in drinking water: 0.1 ppm	(Lenntech, 2004; Smith et al., 1995)
Zinc	Zn occurs in 0 and +2 oxidation states. It forms complexes with a anions, amino acids and organic acids. At high pH, Zn is bioavailable. Zn hydrolyzes at pH 7.0–7.5, forming $\text{Zn}(\text{OH})_2$. It readily precipitates under reducing conditions and may coprecipitate with hydrous oxides of Fe or manganese	Natural concentration of Zn in soils: 30–150 ppm Concentration in plant: 10–150 ppm Plant toxicity: 400 ppm WHO limit in water: 5 ppm	(Evanko and Dzombak, 1997; Lenntech, 2004; Smith et al., 1995)
Cadmium	Cd occurs in 0 and +2 oxidation states. Hydroxide ($\text{Cd}(\text{OH})_2$) and carbonate (CdCO_3) dominate at high pH whereas Cd^{2+} and aqueous sulphate species dominate at lower pH (<8). It precipitates in the presence of phosphate, arsenate, chromate, sulphide, etc. Shows mobility at pH range 4.5–5.5	Soil natural conc: >1 ppm Plant conc: 0.005–0.02 ppm Plant toxicity level: 5–30 ppm USEPA MCL in water: 0.005 ppm	(Matthews and Davis, 1984; Smith et al., 1995)
Arsenic	As occurs in –3, 0, +3, +5 oxidation states. In aerobic environments, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}). It behaves as chelate and can coprecipitate with or adsorb into Fe oxyhydroxides under acidic conditions. Under reducing conditions, As(III) dominates, existing as arsenite (AsO_3^{3-}) which is water soluble and can be adsorbed/coprecipitated with metal sulphides	MCL in drinking water- USEPA: 0.01 ppm WHO: 0.01 ppm	(Bodek et al., 1988; Smith et al., 1995)
Iron	Fe occurs in 0, +2, +3 and +6 oxidation states. Organometallic compounds contain oxidation states of +1, 0, –1 and –2. Fe(IV) is a common intermediate in many biochemical oxidation reactions. Many mixed valence compounds contain both Fe(II) and Fe(III) centers, e.g. magnetite and prussian blue	Tolerable upper intake level (UL) - Dietary Reference Intake (DRI): For adults: 45 mg per day For minors: 40 mg per day	(Holleman et al., 1985; Medscape)
Mercury	Hg occurs in 0, +1 and +2 oxidation states. It may occur in alkylated form (methyl/ethyl mercury) depending upon the Eh and pH of the system. Hg^{2+} and Hg_2^{2+} are more stable under oxidizing conditions. Sorption to soils, sediments and humic materials is pH-dependent and increases with pH	Groundwater natural conc: >0.0002 ppm USEPA regulatory limit in drinking water: 0.002 ppm	(Bodek et al., 1988; Smith et al., 1995)
Copper	Cu occurs in 0, +1 and +2 oxidation states. The cupric ion (Cu^{2+}) is the most toxic species of Cu e.g. $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{2+}$. In aerobic alkaline systems, CuCO_3 is the dominant soluble species. In anaerobic environments $\text{CuS}(\text{s})$ will form in presence of sulphur. Cu forms strong solution complexes with humic acids	Soil natural conc: 2–100 ppm Normal range in plants: 5–30 ppm Plant toxicity level: 30–100 ppm USEPA MCL in water: 1.3 ppm	(Dzombak and Morel, 1990; LaGrega et al., 1994)

dissolved constituents, sorption and ion exchange capacity of the geological materials and organic matter content. Ground-water flow characteristics is vital in influencing the transport of metal contaminants (Allen and Torres, 1991; Evanko and Dzombak, 1997).

The toxicity, mobility and reactivity of heavy metals depend on its speciation, which again depends upon some conditions e.g. pH, Eh, temperature, moisture, etc. In order to determine the speciation of metals in soils, specific extractants are used to solubilize different phases of metals. Through sequential extraction with solutions of increasing strengths, a precise evaluation of different fractions can be obtained (Tessier et al., 1979). The chemical form and speciation of some of the important metals found at contaminated sites are discussed in Table 1.

3. Technologies for treatment of heavy metal contaminated groundwater

Several technologies exist for the remediation of heavy metals-contaminated groundwater and soil and they have some definite outcomes such as: (i) complete or substantial destruction/degradation of the pollutants, (ii) extraction of pollutants for further treatment or disposal, (iii) stabilization of pollutants in forms less mobile or toxic, (iv) separation of non-contaminated materials and their recycling from polluted materials that require further treatment and (v) containment of the polluted material to restrict exposure of the wider environment (Nathanail and Bardos, 2004; Scullion, 2006).

In this review, we have divided the treatment technologies into the following classes: i. Chemical Treatment Technologies ii. Biological/Biochemical/Biosorptive Treatment Technologies, iii. Physico-Chemical Treatment Technologies.

The technologies that have been used over the past few years and are undergoing further tests in laboratory are also discussed. The overall classification has been pictorially presented in Fig. 1.

3.1. Chemical treatment technologies

Groundwater contaminants are often dispersed in plumes over large areas, deep below the surface, making conventional types of remediation technologies difficult to apply. In those cases, chemical treatment technologies may be the best choice. Chemicals are used to decrease the toxicity or mobility of metal contaminants by converting them to inactive states. Oxidation, reduction and neutralization reactions can be used for this purpose (Evanko and

Dzombak, 1997). Reduction is the method most commonly used (Yin and Allen, 1999). All the chemical treatment processes discussed in this section are summarized in Table 2.

3.1.1. In-situ treatment by using reductants

When groundwater is passed through a reductive zone or a purpose-built barrier, metal reductions may occur. Based on both laboratory and field studies, an appropriately created reduced zone can remain in reducing conditions for up to a year (Amonette et al., 1994; Fruchter et al., 1997). Manipulation of sub-surface redox conditions can be implemented by injection of liquid reductants, gaseous reductants or reduced colloids. A six-step enhanced design methodology as proposed by Sevougian et al. (1994) for in-situ chemical barriers is shown in Fig. 2.

Yin and Allen (1999) enlisted several soluble reductants such as sulfite, thiosulphate, hydroxylamine, dithionite, hydrogen sulphide and also the colloidal reductants e.g. Fe(0) and Fe(II) in clays for soil remediation purpose.

3.1.1.1. Reduction by dithionite. Dithionites can reduce redox sensitive metals such as Cr, U and Th to less toxic oxidation states (Yin and Allen, 1999). Dithionites can be injected just downstream of the contaminant plume to create a reduced treatment zone formed by reducing Fe(III) to Fe(II) within the clay minerals of the aquifer sediments. The flowing contaminants will either be degraded or be immobilized while passing through the zone. Amonette et al. (1994) conceptualized the dithionite ion as two sulfoxyl ($\text{SO}_2^\bullet$) radicals joined by a 2.39 pm S–S bond which was considerably longer, and hence weaker than typical S–S bonds (2.00–2.15 pm). Thus, $\text{S}_2\text{O}_4^{2-}$ tends to dissociate into two free radicals of $\text{SO}_2^\bullet$: $\text{S}_2\text{O}_4^{2-} = 2\text{SO}_2^\bullet$. Although direct reduction of trivalent structural Fe(III) in clay minerals by dithionite and strongly alkaline solutions was proposed by Sevougian et al. (1994) for smectite (Equation (1)), it was also likely to be caused by the highly reactive free radicals $\text{SO}_2^\bullet$ as shown in equation (2) (Amonette et al., 1994; Sevougian et al., 1994).

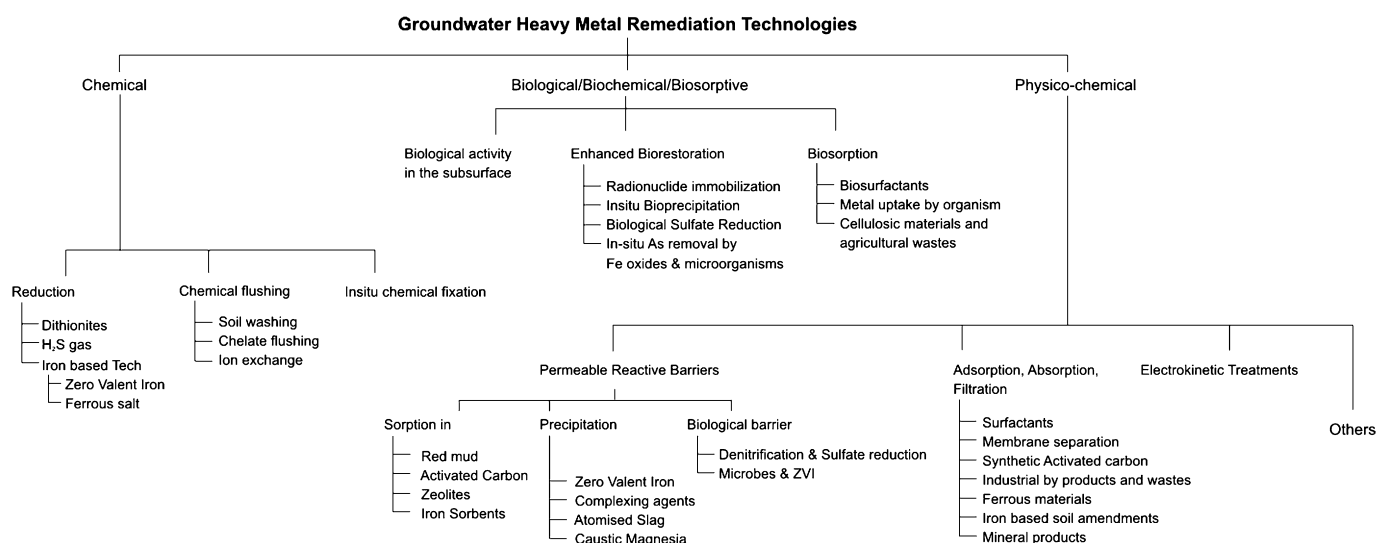
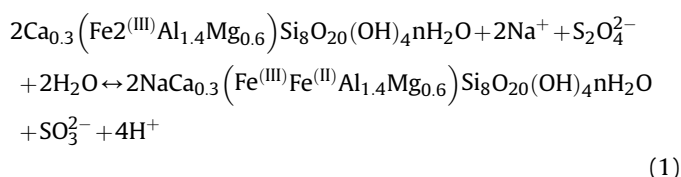


Fig. 1. Classification of groundwater heavy metal remediation technologies.

Table 2
Chemical treatment technologies: comparative overview.

Technology	Scope	Conditions and modes of application	Advantage	Disadvantage	Mechanism and process	Selected references
1. In-situ reduction processes						
1.1 Reduction by dithionites	Redox sensitive elements (Cr, U, Th)	alkaline pH and high permeability of soil. Injected in aquifer.	Active over larger area; Long lasting effect	Toxic gas intermediate; Handling is difficult	Reductive precipitation at alkaline pH	(Amonette et al., 1994; Fruchter et al., 1997; Sevougian et al., 1994)
1.2 Reduction by H ₂ S (g)	Redox sensitive metals (Cr)	In-situ application by carrier gas medium	No secondary waste generation	Toxic gas intermediate; Gas delivery to aquifer is difficult	Sulphide oxidized to sulphate and metal is precipitated as hydroxide	(Thornton and Amonette, 1999; Thornton and Jackson, 1994)
1.3 Reduction by Fe based technologies						
1.3.1 Using ZVI and Colloidal Fe	CrO ₄ ²⁻ , TcO ₄ ⁻ , UO ₂ ²⁺ , As	Injection of Fe ⁰ colloid in treatment trench or in aquifer	Can be injected in deep aquifers without toxic exposure; Regeneration possible	Production of toxic intermediate in aquifer; Modelling is difficult; Barrier integrity cannot be verified	Reductive precipitation of heavy metals and sorption on surface adsorption sites of ZVI	(Cantrell et al., 1995; Gillham et al., 1993; Manning et al., 2002; Su and Puls, 2001)
1.3.2 Cr removal by ferrous salt	Cr(III), Cr(VI)	Acidified ferrous sulphate sol ⁿ injected in wells and trenches	Besides CrO ₄ ²⁻ , it can treat TcO ₄ ⁻ , UO ₂ ²⁺ and MoO ₄ ²⁻ .	Cr(III) may get oxidized to toxic and mobile Cr(VI) under alkaline condition; Lesser depth of soil	Reductive precipitation of Cr(VI) as Cr(OH) ₃ or as the solid solution Fe _x Cr _{2-x} (OH) ₃	(CL:AIRE, 2007; Hong et al., 2007; Puls et al., 1999; Seaman et al., 1999)
2. Soil washing						
2.1 In-situ soil flushing	A wide range of heavy metals e.g. Cr, Fe, Cu, Co, Al, Mn, Mo, Ni.	Surface flooding, sprinklers, basin infiltration systems, leach fields, injection wells	Suitable for using at highly contaminated industrial sites	Mobilized contaminants may escape into environment if not trapped properly. Washing solution treatment is difficult	Desorption of metals at lower pH and recovering of leachate by pump and treat system from aquifer	(McPhillips and Loren, 1991; Moore et al., 1993; USEPA, 1995, 1997)
2.2 In-situ Chelate Flushing	Pb, Cd, Cr, Hg, Cu, Zn, Fe, As	In-situ injection of chelates e.g. EDTA, NTA, DTPA, SDTC, STC, K ₂ BDET	Ligands act at very low dose; Stable complexes formed; Chelates can be regenerated	Some chelates are persistent, toxic; Expensive process	Formation of stable chelate complexes between chelate and contaminants	(Blue et al., 2008; Hong et al., 2008; Lim et al., 2004; Warshawsky et al., 2002)
2.3 In-situ remediation by selective ion exchange	Heavy Metals and Transition Metals	In-situ use of synthetically prepared type II SIRs and ion exchange resins in PRBs	selectively remove low level of metal ions from contaminated aquifer, despite high conc of natural component	High cost; Extremely contaminant specific	Liquid–liquid extraction and ion exchange process involving a separate solid phase	(Korngold et al., 1996; Warshawsky et al., 2002)
3. In-situ chemical fixation	Pb, As and other metals in agricultural soil.	Using red mud and mixture of FeSO ₄ , CaCO ₃ , KMnO and Ca(H ₂ PO ₄) ₂	Laboratory application	Zn and Cd metals may be mobilized with increase in soil acidity	Stabilization of metals by oxidizing and trapping in the structure.	(Lombi et al., 2002; Yang et al., 2007)

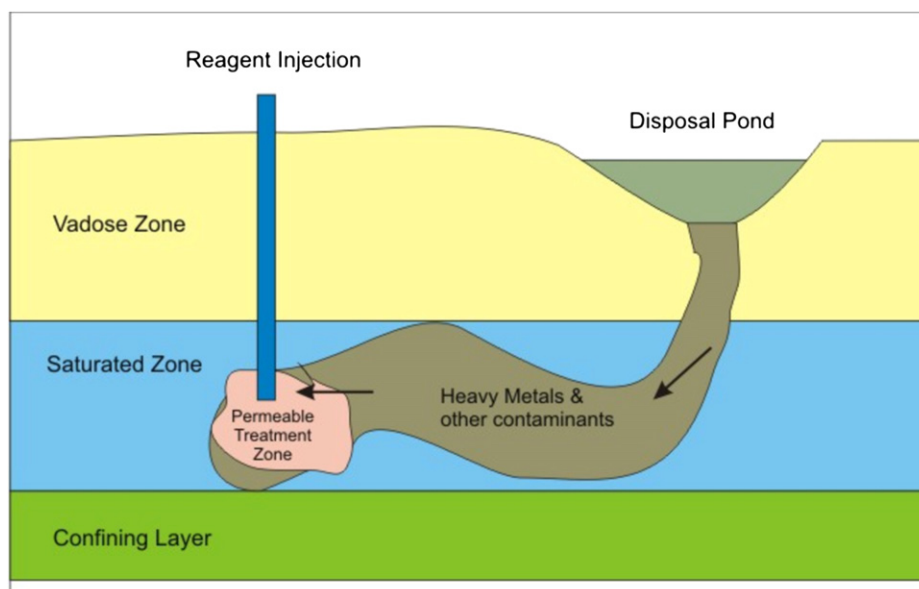
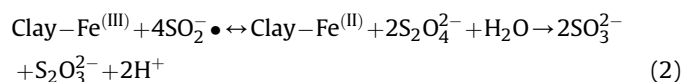


Fig. 2. Creation of a reductive treatment zone, adapted from Fruchter et al. (1997).



Fruchter et al. (1997) proposed the use of alkaline solution buffered with carbonate and bicarbonate while injecting dithionite to reduce the effect of produced H^+ on soil pH. $\text{Fe}(\text{II})$ once produced, would reduce the migrating redox-sensitive contaminants e.g. CrO_4^{2-} , U, Tc and some chlorinated solvents (Fruchter et al., 1997). Yin and Allen (1999) commented that alkaline pH and high permeability of soil are absolute necessity for this process to work. However, dithionite was found to be difficult to handle and generation of toxic gases may be a hazard. Creation of a reductive treatment zone is shown in Fig. 3.

3.1.1.2. *Reduction by gaseous hydrogen sulphide.* Gaseous hydrogen sulphide (H_2S gas) was tested for in-situ immobilization of chromate contaminated soils by Thornton and Jackson (1994), although the delivery of H_2S gas to the contaminated zone posed to be somewhat difficult. Nitrogen could be used as a carrier gas for the delivery and control of H_2S gas during treatment and also for removal of any unreacted agent from the soil after treatment. The H_2S reduced $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{III})$ state and precipitated it as an oxy-hydroxide solid phase, itself being converted to sulphate as indicated in Equation (3) (Thornton and Jackson, 1994). Due to very low solubility of sulphate and $\text{Cr}(\text{III})$ hydroxides, secondary waste generation was not an issue.

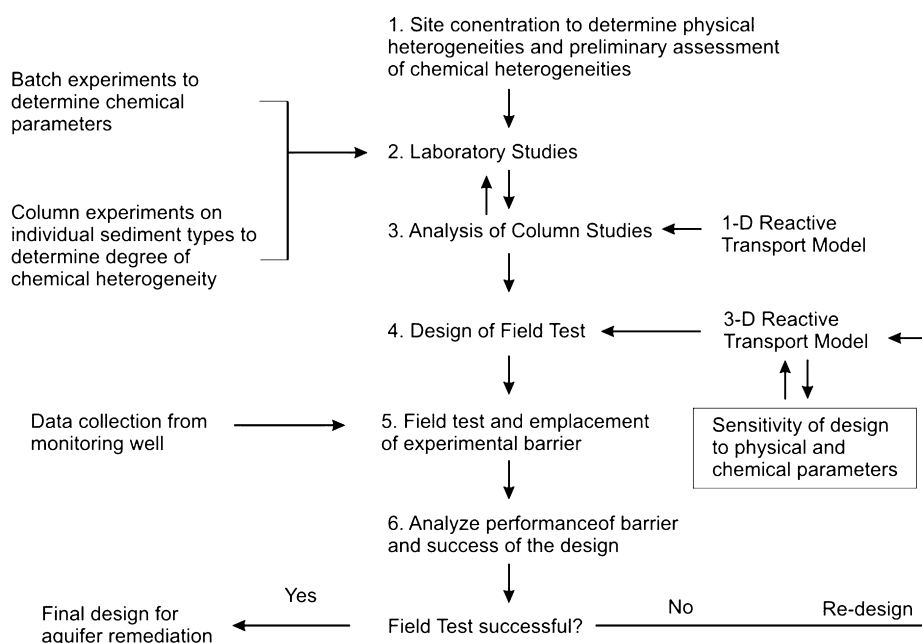
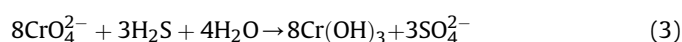


Fig. 3. Enhanced design methodology for in-situ chemical barrier, adapted from Sevougian et al. (1994).

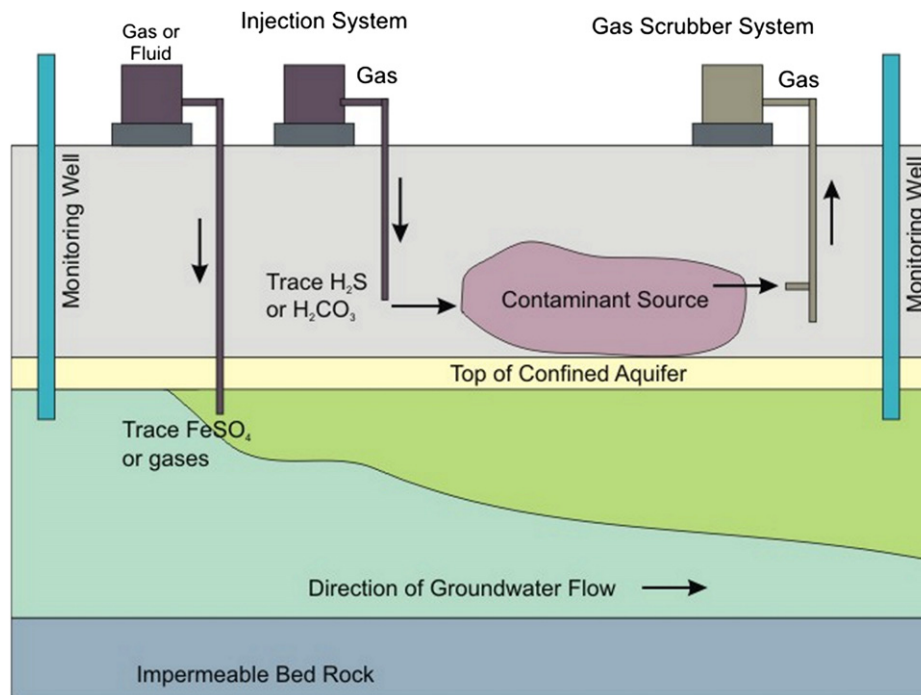


Fig. 4. In-situ gaseous treatment system, adapted from US DoE (1996).

This gaseous treatment is conceptually similar to soil venting. Researchers at the U. S. Department of Energy (1996) proposed a design for the construction of injection and withdrawal wells for in-situ gaseous treatment with H_2S (Fig. 4).

Thornton and Amonette (1999) leached 90% of Cr(VI) dispersed in soil within a column by using 100 ppm aqueous solution of H_2S . The residual Cr(VI) was found to be sequestered in unreacted grain interiors under impermeable coatings formed during H_2S treatment. Thus, this technology may be experimented for chromate contaminated aquifer treatment as well.

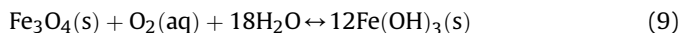
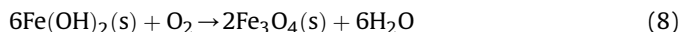
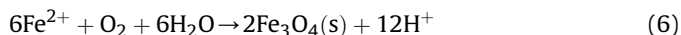
3.1.1.3. Reduction by using iron based technologies. Iron based technologies for remediation of contaminated groundwater and soil is a well documented field. The ability of iron as Fe(0) and Fe(II) to reduce the redox sensitive elements have been demonstrated at both laboratory scale and in field tests (CL:AIRE, 2007; Kim et al., 2007; Ludwig et al., 2007; Puls et al., 1999). More iron based removal processes will be discussed under the sub-sections 3.2.2.4, 3.3.1.1.1, 3.3.1.1.4, 3.3.1.2.1, 3.3.1.2.2, 3.3.1.3.2, 3.3.2.5 and 3.3.2.7.

3.1.1.3.1. Zero-valent colloidal iron (colloidal ZVI¹). ZVI (Fe^0) was found to be a strong chemical reductant and was able to convert many mobile oxidized oxyanions (e.g., CrO_4^{2-} and TcO_4^-) and oxy-cations (e.g. UO_2^{2+}) into immobile forms (Blowes et al., 1995). Colloidal ZVI of micro-nanometer particle size can be injected into natural aquifers and this was advantageous than a treatment wall filled with ZVI since no excavation of contaminated soil was needed, human exposure to hazardous materials was minimum and injection wells could be installed much deeper than trenches (Cantrell and Kaplan, 1997; Gillham et al., 1993). Furthermore, the treatment barrier created this way could be renewed with minimal cost or disturbance to above-ground areas (Yin and Allen, 1999).

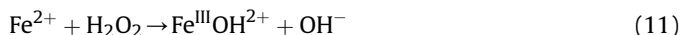
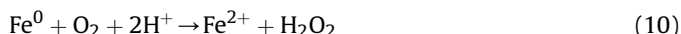
Manning et al. (2002) suggested that the As(III) removal was mainly due to the spontaneous adsorption and coprecipitation of As(III) with Fe(II) and Fe(III) oxides/hydroxides formed in-situ during ZVI oxidation (corrosion). The oxidation of ZVI by water and oxygen produces Fe(II) (Ponder et al., 2000):



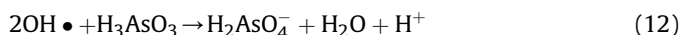
Fe(II) further reacts to give magnetite (Fe_3O_4), ferrous hydroxide ($Fe(OH)_2$) and ferric hydroxide ($Fe(OH)_3$) depending upon redox conditions and pH:



Recent research suggests that the formation of Fe^{2+} and H_2O_2 on the corroding Fe^0 surface in turn forms $OH^\bullet$ radical (Joo et al., 2004):



The As (III) oxidation reaction then proceeds as:

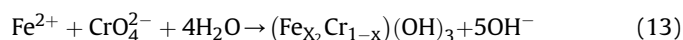


Toxic intermediates may be generated as by-product from this technique. Also, the barrier-integrity verification, effective

¹ Heavy metals are mentioned with their IUPAC symbols.

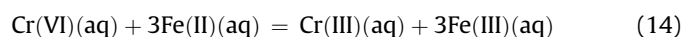
emplacement of barriers and modelling were found to be quite difficult (Joo et al., 2004).

3.1.1.3.2. Removal of chromium by ferrous salts. Puls et al. (1999) suggested the following reaction for chromate reduction and immobilization by Fe:



The toxic or carcinogenic Cr(VI) was reduced to the less toxic Cr(III) form, which readily precipitated as $\text{Cr}(\text{OH})_3$ or as the solid solution $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$. CL:AIRE (2007) reported a case where at the site of a former paper mill on the Delaware River, USA, the in situ application of an acidified solution of ferrous sulphate heptahydrate, via a combination of wells and trenches, reduced concentrations of Cr(VI) in groundwater from 85,000 $\mu\text{g L}^{-1}$ to 50 $\mu\text{g L}^{-1}$ by reductive precipitation. Here, ferrous-ammonium sulphate could also have been applied which would act relatively rapidly over neutral to alkaline pHs, thus avoiding the need for acidification.

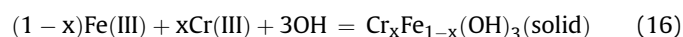
Brown et al. (1998) suggested the following reaction of ferrous sulphate to reduce Cr(VI) from the metal industry process effluents as:



If the pH of the solution was near neutral, then the following precipitates could be formed rapidly (Walker and Pucik-Ericksen, 2000):



and if excess Fe was present, then the reaction will be:



The mobile contaminants such as TcO_4^- , UO_2^{+2} and MoO_4^{2-} were also thought to be suitable for precipitation by Fe^0 . Numerous halogenated-hydrocarbon compounds and CrO_4^{2-} had been reported to be removed effectively from groundwater by this mechanism (Cantrell et al., 1995).

Seaman et al. (1999) also similarly used buffered and unbuffered Fe(II) solutions to stabilize Cr(VI) by converting it to Cr(III) and dichromate which were trapped in Fe–Al system to prevent future leaching. They concluded that this process of Cr(VI) binding might be successful at lesser depth of soil.

3.1.2. Soil washing

This technique involves washing of contaminated soil by water and other extracting agents, i.e. acid or chelating ligands added to the water to leach out the reactive contaminants from the soil (Tuin et al., 1987). According to Sikdar et al. (1998), two approaches are taken for soil washing. In the first approach, soil washing as is considered as a fractionating technique for isolating the finer particles i.e. clay, silt, or humic substances which captivates the contaminants in the soil. The washed oversize fraction can be used for refill. The wash water, remain hazardous on account of the presence of a fraction of the contaminants in it. The second approach is based on washing the entire soil with a fluid that extracts the contaminants from all size fractions. The in situ soil washing and surfactant- or solvent-assisted soil washing techniques use organic solvents, such as alcohols, polymers, poly-electrolytes, chelants, inorganic acids, or surfactants depending on site-specific circumstances. A comprehensive review on the use of chelating agents for soil heavy metal remediation was undertaken by Leštan et al. (2008). Sikdar et al. (1998) stated that soil permeability was an important determinant for in situ washing (soil flushing) since low-permeability limited the transport of liquid or

vapor through the soil. An inherent part in contaminant removal by soil washing is the use of membranes or some other technology to segregate the contaminants from the wash liquids. Dermont et al. (2008) reviewed the basic principles, applicability, advantages and limitations, methods of predicting and improving the performance of physical and chemical technologies for soil washing practiced between the period of 1990–2007. The role of membranes in the contaminant separation will be discussed later in section 3.3.2.2.

3.1.2.1. In-situ soil flushing. The flushing fluid (water or chemical extractant solutions) is applied on the surface of the site or injected into the contaminated zone. The resulting leachate can then be recovered from the underlying groundwater by pump-and-treat methods (DoD Environmental Technology Transfer Committee, 1994). In contaminated soil, metal ions remain sorbed to soil particles of natural aquifer (Evanko and Dzombak, 1997; Yin and Allen, 1999). The injection of dilute acids reduces the aquifer pH to much lower values resulting in desorption of metal ions from solid surfaces due to proton competition. Most commonly used acids for soil washing are sulphuric acid, hydrochloric acid and nitric acid (Smith et al., 1995). The fluids can be introduced by surface flooding, surface sprinklers, basin infiltration systems, leach fields, vertical or horizontal injection wells or trench infiltration systems (USEPA, 1997).

Earlier, this technique was mostly followed for the treatment of organic contaminants rather than metals. At two Superfund sites of USA, Lipari Landfill in New Jersey and the United Chrome Products site in Oregon, in-situ soil flushing was reported to be operational (USEPA, 1995). At the United Chrome Products site, Cr levels in groundwater was reduced from more than 5000 mg L^{-1} to less than 50 mg L^{-1} in areas of high concentration (McPhillips and Loren, 1991). Moore et al. (1993) suggested the use of solutions of hydrochloric acid, EDTA and calcium chloride as soil flushing agents. However, treating the washing solution for reuse can be more difficult than the soil flushing itself (Mulligan et al., 2001).

Navarro and Martínez (2010) performed soil flushing experiments to dissolve metals by water from an old mining area of size 0.9 ha contaminated by uncontrolled dumping of base-metal smelting slags. The results of the pilot-scale study showed the removal of Al (43.1–81.1%), Co (24.5–82.4%), Cu (0–55%), Fe (0–84.7%), Mn (66.2–85.8%), Mo (0–51.7%), Ni (0–46.4%) and Zn (0–83.4%). Few other metals such as As, Se, Sb, Cd and Pb were mobilized or removed in negligible amounts from the groundwater. Geochemical modelling of groundwater indicated the presence of ferrihydrite which may have caused the mobilization of As, Sb and Se.

The technical options for soil cleanup resulting in soil wash water and subsequent treatment options are shown in Fig. 5.

3.1.2.2. In-situ chelate flushing. Injecting chelating agents in contaminated soil may give rise to very stable soluble metal–chelate complexes pulling out the metals from solid phase to the solution phase. The most frequently used chelating agents are EDTA, citric acid and diethylene triamine pentaacetic acid (DTPA) (Smith et al., 1995).

Peters (1999) did some detailed work on the treatability of representative soils from a contaminated site for extracting Cu, Pb and Zn by EDTA, citric acid, nitrilotriacetic acid (NTA), gluconate, oxalate, Citranox®, ammonium acetate, phosphoric acid and pH-adjusted water. NTA, being a class II carcinogen, was avoided while EDTA and citric acid offered the greatest potential as chelating agents for removing Cd, Cu, Pb, Zn, Fe, Cr, As, and Hg simultaneously. The overall removal of Cu, Pb and Zn after multiple-stage washing were 98.9%, 98.9%, and 97.2%, respectively. Lim et al. (2004) assessed the suitability of using EDTA, NTA and DTPA to cleanup Pb(II), Cd(II)

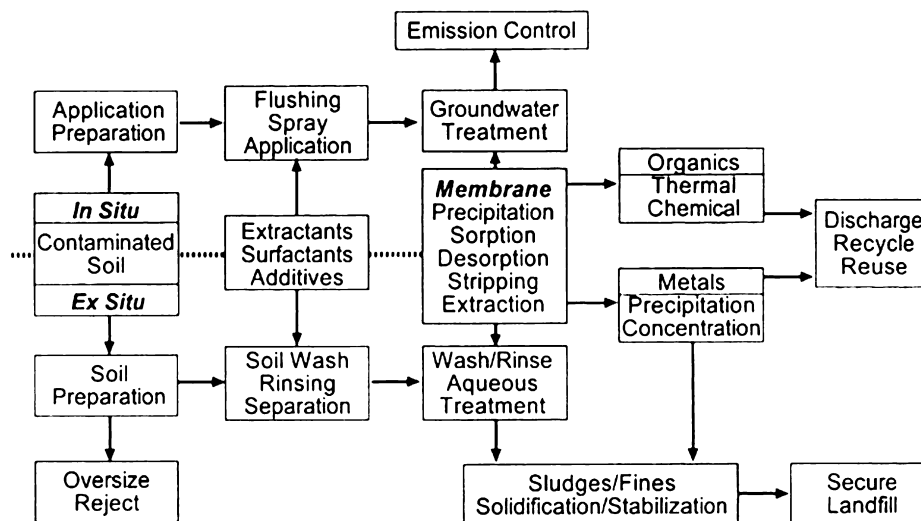


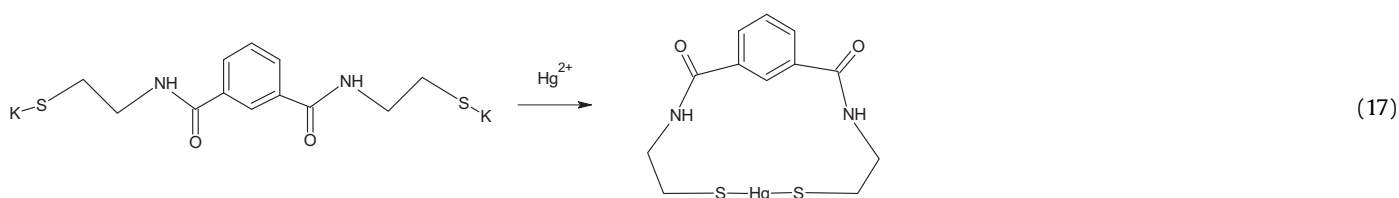
Fig. 5. A generic flow sheet for soil washing/flushing and treatment of the soil washing solution, adapted from Sikdar et al. (1998).

and Cr(III). Pb and Cd were quickly removed at low dose of the ligand. However, Cr could not be extracted by any of the 3 ligands due to its tendency to hydrolyze and slow ligand exchange kinetics of the hydrolyzed Cr species. Hong et al. (2008) reported complete extraction of Pb from a soil contaminated with 3300 mg kg^{-1} of Pb by using 100 mM EDTA within 10 min at 150 psi (10 atm) pressure. Pocięcha and Lestan (2010) also extracted 67.5% of Pb from the contaminated soil by EDTA solution, yielding washing solution with 1535 mg L^{-1} Pb and 33.4 mM EDTA. Notably, they used an aluminium anode to regenerate the EDTA by removing the extracted Pb from EDTA solution at current density 96 mA cm^{-2} and pH 10. This process removed 90% of Pb from the solution through the electrodeposition on the stainless steel cathode. Di Palma et al. (2003) proposed a two-step recovery of EDTA after washing soils contaminated with Pb or Cu. Initial evaporation led to a reduction of extractant volume by 75% and subsequent acidification resulting in precipitation of more than 90% of the EDTA complexes.

Blue et al. (2008) found out that among K_2BDET (1,3-benzenediamidoethanethiol), sodium dimethyldithiocarbamate (SDTC), sodium sulfide nonahydrate, disodium thiocarbonate (STC) and trisodium 2,4,6-trimercaptotriazine nonahydrate (TMT-55), BDET was most effective in removing Hg. One gram of BDET could treat 353 L of a sample containing 66 ppb Hg and 126 L of sample containing 188 ppb of Hg (Blue et al., 2008). The reaction between BDET and Hg is shown in equation 17.

form EDTA complexes. Recovery of EDTA up to 91.6% was achieved by evaporating and acidifying the extracted solution after filtration. Under alkaline conditions, about 99.5% of the extracted Cu was recovered. Some researchers used soil washing to reduce the amount of labile contaminant in soil before stabilizing the rest of the contaminants by using soil stabilization techniques such as in situ chemical fixation (Isoyama and Wada, 2007; Tokunaga et al., 2005). It was reported by Zhang et al. (2010) that pre-washing of contaminated soil fractions with EDTA facilitated the subsequent chemical immobilization of Cu and Cr, while Pb and Zn were mobilized, especially when $\text{Ca}(\text{OH})_2$ was added as the immobilizing agent. The influence of soil washing by chelate on the subsequent immobilization of heavy metals was found to be dominated by three competitive processes viz. the removal of labile fractions, the destabilization of less labile fractions, and chemical immobilization.

Heavy metals such as Cu, Pb and Zn were removed from few contaminated soil samples pre-treated by conventional water washing by using some chelating agents viz. [S,S]-ethylenediaminedisuccinic acid (EDDS), methylglycinediacetic acid (MGDA) and citric acid. EDDS and MGDA were equally efficient in removing Cu, Pb, and Zn after 10–60 min, reaching to maximum efficiency after 10 days. After this, the biodegradable amino polycarboxylic acids were used as a second step resulting in the release of most of the remaining metals (Cu, Pb and Zn) from the treated soils after long leaching time. This indicated that a 2 step leaching



Di Palma et al. (2005) extracted Cu by $\text{Na}_2\text{-EDTA}$ from an artificially contaminated soil and evaluated the influence of the speed of percolation and chelating agent concentration on the removal efficiency. At pH of 7.3, the flushing solution viz 500 ml of $\text{Na}_2\text{-EDTA}$ 0.05 M solution and 100 ml of pure water at 0.792 cm h^{-1} extracted up to 93.9% of the Cu. Under these operating conditions, the competitive cations such as Ca and Fe did not get the chance to

procedure with different wash liquids may be effective and time consuming (Arwidsson et al., 2010).

The problem associated with using the chelates is that most effective chelates such as EDTA and DTPA are not biodegradable and may be hazardous to environment while NTA is a carcinogen. Moreover, the chelates are expensive to use, but they can be recovered by various separation processes (Kos and Lestan, 2004;

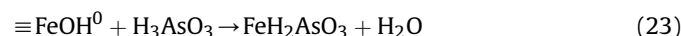
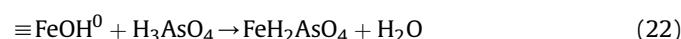
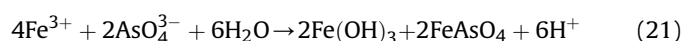
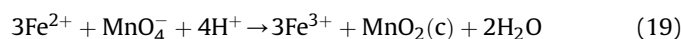
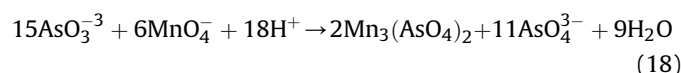
Lim et al., 2004; Luo et al., 2006; Means et al., 1980; Pocięcha and Leston, 2010; Römkens et al., 2002).

3.1.2.3. In-situ remediation of heavy metals by selective ion exchange methods. An important class of ion-exchange resins includes solvent-impregnated resins (SIRs). These materials combine the advantages of liquid–liquid extraction and ion exchange involving a separate solid phase. Korngold et al. (1996) suggested the idea to use ion-exchange resins for tap water remediation. SIRs removed very low concentration ($>1 \text{ mg L}^{-1}$) of contaminants in the presence of high concentration of microelements (e.g. calcium, magnesium, sodium, potassium and chloride) present in water at nearly neutral pH and the presence of other anions, all of which compete for available sites on the SIRs. Vilensky et al. (2002) studied the feasibility of commercial ion-exchange resins and synthetically prepared type II SIRs (Duolite GT-73 and Amberlite IRC-748, produced by Rohm and Haas) for groundwater remediation as a material for using in Permeable Reactive Barriers (PRBs). In type II SIRs, extractant molecules were bound to a functional matrix due to acid–base interactions. A major advantage of ion-exchange resins over other adsorbents is that they can be effectively regenerated up to 100% efficiency (Korngold et al., 1996; Warshawsky et al., 2002).

3.1.3. In-situ chemical fixation

Lombi et al. (2002) investigated the ability of red mud (an iron rich bauxite residue), lime and beringite (a modified aluminosilicate) to chemically stabilize heavy metals and metalloids in agricultural soil. A 2% red mud performed as effectively as 5% beringite. The red mud amendment decreased acid extractability of metals by shifting metals to the iron-oxide fraction from the exchangeable form and was much reliable.

Yang et al. (2007) tried out a new method of in-situ chemical fixation of As through stabilizing it with FeSO_4 , CaCO_3 and KMnO_4 . The initial design of the remediation experiments was based on the following possible reactions:



FeSO_4 was used as the major component of the fixation solutions due to the close association of iron compounds with arsenic and the low solubility of ferric arsenate. In two of the treatment solutions, KMnO_4 was used to oxidize any As(III) in the soil samples into the less toxic and more stable As(V). They also tested different treatment solutions, viz only FeSO_4 , $\text{FeSO}_4 + \text{KMnO}_4$ and $\text{FeSO}_4 + \text{CaCO}_3 + \text{KMnO}_4$ on sample. Although soils treated with KMnO_4 solutions showed lower mobility of arsenic than those treated with only FeSO_4 for aggressive TCLP sequential leaching, KMnO_4 treatments actually left large portions of the soil arsenic vulnerable to environmental leaching simulated using SPLP. Finally, treatment with the solution containing only FeSO_4 was considered optimal (Yang et al., 2007).

Pb and As in contaminated soil could be immobilized by the addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and FeSO_4 as stabilizing agents. Singular

addition of phosphate decreased Pb leachability, but significant mobilization and plant uptake of As was noticed. Mixtures of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and FeSO_4 immobilized both Pb and As by reducing their water solubilisation. However, the soil pH decreased from 7.8 to 5.6, mobilizing Zn and Cd (Xenidis et al., 2010).

3.2. Biological, biochemical and biosorptive treatment technologies

3.2.1. Biological activity in the sub-surface

Biological treatment methods exploit natural biological processes that allow certain plants and micro-organisms to help in the remediation of metals in soil and groundwater. Plant based remediation methods for slurries of dredged material and metal contaminated soils had been proposed since the mid-1970s (Cunningham and Berti, 1993). A number of researchers (Barona et al., 2001; Boopathy, 2000; Salt et al., 1995) were sceptical about significant metal extraction capability of plants. However, Salt et al. (1995) reported a research group in Liverpool, England, making three grasses commercially available for the stabilization of Pb, Cu and Zn wastes. Recently, a review paper focusing on the use of plants and micro-organisms in the site restoration process have been published (Kavamura and Esposito, 2010). The biological processes for heavy metal remediation of groundwater or sub-surface soil occur through a variety of mechanisms including adsorption, oxidation and reduction reactions and methylation (Means and Hinchey, 1994). According to Boopathy (2000), some of the examples of in-situ and ex-situ heavy metal bioremediation are land-farming, composting, use of bioreactors, bioventing by oxygen, using biofilters, bioaugmentation by microbial cultures and bio-stimulation by providing nutrients. Some of the other processes include bioaccumulation, bioleaching and phytoremediation. Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction, phytostabilization and rhizofiltration (Evanko and Dzombak, 1997; USDOE, 1996; Vangronsveld et al., 1995). A hyperaccumulator is defined as a plant with the ability to yield 0.1% Cr, Co, Cu, Ni or 1% Zn, Mn in the above-ground shoots on a dry weight basis (Evanko and Dzombak, 1997). Since metal hyperaccumulators generally produce small quantities of biomass, they are not suitable agronomically for phytoremediation. Nevertheless, such plants are valuable stores of genetic and physiologic material and data (Cunningham and Berti, 1993). In order to provide effective cleanup of contaminated soils, it is essential to find, breed, or engineer plants that absorb, translocate and tolerate levels of metals in the 0.1%–1.0% range and are native to the area (Salt et al., 1995). Wang and Zhao (2009) evaluated the feasibility of using biological methods for the remediation of As contaminated soils and groundwater. Ex-situ bioleaching, bio-stimulation such as addition of carbon sources and mineral nutrients, ex-situ or in-situ biosorption, coprecipitation with biogenic solids or sulphides and introduction of proper biosorbents or micro-organisms to produce active biosorbents inside the aquifer or soil were found to be suitable techniques for this purpose. Salati et al. (2010) reported a highly efficient technique of augmenting phytoremediation process by using organic fraction of municipal solid wastes (OFMSW) to enhance heavy metal uptake from contaminated soil by maize shoots. High presence of dissolved organic matter, 41.6 times greater than soil control, exhibiting ligand properties due to presence of large amount of carboxylic acids made the process very much efficient (Salati et al., 2010).

3.2.1.1. Natural biological activity. In oxygen containing aquifers, the aerobic bacteria was found to degrade a variety of organic contaminants e.g. benzene, toluene and xylenes. When all the oxygen got depleted, anaerobic bacteria, e.g. methanogens as well as sulphate and nitrate respiring bacteria continued the

degradation (Wilson et al., 1986). Baker (1995) observed that some plants such as *Urtica*, *Chenopodium*, *Thlaspi*, *Polygonum sachalae* and *Alyssim* possessed the capability of accumulating heavy metals such as Cu, Pb, Cd, Ni and Zn. So these could be considered for indirectly treating contaminated soils. To date, this field of study used to identify the botanical population of contaminated sites and selected some plants for either phytoextraction or phytostabilization purposes (Li et al., 2007; Regvar et al., 2006). However, more detailed genetic level study must be done to understand the metal uptake capability of plants. Yong and Mulligan (2004) stated that the natural attenuation level of different heavy metals varied from moderate to low levels with passage of considerable amount of time. A review paper discussing various mechanisms of natural attenuation for both organic and inorganic contaminants in soil, role of monitoring, use of models and protocols and case studies had been published by Mulligan and Yong (2004).

Practically, when large tracts of land gets contaminated, then natural vegetation such as heavy metal accumulating willow trees can cleanup the area over a long period of time (6 to 10 years) and also can generate economically valuable products (Bañuelos, 2006; Sas-Nowosielska et al., 2004). Also, *Brassica napus* (canola) and *Raphanus sativus* (radish) are shown to be effective in remediating multi-metal contaminated soil (Marchiol et al., 2004). Hellerich et al. (2008) evaluated the potential for natural attenuation of Cr(VI) for sub-wetland ground water at a Cr-contaminated site in Connecticut and concluded that the attenuation capacity could be exceeded only with high Cr(VI) concentration and extremely long Cr source dissolution timeframes. Based on the 1-D transport modelling and incorporating input parameter uncertainty, they calculated a very high probability that the Cr(VI) level will remain under the regulatory limit after the natural attenuation process. Both willow (*Salix* sp. 'Tangoio') and poplar (*Populus* sp. 'Kawa') were shown to uptake B, Cr and Cu from contaminated soils (Mills et al., 2006). Kim and Owens (2010) reviewed the potential of phytoremediation by using biosolids in contaminated sites or landfills. Moreno-Jiménez et al. (2011) performed a study on phytostabilization of heavy metals such as As, Zn, Cu, Cd and Al in the Guadamar river valley at Southern Spain and identified a native Mediterranean shrub *Retama sphaerocarpa* having promising ability to phytostabilize the heavy metal contaminated soils (Moreno-Jiménez et al., 2011). However, these processes are still not applied for groundwater remediation.

3.2.2. Enhanced bioremediation

Many of the bioremediation processes first pumped out the leaked contaminants as far as possible. Then the micro-flora population was enhanced by pumping down nutrients and oxygen through injection wells in the aquifer (Raymond, 1974). Sometimes, micro-flora such as bacteria, fungi, plant growth promoting rhizobacteria (PGPR) and *pseudomonads* were used for assisting the plant in metal uptake (Leung et al., 2006; Wu et al., 2006). In recent years, many more bioprocesses have been developed to remove a variety of heavy metals through enhanced bioremediation. Some of them have been discussed here.

3.2.2.1. Immobilization of radionuclides by micro-organisms. Researchers working on U(VI) reduction in contaminated aquifers had suggested the use of acetate as an electron donor to stimulate the activity of dissimilatory metal-reducing micro-organisms (Finneran et al., 2002a, 2002b). It was reported that the *Geobacteraceae* species available in pure culture were capable of U(VI) reduction (Lovley et al., 1991). In an experiment conducted by Anderson et al. (2003), U(VI) was substantially removed within 50 days of initiation of acetate injection. All the Fe(III) got reduced to Fe(II) thereby switching the terminal electron accepting process for

oxidation of the injected acetate from Fe(III) reduction to sulphate reduction. Sulphate reducing species of bacteria replaced the *Geobacteraceae* species resulting in the increase of U(VI) concentration once again. So optimization of acetate application was suggested to ensure long term activity of *Geobacteraceae*. Mouser et al. (2009) suggested that ammonium influenced the composition of bacterial community prior to acetate amendment. *Rhodoferrax* species predominated over *Geobacter* species at higher ammonium concentration while *Dechloromonas* species dominated the sites with lowest ammonium. However, *Geobacter* species became the predominant at all locations once acetate was added and dissimilatory metal reduction was stimulated. A number of researchers worked on the stimulation of dissimilatory metal reducing activity by micro-organisms using carbon donor amendments to immobilize U and Tc from the contaminated groundwater containing nitrate (Cardenas et al., 2008; Istok et al., 2003; North et al., 2004). Cardenas et al. (2008) reduced U(VI) concentration in a contaminated site of the U.S. Department of Energy in Oak Ridge, TN from 60 $\mu\text{g L}^{-1}$ to 30 $\mu\text{g L}^{-1}$ by conditioning the groundwater above ground thereby stimulating in-situ growth of Fe(III)-reducing, denitrifying and sulphate-reducing bacteria by injecting ethanol every week into the sub-surface.

In-situ biobarrier was used by Michalsen et al. (2009) to neutralize pH and remove nitrate and radionuclides from groundwater contaminated with nitric acid, U, and Tc over a time period of 21 months. Addition of ethanol effectively promoted the growth of a denitrifying community, increased pH from 4.7 to 6.9, promoting the removal of 116 mM nitrate and immobilizing 94% of total U(VI). *Betaproteobacteria* were found to be dominant (89%) near the source of influent acidic groundwater, whereas members of *Gamma-* and *Alphaproteobacteria* and *Bacteroidetes* increased along the flow path with increase in pH and decrease in nitrate concentrations. Groudev et al. (2010) treated experimental plots heavily contaminated with radionuclides (mainly U and Ra) and non-ferrous heavy metals (mainly Cu, Zn, Cd and Pb) in-situ using the indigenous soil micro-flora. The contaminants were solubilised and removed from the top soil layers by the dual role played by the acidophilic chemolithotrophic bacteria and diluted sulphuric acid in the acidic soil, and various heterotrophs and soluble organics and bicarbonate in the alkaline soil. The dissolved contaminants from top layer either drained away as effluent or got transferred to the deeper soil subhorizon. The sulphate-reducing bacteria inhabiting this soil subhorizon precipitated the metals in their insoluble forms such as uranium as uraninite, and the non-ferrous metals as the relevant sulphides.

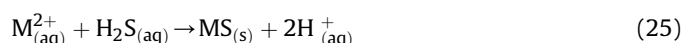
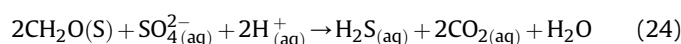
3.2.2.2. In-situ bioprecipitation process (ISBP). In situ bioprecipitation (ISBP), involves immobilizing the heavy metals in groundwater as precipitates (mainly sulphides) in the solid phase. Carbon sources such as molasses, lactate, acetate and composts are injected in the aquifer where they undergo fermentation and trap the metal ions in an organic matrix. The ISBP process was investigated for stabilizing heavy metals such as Cu, Zn, Cd, Ni, Co, Fe, Cr, As and was shown to be feasible as a strategy for improving groundwater quality (Geets et al., 2003). However, the stability of the heavy metal precipitates in the ISBP remains to be a questionable issue. Janssen and Temminghoff (2004) assessed the ISBP based on bacterial sulphate reduction (BSR) with molasses as carbon source for the immobilization of a Zn plume of concentration 180 mg L^{-1} in an aquifer with high E_h , low pH, low organic matter content and low sulphate concentrations. They used deep wells for substrate injection. Batch experiments revealed the necessity of adding a specific growth medium to the groundwater to an optimal molasses concentration range of 1–5 g L^{-1} without which, BSR could not be triggered. In an in-situ pilot experiment, Zn concentrations was

reduced from around 40 mg L⁻¹ to below 0.01 mg L⁻¹. The BSR process continued for at least 5 weeks even after termination of substrate supply (Janssen and Temminghoff, 2004).

Diels et al. (2005) observed that the interruption in the carbon source delivery stopped the ISBP. Another noticeable point was that while Cd–Zn formed stable precipitates, Ni–Co formed less stable precipitates which can undergo leaching (Diels et al., 2005). Satyawali et al. (2010) investigated the stability of Zn and Co precipitates formed after ISBP in an artificial and a natural solid liquid matrix. In the artificial matrix, the Zn precipitate was not affected by redox changes, but 58% of it got mobilized with sequential pH change. In case of the natural matrices, the stability of metal precipitates, mainly sulphur compounds Zn and Co, was largely affected by the applied carbon source.

3.2.2.3. Biological sulphate reduction (BSR). BSR is the process of reduction of sulphate to sulphide, catalyzed by the activity of sulphate-reducing bacteria (SRB) using sulphate as electron acceptor (Gibson, 1990). BSR was proved to be an effective means in reducing heavy metal concentrations in contaminated water (Suthersan, 1997). Moreover, metal sulphides due to their low solubility precipitate with metal ions already present in the solution. BSR was investigated for treatment of AMD on-site in reactive barriers (Benner et al., 1999; Blowes et al., 1995, 1998; Waybrant et al., 1998) as well as off-site in anaerobic bioreactors (Grebner et al., 2000; Hammack and Edenborn, 1992). AMD is characterized by low Eh, low pH and high concentrations of sulphate, Fe and heavy metals. The use of BSR was aimed at pH increase and sulphate and metal removal. A wide range of electron donors such as ethanol, lactate, hydrogen and economically favorable waste products, pure substrates or inoculated with monocultures or media (manure, sludge, soil) containing SRB had been reported to be quite effective in the BSR process (Annachhatre and Suktrakoolvatt, 2001; Dvorak and Hedin, 1992; Hammack and Edenborn, 1992; Lens et al., 2000; Prasad et al., 1999; van Houten et al., 1994; Waybrant et al., 1998).

According to Gibert et al. (2002), biologically mediated reduction of sulphate to sulphide, accompanied with the formation of metal sulphides occurred through the reaction sequence:



Here, CH₂O is an organic carbon and M²⁺ is a divalent metal cation. Other processes related to the pH increase and the redox potential decrease could also precipitate metals as hydroxides and carbonates (Gibert et al., 2002).

3.2.2.4. In-situ As removal from contaminated groundwater by ferrous oxides and micro-organisms. High concentration of arsenic in sub-surface aquifer may arise due to the presence of bacteria, using As bearing minerals as a energy source, reducing insoluble As(V) to soluble As(III). Das et al. (1994) reported As in groundwater of West Bengal in massive scale while Camacho et al. (2011) did a detailed study on the occurrence of As in groundwater of Mexico and south western USA.

The micro-organisms *Gallionella ferruginea* and *Leptothrix ochracea* were found to support biotic oxidation of iron by Katsoyiannis and Zouboulis (2004), who performed some experiments in laboratory where iron oxides and these micro-organisms were deposited in the filter medium, offering a favorable environment for arsenic adsorption. These micro-organisms probably oxidized As(III) to As(V), which got adsorbed in Fe(III) resulting in

overall arsenic removal of up to 95% even at high initial As concentrations of 200 µg L⁻¹ Leupin and Hug (2005) passed aerated artificial ground water with high arsenic and iron concentration through a mixture of 1.5 g iron fillings and 3–4 g quartz sand in a vertical glass column. Fe(II) was oxidized to hydrous ferric oxides (HFO) by dissolved oxygen while As(III) was partially oxidized and As(V) adsorbed on the HFO. Four filtrations reduced total As below 50 µg L⁻¹ from 500 µg L⁻¹ without any added oxidant.

Sen Gupta et al. (2009) successfully applied this principle in the field when he reversed the bacterial arsenic reduction process without using any chemical, by recharging calculated volume of aerated water (DO > 4 mg L⁻¹) in the aquifer to create an oxidized zone. This boosted the growth of iron oxidizing bacteria and suppressed the growth of As reducing anaerobic bacteria and promoted the growth of chemoautotrophic As oxidizing bacteria (CAOs) over a period of six to eight weeks. Subterranean groundwater treatment turned the underground aquifer into a natural biochemical reactor and adsorber that oxidizes and removes As along with Fe and Mn at an elevated redox value of groundwater (Eh > 300 mV in the oxidation zone). The technical diagram of the arsenic removal facility is shown in Fig. 6. The success of the process depended on controlled precipitation of Fe on the aquifer sand so that the precipitate could acquire a dense goethite or lepidocrocite type structure. Controlled precipitation of Fe(III) also ensured that it trapped As(V) as it got adsorbed on the aquifer sand and is subsequently oxidized to form a dense and compact structure, without affecting the permeability of the aquifer sand (Sen Gupta et al., 2009). The method was very effective in reducing the concentration of As below the regulatory standard of 10 µg L⁻¹ from initial concentrations of 250 µg L⁻¹ and was tested extensively in field conditions (www.insituarsenic.org). van Halem et al. (2010) also tested a community-scale facility in Bangladesh for injection of aerated water (~1 m³) into an anoxic aquifer with elevated iron (0.27 mMol L⁻¹) and arsenic (0.27 µMol L⁻¹) concentrations with successful outcomes. Saalfeld and Bostick (2009) demonstrated a process in laboratory, where biologically mediated redox processes affected the mobility of As by binding it to iron oxide in reducing aquifers through dissimilatory sulphate reduction and secondary iron reduction processes. Incubation experiments were conducted using As(III/V)-bearing ferrihydrite in carbonate-

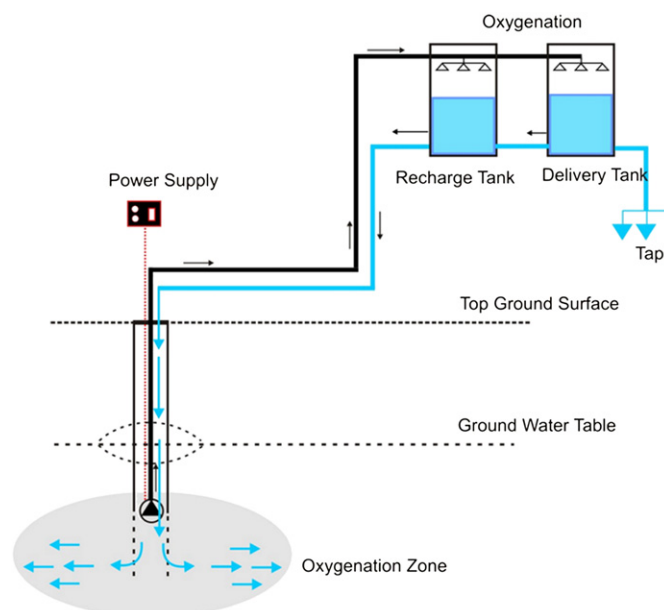


Fig. 6. Technical diagram of SAR technology.

buffered artificial groundwater enriched with sulphate (0.08–10 mM) and lactate (10 mM) and inoculated with *Desulfovibrio vulgaris* (ATCC 7757), which reduces only sulphate but not Fe or As. Magnetite, elemental sulphur and trace Fe sulphides were formed as the end products through sulphidization of ferrihydrite. It was suggested that only As(III) species got released under reducing conditions and bacterial reduction of As(V) was necessary for As sequestration in sulphides.

3.2.3. Biosorption of heavy metals

This field of remediation technology is an emerging and ever developing field but somewhat lacking in field application. Experiments with various biosorbents showed promising results. There are a number of advantages of biosorption over conventional treatment methods such as low cost, minimization of chemical or biological sludge, high efficiency, regeneration of biosorbents and possibility of metal recovery.

3.2.3.1. Metal removal by biosurfactants. Surfactants lower the surface tension of the liquid in which it is dissolved by virtue of its hydrophilic and hydrophobic groups. Decrease in the surface tension of water makes the heavy metals more available for remediation from contaminated soils (Ron and Rosenberg, 2001). Biosurfactants are biological surfactant compounds produced by micro-organisms and other organisms while glycolipids or lipopeptides are low-molecular-weight biosurfactants.

Biologically produced surfactants e.g. surfactin, rhamnolipids and sophorolipids could remove Cu, Zn, Cd and Ni from a heavy metal contaminated soil (Mulligan et al., 1999a, b; Wang and Mulligan, 2004). Mulligan and Wang (2006) used a rhamnolipid for studying its metal removal capacity both in liquid and foam forms. Rhamnolipid type I and type II, with surface tensions of 29 mN m⁻¹, were found to be suitable for soil washing and heavy metal removal (JENEIL Biosurfactant Co. LLC, 2001). The metals were removed by complex formation with the surfactants on the soil surface due to the lowering of the interfacial tension and hence associating with surfactant micelles. The best removal rates, 73.2% of the Cd and 68.1% of the Ni, were achieved by adjusting the initial solution pH value to 10. A 11% and 15% increase in Cd and Ni removal was observed by rhamnolipid foam than rhamnolipid solution of same concentration (Mulligan and Wang, 2006).

Aşçı et al. (2010) also experimented with rhamnolipids for extracting Cd(II) and Zn(II) from quartz. When 0.31 mMol kg⁻¹ Cd(II) in quartz was treated with 25 mM rhamnolipid, 91.6% of the sorbed Cd(II) was recovered. In case of Zn(II), approximately 87.2% of the sorbed Zn(II) or 0.672 mMol kg⁻¹ was extracted by using 25 mM rhamnolipid concentration. On an average, 66.5% of Zn(II) and 30.3% of Cd(II) were released at high or saturation metal ion loadings on quartz. This indicated that a fairly large portion of the metal ions was irreversibly retained by quartz (Aşçı et al., 2010).

3.2.3.2. Metal uptake by organisms. Prakasham et al. (1999) demonstrated 85–90% removal of Cr by adsorption in non-living *Rhizopus arrhizus* biomass at acidic pH of 2 in a stirred tank reactor at 100 rpm and at 1:10 biomass–liquid ratio for 4 h contact time. However, fluidized bed reactors was more efficient. At solid–liquid ratio of 1:10, the Cr ion removal was observed to be 73% for 1 h and 94% for 4 h of contact time. Braud et al. (2006) revealed that *Pseudomonas aeruginosa* and *Pseudomonas fluorescens* could extract Pb from its carbonates to an exchangeable fraction although the Pb bound to Fe–Mn oxides, organic matter and in the residual fractions remained stable. Abou-Shanab et al. (2006) reported a 15 times increase of extractable Ni with *Microbacterium arabinogalactanolyticum* depending on the initial Ni concentration in the soil. Rangsayatorn et al. (2002) studied a cyanobacteria *Spirulina*

(*Arthrospira*) *platensis* TISTR 8217 for removing low level Cd (>100 mg L⁻¹) from water. Metal sorption amounting to 78% was completed within 5 min at pH 7 and in a temperature range of 0–50°C. Earlier, *Spirulina* was used both for industrial and domestic wastewater treatments.

Pandey et al. (2008) found that *Calotropis procera*, a wild perennial plant had high uptake capacity of Cd(II) at pH 5.0 and 8.0. The adsorption equilibrium of ≥90% removal was attained within 5 min, irrespective of the Cd ion concentration. Pandey et al. (2008) deduced that at lower adsorbate concentration, monolayer adsorption or Langmuir isotherm was followed while multilayer adsorption or Freundlich isotherm was followed at higher concentrations. Other cations, viz. Zn(II), As(III), Fe(II) and Ni(II) also interfered in the adsorption process when their concentration was higher than the equimolar ratio. The involvement of hydroxyl (–OH), alkanes (–CH), nitrite (–NO₂) and carboxyl group (–COO) chelates in metal binding was indicated by the FTIR analysis. The presence of common ions viz. Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, PO₄³⁻ did not significantly interfere with metal uptake properties even at higher concentrations. The complete desorption of the Cd was achieved by 0.1 M H₂SO₄ and 0.1 M HCl.

In an innovative approach, Kim et al. (2009) used single-stranded DNA aptamers to remove As from Vietnamese groundwater. One of the As binding DNA aptamers, Ars-3, was found to have the highest affinity to both As(V) and As(III) with dissociation constants (K_d) of 4.95 ± 0.31 nM and 7.05 ± 0.91 nM, respectively. Different As concentrations ranging from 28.1 to 739.2 µg L⁻¹ were completely removed after 5 min of incubation with Ars-3.

Srivastava et al. (2011) isolated fifteen fungal strains from soils of West Bengal, India to test the biological removal of As. The *Trichoderma* sp., sterile mycelial strain, *Neocosmospora* sp. and *Rhizopus* sp. fungal strains were found to be most effective in biological uptake of As from soil, the removal rate ranging between 10.92 and 65.81% depending on pH. More research can be done with these strains to apply them in As contaminated aquifers after properly creating aerobic environment.

Therefore, a number of living organisms, micro and macro, either up took metals in their body or increased the extracted the heavy metals from their bound condition. These organisms can be applied in suitable condition for aquifer remediation but more research is required to suit them to field conditions.

3.2.3.3. Biosorption of heavy metals by cellulosic materials and agricultural wastes. Unmodified cellulose had been reported to possess low heavy metal adsorption capacity and also variable physical stability, forcing the researchers to carry out chemical modification of cellulose to achieve adequate structural durability and higher adsorption capacity for heavy metal ions (Kamel et al., 2006). O'Connell et al. (2008) reviewed a range of modified cellulose materials mainly produced by esterification, etherification, halogenation and oxidation. Some modified cellulose materials used by a number of researchers over years to remove various heavy metals have been listed in Table 3. Sud et al. (2008) also reviewed cellulosic agricultural waste materials for their capacity of significant metal biosorption. The functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino and sulphhydryl groups present in agricultural waste biomass formed metal complexes or chelates with heavy metal ions. The biosorption process occurred by chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange mechanisms.

Han et al. (2009) described the use of electrospinning process to fabricate oxidized cellulose (OC) by introducing a more porous structure inside the OC matrix, thereby increasing its capacity to chelate with metal ions. These OCs were shown to be uptaking Th and U from groundwater. The optimum pH conditions for heavy

Table 3
Heavy metal removal by modified cellulose materials.

Modified cellulose materials	Metals removed	Operating concentration (mg g ⁻¹)	References
Peanut hulls	Cu(II)	65.6	(Periasamy and Namasivayam, 1996)
Tree bark	Cu(II)	21.6	(Gaballah and Kilbertus, 1998)
Sugar cane bagasse	Pb(II)	133.6	(Peternele et al., 1999)
Orange peel	Ni(II)	80.0	(Ajmal et al., 2000)
<i>P. chrysosprum</i>	Cu(II)	26.5	(Say et al., 2001)
	Pb(II)	85.9	
	Cd(II)	27.8	
<i>P. versicolor</i>	Ni(II)	57.0	(Dilek et al., 2002)
Hazelnut shell	Ni(II)	10.1	(Demirbas et al., 2002)
<i>Trametes versicolor</i>	Cu(II)	116.9	(Bayramoglu et al., 2003)
	Pb(II)	229.9	
	Zn(II)	109.2	
Sugar beet pulp	Pb(II)	73.8	(Reddad et al., 2003)
Grape stalk waste	Ni(II)	10.6	(Villaescusa et al., 2004)
	Cu(II)	10.1	
	Pb(II)	49.9	

metal binding on modified cellulose materials were mostly observed to occur in the pH range of 4.0–6.0. Most of the adsorption mechanisms between the modified cellulose adsorbents and heavy metals were characterized either by the Langmuir model or in a lesser number of cases by the Freundlich model of adsorption. Hasan et al. (2000) indicated rubber-wood ash to be a suitable adsorbent for the Ni(II) cation from dilute solution. The adsorption reaction could be described as first order reversible reaction and the equilibrium was reached within 120 min. The optimum efficiency of adsorbing 0.492 mMol g⁻¹ of Ni(II) was obtained at pH 5 and 30 °C temperature. Above pH value of 5.5, precipitate of Ni(OH)₂ was formed, thus reducing number of available free Ni ions.

Tabakci et al. (2007) studied the sorption properties of adsorbents prepared from cellulose grafted with calix[4]arene polymers (CGC[4]P-1 and CGC[4]P-2) for adsorbing some heavy metal cations such as Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ and dichromate anions, Cr₂O₇²⁻/HCr₂O₇⁻. CGC[4]P-2 exhibited excellent sorption properties for heavy metal ions and dichromate anions at pH 1.5 but CGC[4]P-1 was not much effective (Tabakci et al., 2007).

Grape stalk, a by-product of wine production, was utilized by Martínez et al. (2006) for sorption of lead and cadmium from aqueous solutions. Maximum sorption capacities was found to be 0.241 and 0.248 mMol g⁻¹ for Pb(II) and Cd(II), respectively, at a pH value of 5.5. However, HCl or EDTA solutions desorbed 100% of Pb and 65% of Cd from the grape stalks. In addition to ion exchange process, other mechanisms, such as surface complexation and electrostatic interactions, were thought to be involved in the adsorption process. Amin et al. (2006) used untreated rice husk for complete removal of both As(III) and As(V) from aqueous solution at an initial As concentration of 100 µg L⁻¹ in 6 g of rice husk at a pH range of 6.5 to 6.0. Desorption in the range of 71–96% was observed when rice husk was treated with 1 M of KOH. Sahu et al. (2009b) used activated rice husk to achieve maximum Pb and BOD reduction of 77.15% and 19.05%, respectively in a three phase modified multi-stage bubble column reactor (MMBCR). Walnut hull was studied for Cr(VI) adsorption from solution and was found to be pH-dependent, reaching 97.3% at pH 1.0. The efficiency increased with temperature and with increasing initial Cr(VI) concentration up to 240–480 mg L⁻¹, and decreased with increasing adsorbent concentration ranging from 1.0 to 5.0 g L⁻¹. Sodium chloride, as supporting electrolyte in the medium,

induced a negative effect on the efficiency. So, besides the modified cellulose materials, the simple walnut hull demonstrated good performance and can be tested out in field application (Wang et al., 2009).

Munagapati et al. (2010) studied the kinetics, equilibrium and thermodynamics of adsorption of Cu(II), Cd(II) and Pb(II) from aqueous solution on *Acacia leucocephala* bark powder. The biosorption capacity followed the order Pb(II) > Cd(II) > Cu(II) at optimum conditions of pH 4.0, 5.0 and 6.0 at biosorbent dosage of 6 g L⁻¹. The biosorption process best fitted the pseudo-second-order kinetic model, was exothermic and spontaneous. It was concluded that *A. leucocephala* bark powder could be used as a low cost, effective biosorbent for the removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solution (Munagapati et al., 2010). The cellulose materials and agricultural wastes therefore show promising results depending on pH and polymerization reactions. Nevertheless, more extensive research is required for their field application.

The biological, biochemical and biosorption treatment processes are summarized in Table 4.

3.3. Physico-chemical treatment technologies

The techniques are dependent upon physical processes or activities such as civil construction of barriers, physical adsorption or absorption, mass transfer as well as harnessed chemical or biochemical processes are discussed here. Most of the times, two or more processes are coupled together to deal with the contamination problem. The physico-chemical treatment processes are summarized in Table 5.

3.3.1. Permeable reactive barriers (PRB)

USEPA (1989) defined Permeable Reactive Barrier (PRB) as 'an emplacement of reactive media in the sub-surface designed to intercept a contaminated plume, provide a flow path through the reactive media and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier'. The concept behind PRB is that a permanent, semi permanent or replaceable reactive media is placed in the sub-surface across the flow path of a plume of contaminated groundwater which must move through it under its natural gradient, thereby creating a passive treatment system. Treatment walls remove contaminants from groundwater by degrading, transforming, precipitating, adsorbing or adsorbing the target solutes as the water flows through permeable reactive trenches (Vidic and Pohland, 1996). PRBs are designed to be more permeable than the surrounding aquifer materials so that water can readily flow through it maintaining groundwater hydrogeology while contaminants are treated (Yin and Allen, 1999). The reactive cell is generally constructed approximately 0.6 m above the water table and 0.3 m keyed into the aquitard, deeper in case of the funnel-and-gate system. Such construction would prevent contaminants from flowing either on top or bottom of the reactive cell. Gavaskar et al. (1998) summarized four possible arrangements for construction of the reactive cell (Fig. 7). Adequate site characterization, bench-scale column testing, and hydrogeologic modelling are essential for designing and constructing PRBs (Gavaskar, 1999). Lee et al. (2009) proposed a design-specific site exploration approach for PRB designing called quantitatively directed exploration (QDE), employing three spatially related matrices such as covariance of input parameters, sensitivity of model outputs and covariance of model outputs to identify the ideal location for the PRB (Lee et al., 2009).

Table 4

Biological/biochemical treatment technologies: comparative overview.

Technology	Scope	Conditions and modes of application	Advantage	Disadvantage	Mechanism and process	Selected references
1. Biological activity in the sub-surface	Cr, Co, Cd, Ni, Zn, Pb, Cu	In-situ culture of aerobic bacteria and planting of trees. Only in shallow sub-surface	Very little cost; Applicable to large tract of land over long time	Not suitable for aquifer remediation; Very slow process; No modelling can be done	Oxidation, precipitation, bioaccumulation	(Baker, 1995; Salati et al., 2010; Wilson et al., 1986; Yong and Mulligan, 2004)
2. Enhanced bioremediation						
2.1 Immobilization of radionuclides by micro-organisms	U, Ra, Tc	Injecting carbon donor e.g. acetate to support <i>Geobacter</i> species of bacteria in biobarrier	No harmful byproducts are produced	Acetate injection to be optimized to prevent growth of SRB	Reduction, agglomeration, absorption of U(IV) into sediments	(Anderson et al., 2003; Finneran et al., 2002a; Finneran et al., 2002b; Mouser et al., 2009)
2.2 ISBP	Cu, Zn, Cd, Ni, Co, Fe, Cr, As	Injection of Carbon source (e.g. molasses) in aquifer by deep wells	Cheap carbon sources available	Heavy metal ppts (e.g. Ni and Co) may remobilize with changing soil pH	Fermentation of carbon sources inside aquifer and trapping of heavy metals inorganic matrix	(Diels et al., 2005; Geets et al., 2003; Janssen and Temminghoff, 2004; Satyawali et al., 2010)
2.3 BSR	Divalent metal cations	Injection of electron donors and inoculating the soil or aquifer with bacterial cultures.	On-site remediation of AMD; Offsite use in bioreactors; Can be used in PRBs	Reaction rate limited and requires sufficient residence time.	Reduction of sulphate to metal sulphide ppts, catalyzed by the activity of SRB.	(Dvorak and Hedin, 1992; Gibert et al., 2002; Hammack and Edenborn, 1992; Hammack et al., 1994; Waybrant et al., 1998)
2.4 In-situ As removal by ferrous oxides and micro-organisms	As, Fe, Mn	In-situ oxidation of Fe(II) and As(III) by injecting aerated water in aquifer by boosting aerobic As oxidizing bacteria	No chemicals used; No waste produced; Low operating cost	Regular injection of aerated water needed to maintain oxidation zone	Oxidation of Fe(II) and As(III) by elevating Eh and boosting microbial growth and then co-precipitating As, Fe and Mn	(Camacho et al., 2011; Katsoyiannis and Zouboulis, 2004; Leupin and Hug, 2005; Sen Gupta et al., 2009)
3. Biosorption of heavy metals						
3.1 Biosurfactants	Cd, Zn, Ni	Experimental use in laboratory with rhamnolipids solution and foam	High metal retention capacity	Not tested in field. Foam is supposed to be more suitable, but transportation to deep aquifers can be tough	Bioadsorption through metal complex forming with surfactants due to lowering of interfacial tension	(Asçi et al., 2010; Mulligan and Wang, 2006; Ron and Rosenberg, 2001)
3.2 Uptake by organisms	Cd, Cr, Zn, As, Fe, Ni	Laboratory experiments done within pH 2–8 to remove Cd and Cr from aqueous solution.	Zn, As, Fe, Ni can also get adsorbed, anions do not interfere	Desorption of the Heavy metals under high acidic condition	Bacteria, fungus, plants and DNA aptamers uptook metals in cell cytoplasm, or stabilized them	(Kim et al., 2009; Pandey et al., 2008; Prakasham et al., 1999; Srivastava et al., 2011)
3.3 Cellulosic materials and agricultural wastes	Pb, Ni, Cu, Cd, Zn	Lab expt with a range of modified cellulose materials	Low cost cellulose materials. Large range of heavy metals can be treated	No significant field study done	Bioadsorption of heavy metals in modified cellulose structure at pH range 4–6	(Han et al., 2009; Hasan et al., 2000; Kamel et al., 2006; Sahu et al., 2009a; Sud et al., 2008; Tabakci et al., 2007)

Table 5

Physico-chemical treatment technologies: comparative overview.

Technology	Scope	Conditions and modes of application	Advantage	Disadvantage	Mechanism and process	Selected references
1. Permeable reactive barriers						
1.1 Sorption process in PRBs						
1.1.1 Red mud	Pb, As, Cd, Zn	In-situ application (acidified or non acidified) in PRBs in aquifers	Cheap by-product from Al industry; High sorption capacity, adsorbed metals remain immobile	Sorbs cations with lesser ionic radii; Depends on pH	Sorption of metal cations in the channels of negatively charged cancrinite framework	(Apak et al., 1998; Brunori et al., 2005; Gupta and Sharma, 2002; Santona et al., 2006)
1.1.2 Activated Carbon and peat	Cr, Cd and other heavy metals	In-situ application in PRBs mainly in granular form (GAC)	High adsorption capacity; Regeneration possible; Acts better when coupled with microbes	More field-scale studies on inorganic and metal adsorption is needed	Adsorption by high surface area (about 1000 m ² g ⁻¹) and presence of surface functional groups	(Fine et al., 2005; Han et al., 2000; Huttenloch et al., 2001; Thiruvengkatachari et al., 2008)
1.1.3 Zeolites, (clinoptilolite, chabazite-phillipsite, clinoptilolite, fly ash zeolites)	Cd, Cu, Ni, Cr, As	In-situ application in PRBs	Very high adsorbing capacity; Hundreds of natural zeolites are available	Selective adsorption capacity	Adsorption, ion exchange, catalytic and molecular sieving through 3D aluminosilicate structure	(ITRC, 2005; Roehl et al., 2005; Ruggieri et al., 2008; Xenidis et al., 2010)
1.1.4 Iron sorbents (ZVI and pyrite)	As(III), As(V), Hg	In-situ application in PRBs	ZVI and pyrite are cheap; Handling is easy	As gets released in presence of silicate and phosphate in aquifer or soil	As trapped by rust of ZVI and Hg trapped by complex formation on pyrite adsorption sites.	(Bower et al., 2008; Su and Puls, 2001; Sun et al., 2006)
1.2 Chemical precipitation						
1.2.1 Reaction with ZVI	Cr, As, Cr, Ni, Pb, Mn, Se, Co, Cu, Cd, Zn, Ca, Mg, Sr and Al	In-situ application in PRBs synergistically with electrokinetic treatment	With support of electrokinetic method, natural reactions can be mimicked	Clogging of barrier by metal hydroxides and carbonates. ZVI also gets corroded	With corrosion of ZVI, pH increased, redox potential decreased, DO was consumed and Fe(II) was generated with reduction and precipitation of other metals	(Faulkner et al., 2005; Hopkinson and Cundy, 2003; Jeon et al., 2011; Jun et al., 2009; Puls et al., 1999; USEPA, 1998)
1.2.2 Alkaline Complexation agents (lime, CaCO ₃ , hydroxides)	Heavy metals in AMD	In-situ application of Hydrated lime in PRBs	Cheap reagent; Can remediate a no of anionic and cationic contaminants	Alkaline agent gets spent with passage of time	pH becomes 12, metal hydroxides are formed and metal solubility decreases	(ITRC, 2005; Roehl et al., 2005)
1.2.3 Atomized Slag	Cd, As, Pb, Cr, Cu	In-situ combination of atomized slag and sand system in PRBs	Cheap slag material from Fe and steel industry; Can treat wastewater and leachate	Highly sensitive to pH and presence of other organic materials	Metal precipitation depending on pH and then sorption in the atomized slag	(Ahn et al., 2003; Chung et al., 2007)
1.2.4 Caustic Magnesia	Co, Cd, Ni, Zn, Cu, Pb, Mn, Al, Fe	In-situ application in PRBs	Traps multiple metals; Cheap material	At later stage Cd, Co and Ni may dissolve	Mg(OH) ₂ formed and pH becomes 8.5 when metals form hydroxides and precipitates	(Cortina et al., 2003; Rötting et al., 2006)
1.3 Biological barriers in PRB						
1.3.1 Denitrification and BSR	Fe, Ni, Zn, Al, Mn, Cu, U, Se, As, V, Cr	In-situ application of organic carbon and SRBs in PRBs for AMD	Removes both divalent and trivalent heavy metal species; 95% metal removal in PRBs	Steady supply of nutrients should be provided to sustain microbial population	Divalent metals get removed as sulphide while trivalent metals form hydroxide and oxyhydroxide	(Benner et al., 1999; Jarvis et al., 2006; Jeyasingh et al., 2011; Thiruvengkatachari et al., 2008)
1.3.2 Mixing biotic components with ZVI	Cr, As, Pb, Cd, Zn, Sr, Ni	In-situ application of Fe ⁰ , bacteria and organic nutrients in PRBs	Able to treat mixtures of contaminants (nitrate, organic and heavy metals) together	PRB should provide C,N and P for growth and reproduction of microbes	Bacteria reduces metals to sulphides and hydroxides and Fe ⁰ traps the precipitates	(ARS Technologies Inc., January 2005; Ludwig et al., 2009; Van Nooten et al., 2008; Wrenn, 2004)
2. Adsorption, filtration and absorption mechanisms						
2.1 Absorption by using inorganic surfactants	Cd, Pb, Zn, As, Cd, Cu, Ni	Application of anionic surfactants on surface of soil or in aquifer	Many surfactants are available; Complexing agents work well with surfactants	pH-dependent process, high permeability aquifer needed	metal sorption depending on charge of surfactant	(Mulligan et al., 2001; Scherer et al., 2000; Torres et al., in press)

(continued on next page)

Table 5 (continued).

Technology	Scope	Conditions and modes of application	Advantage	Disadvantage	Mechanism and process	Selected references
2.2 Membrane and filtration technology	Cu, Cd, Pb, Cr, Hg, Pb, Zn, U, Tc, As	electrodialytic membrane, emulsion liquid membrane, polymer membrane, UF, EUF, nanofibre membrane, microfiltration	High removal efficiency observed	Filter clogging; recharge or regeneration of filter materials	All the membranes and filters have separate mechanisms e.g. electrostatic capture, complexation, dialysis, micellar capture in 3-D structure	(Hsieh et al., 2008; Sang et al., 2008b; Sikdar et al., 1998)
2.3 Adsorption by commercial and synthetic activated carbon	As, Pb, Cr, Cd, Ni, Zn	Activated carbon with higher ash content, GAC, IMC, PHC, tamarind wood carbon are used	High BET surface area and surface active agents provide adsorption sites for heavy metal cations	Regeneration of spent materials may be frequently needed	AC activated with Fe, ZnCl ₂ , etc and high BET surface area provide active sites for cation adsorption	(Acharya et al., 2009b; Dwivedi et al., 2008; Navarro and Alguacil, 2002; Sahu et al., 2010; Singh et al., 2008)
2.4 Adsorption in industrial byproducts and wastes	As, Cd, Pb	Bone-char, bio-char, rice husk, maple wood ash were tested in laboratory	These are readily available from industry; Show promising result	Field application needed	Adsorption on surface sites	(Amin et al., 2006; Mohan and Chander, 2006; Mohan et al., 2007; Sneddon et al., 2005)
2.5 Use of ferrous materials as adsorbents	As(V), Cr, Hg, Cu, Cd, Pb	Injection of Fe(III) salts, Fe ₃ O ₄ nanoparticles coated with HA, FMBO, mixed magnetite and maghemite nanoparticles	As(V) and other metal cations bind with Fe(III) as strong inner-sphere complexes due to their strong geochemical association	As(III) oxidation is difficult to achieve in anaerobic aquifers; Ferrous materials get used up & need to be replaced frequently	Sorption by Fe oxides, oxyhydroxides and sulphides and microbe mediated reactions involving Fe as an e ⁻ acceptor	(Chowdhury and Yanful, 2010; Rao and Karthikeyan, 2007; Ruiping et al., 2009; Smedley and Kinniburgh, 2002; Sylvester et al., 2007)
2.6 Ferrous salts as in-situ soil amendments	Various heavy metals at industrial sites	In-situ application of goethite and Fe grit in soil and spreading over contaminated land surface to help in vegetation growth	Show result over long period of time (few years); Applicable to highly contaminated sites	Some amendments have negative effect on vegetation growth; Not effective for all pollutants	Adsorption to mineral surfaces, surface precipitation, formation of stable complexes with organic ligands and ion exchange	(Cundy et al., 2008; Hartley and Lepp, 2008; Kumpiene et al., 2006; Mench et al., 2003)
2.7 Minerals and derived materials	Cr, As, Se, Cs, Pd, Cu, Cd, Ni	Laboratory experiment with fullers beads and hydrotalcite type minerals	A wide range of heavy metals can be removed from aqueous solutions	Application in groundwater treatment is not performed	Precipitation under alkaline conditions (Fuller's bead) & adsorption through large surface area (hydrotalcite)	(Hasan et al., 2007; Hu et al., 2005; Lazaridis, 2003; Regelin and Temminghoff, 2011; Yang et al., 2005)
3. Electrokinetic remediation	As, Cd, Cr, Co, Hg, Ni, Mn, Mo, Zn, Sb, Pb	DC current applied via electrodes inserted in soil, cations migrate towards cathode, anions towards anode where they are recovered	85–90% efficient in removing metals; Applicable to wide range of metals	The process depends on soil pore, water current density, Grain size, Ionic mobility, Contaminant concentration and Total ionic concentration	Process involves electro-osmosis, electromigration and electrophoresis	(Chilingar et al., 1997; Colacicco et al., 2010; Giannis et al., 2007; Lee and Kim, 2010; Scullion, 2006; Virkutyte et al., 2002; Yuan et al., 2009)

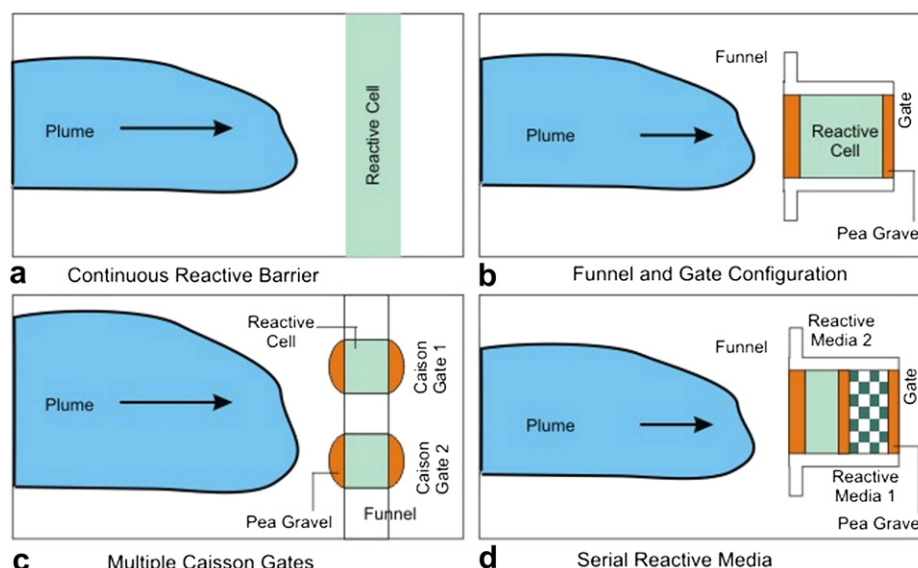


Fig. 7. Construction of the reactive cell, adapted from Gavaskar et al. (1998).

Scherer et al. (2000) classified the permeable barrier technologies into three types, according to the separation process used in them. They are:

1. Sorption – zeolites, humic materials, oxides, precipitating agents
2. Chemical Reaction – zero-valent metals (Fe, etc), minerals
3. Biological Treatment – oxygen and nitrate releasing compounds, organic materials

3.3.1.1. Sorption process in PRB. Contaminants in an aquifer migrating through an installed reactive wall can be passively fixed in-situ by sorption onto the reactive materials contained in the treatment wall via ion exchange, surface complexation, surface precipitation or hydrophobic partitioning (Dzombak and Morel, 1990; Schwarzenbach et al., 1993). For such a sorption technique to be effective, pH range of the barrier chemical needs to be selected depending on the metal to be removed and sorbents used. This technology is meant for shallower depth of 3 to 12 m. The immobilized contaminants may be re-mobilized with changing environmental condition (Yin and Allen, 1999).

3.3.1.1.1. Sorption within red mud at PRB. Red mud with a composition of fine particles of aluminum, iron, silica, calcium and titanium oxides and hydroxides, derived from the digestion of bauxite during the Bayer process, was reported to have high surface reactivity (Apak et al., 1998; Chvedov et al., 2001). Red mud had been investigated by many researchers for its ability to remove various contaminants and heavy metals from wastewater (Apak et al., 1998; Gupta et al., 2004a; Gupta and Saini, 2004b; Gupta and Sharma, 2002) and acid mine drainage (AMD) (Komnitsas et al., 2004).

Brunori et al. (2005) studied the metal trapping ability of treated red mud. After 48 h of contact, 35% of As from initial concentration of $230 \mu\text{g L}^{-1}$, was removed with 2 g L^{-1} red mud. The percentage significantly increased with 10 g L^{-1} red mud that removed up to 70% of As from initial concentration of $400 \mu\text{g L}^{-1}$. Metal release was generally low at acidic pH.

The adsorption behavior of Pb, Cd and Zn on non-treated and acid-treated red mud was studied and the adsorbed heavy metals were found to be immobile (Santona et al., 2006). Red mud with

cancrinite structure had a negative charge density in its lattice at the equilibrium pH of the conducted adsorption experiments. This negative charge density was neutralized by the incorporation of metals in the cages and channels of cancrinite framework (Mon et al., 2005). It was also observed that on treating with red mud, the Cu concentration in samples of polluted river water decreased from 0.537 mg mL^{-1} to 0.369 mg mL^{-1} and $\text{Cu}(\text{NO}_3)_2$ concentration decreased from 0.506 mg mL^{-1} to 0.367 mg mL^{-1} . The experiments were performed at pH between 3 and 11 and at 30°C . It was concluded that Cu ions could be successfully removed from the aqueous solutions by using red mud (Nadaroglu et al., 2010).

Ferrous based red mud sludge combines the ability of forming Fe–As coprecipitate as amorphous hydrous oxide-bound arsenic and high arsenic adsorption features. A dosage of 0.2 or 0.3 g L^{-1} of the red mud sludge can be used to remove As(V) at an initial concentration of 0.2 or 0.3 mg L^{-1} at a pH range of 4.5–8.0. At the lower pH value of 4.5, the As(V) was not released from the red mud sludge. Phosphate was found to greatly reduce the arsenic removal efficiency (Li et al., 2010).

3.3.1.1.2. Activated carbon and peat in PRB. Activated carbon and peat were reported to be chemically stable materials and presented a high adsorption capacity for many organic and inorganic contaminants due to their large surface area, about $1000 \text{ m}^2 \text{ g}^{-1}$ and presence of different types of surface functional groups, e.g. hydroxyl, carbonyl, lactone, carboxylic acid (Huttenlocher et al., 2001). Han et al. (2000) found the granular activated carbon (GAC) highly suitable for using in permeable barriers, especially for removing Cr(VI) from contaminated groundwater. Regeneration of carbon by phosphate extraction and acid washing also appeared to be successful (Han et al., 2000), allowing the possibility for repeated use of the material (Thiruvengatchari et al., 2008). Microbial regeneration of activated carbon used inorganic sorption in PRB is a promising area which needs to be explored. A study conducted by Leglize (2004) with PRB using activated carbon and microorganism increased the degradation efficiency of PAH which was adsorbed on the carbon.

Column experiments carried out using peat activated with NaOH effectively captured transition metals from aqueous media by non-exchange mechanisms. Only 1 g of the NaOH-activated peat showed 100% removal efficiency of Cd from over 200 mL of a 200 mg L^{-1} Cd solution whereas 1 g of non-activated peat

adsorbed 25% less Cd from the same solution. FTIR spectroscopic studies revealed crucial role of carboxyl groups in the sorption mechanism (Fine et al., 2005). This activated peat can also be considered for using in PRBs.

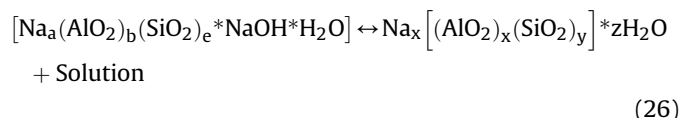
3.3.1.1.3. Zeolites in PRB. Zeolites are tectosilicate minerals with 3D aluminosilicate structure containing water molecules, alkali and alkaline earth metals in their structural framework. These have potentials to be used as treatment mineral in the PRBs due to high ion exchange, adsorbing, catalytic and molecular sieving capacities (ITRC, 2005; Roehl et al., 2005). Zeolitic mineral clinoptilolite [(Ca, Mg, Na₂, K₂) (Al₂Si₁₀O₂₄ • 8H₂O)] had been researched by many research groups (ITRC, 2005). Park et al. (2002) observed 80% cation removal ability by 1 g of clinoptilolite, except for very high initial concentrations of ammonium (80 ppm) and copper (40 ppm). Highest permeability of 2×10^{-3} to 7×10^{-4} cm s⁻¹ was achieved by mixing washed clinoptilolite of diameter 0.42–0.85 mm with Jumunjin sands in 20:80 ratio (w/w). Kocaoba (2009) studied clinoptilolite for its removal efficiency of Cd(II), Cu(II) and Ni(II) from aqueous solutions. The selectivity was determined as Cd (II) > Ni (II) > Cu (II). The sorption kinetics indicated the process to follow pseudo-second order reaction (Kocaoba et al., 2007). Again, natural sepiolite showed better adsorption of Cr³⁺ and Cd²⁺ ions than Mn²⁺ ions within pH range of 3–5 (Kocaoba, 2009).

Natural zeolitic rocks such as chabazite-phillipsite, clinoptilolite, and volcanic glass could also remove arsenic from different types of waters having varying mineralization degree. The arsenic removal efficiency were 60 to 80% for chabazite-phillipsite and 40–60% for clinoptilolite-bearing rocks. The three key factors influencing the arsenic removal are firstly, mineralogy of the zeolites occurring in the volcanic rock, secondly, zeolite content of the zeolitic rock and lastly, the water mineralization degree (Ruggieri et al., 2008).

Some researchers are trying to use 'Surface Modified Zeolites' for metal sorption as well. The mechanism of absorption of oxy-cations and oxyanions in zeolites is shown in Fig. 8.

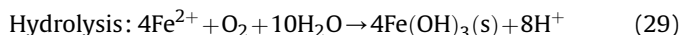
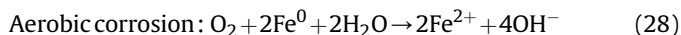
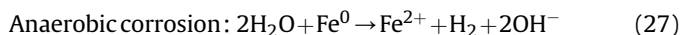
Fly ash zeolites are byproducts from hydrothermal treatment processes of hard coal fly ash (HCF) by NaOH solutions. They are tectosilicates showing different dimensions of their channels and cages forming the crystal lattice. Czurda (1998) mentioned about the zeolitization of the fly ash (equation 26) when it was treated

with NaOH solution. This reaction represented an equilibrium reaction between the solution and the solid phase.

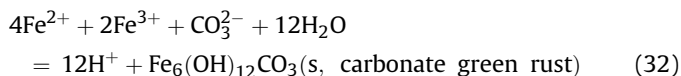
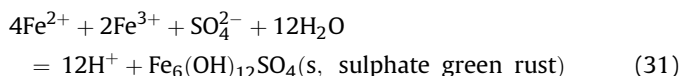
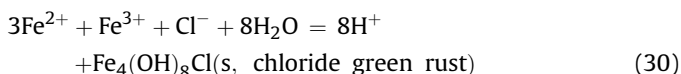


The zeolitization was proposed to be dependent on temperature, molarity of NaOH solution, reaction time and Si/Al proportions leading to development of different phases e.g. zeolite Na–P and zeolite X (Czurda, 1998). These FAZs could be used in funnel and gate type PRBs for site cleanup similar to natural clay, zeolites and Zero Valent Iron (ZVI). Electrokinetic methods were suggested to induce hydraulic flow through the reactive zone or wall of FAZ (Czurda and Haus, 2002).

3.3.1.1.4. Iron sorbents in PRB. Su and Puls (2001) investigated the effectiveness of ZVI in removing arsenic. They interacted 1 g of Fe⁰ at 23 °C for up to 5 days in the dark with 41.5 mL of 2 mg L⁻¹ As(V), As(III) and 1:1 As(V) + As(III) in 0.01 M NaCl when As concentration decreased exponentially with time and decreased below 0.01 mg L⁻¹ within 4 days. Both As(V) and As(III) were suggested to form stronger surface complexes or migrated further inside the interior of the sorbent with increasing time. Also, the oxide films developed on Fe⁰ particles were observed to be porous and incoherent, providing adsorption sites for both As(III) and As(V). However, more studies were recommended on the effects of temperature, pH, dissolved salts and micro-organisms on the removal efficiency of Fe. Again, Su and Puls (2003) observed that in presence of silicate and phosphate, which compete with As for adsorption sites, the already adsorbed As species breaks through. The ZVI first underwent corrosion to Fe²⁺ and Fe³⁺ through the following mechanisms:



Following these, formation of chloride green rust, sulphate green rust and carbonate green rust trapped the As species by the mechanism shown below (Wilkin et al., 2002):



Sulphate or carbonate green rusts were reported to form in ZVI columns fed with sulphate-rich or bicarbonate-rich influent solutions (Gu et al., 1999).

Sun et al. (2006) reported that under anaerobic conditions arsenite removal was easier by ZVI while arsenate removal was more efficient under aerobic conditions, predominated by two different mechanisms. Arsenite was precipitated in anaerobic conditions and arsenate was adsorbed to iron and iron corrosion

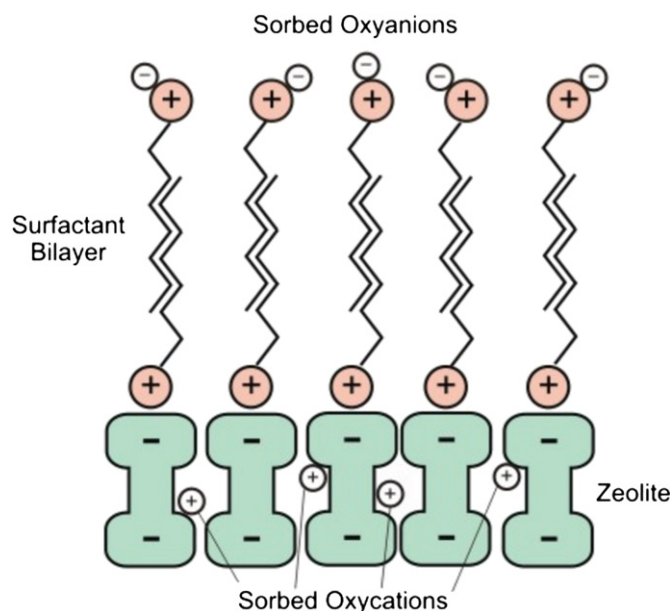


Fig. 8. Proposed mechanism of sorption of oxyanions and metal cations in surface modified zeolites, adapted from Scherer et al. (2000).

products in aerobic conditions. Low pH or acidic conditions helped in arsenic removal both in aerobic and anaerobic conditions while in relative anaerobic condition, alkaline condition seemed to be favorable for arsenite removal. Low concentration of sulfate and nitrate and high level of phosphate inhibited arsenate removal. More than 98% of arsenate could be removed with a hydraulic resident time (HRT) of 2 h at least, making this technique suitable for slow flowing aquifer PRBs (Sun et al., 2006).

Pyrite (FeS₂) was used to adsorb Hg(II) on its surface by complexation reactions in batch and column experiments. Hg(II) adsorption rate and capacity increased with increasing pH. When column experiment was continued for 2 weeks at low pH, an ordered monolayer of Hg–Cl complexes on pyrite was formed. At high pH, Hg–OH was formed on pyrite surface. These complexes were immobile under leaching conditions. However, the effectiveness of the process underwent 4-fold decrease in presence of dissolved oxygen. Pyrite was suggested to be an effective agent in PRBs for Hg adsorption from groundwater (Bower et al., 2008).

3.3.1.2. Chemical precipitation in PRB. The reactive chemical agents can also be used in PRBs to precipitate contaminants. These chemicals can modify the pH and redox conditions resulting in metal precipitation as hydroxides. Blowes et al. (2000) suggested that calcite dissolution and sulphate reduction filters could be constructed in the acidic drainage path in the form of reducing and alkalinity producing systems (RAPS) and PRBs. The reactive materials that can be used include ferrous salts, lime, limestone, fly ash, phosphate, chemicals such as Mg(OH)₂, MgCO₃, CaCl₂, CaSO₄ and BaCl₂ and zero-valent metals. The immobilized contaminants and toxic degradation intermediates might be re-mobilized upon environmental condition changes (Yin and Allen, 1999). Some processes are discussed below.

3.3.1.2.1. Reaction with zero valent iron in PRB. Iron was first used as a reactive material in permeable reactive barriers in the 1990s (USEPA, 1998). After that, a number of researchers have used ZVI successfully in removing heavy metals, organic and inorganic pollutants from groundwater by chemically bonding with them (Cundy et al., 2008; Morrison et al., 2002; Thiruvengatchari et al., 2008; Wilkin and McNeil, 2003; Wilkin et al., 2002). Morrison et al. (2002) noticed precipitation of reduced oxides (UO₂, V₂O₃), sulfides (As₂S₃, ZnS), iron minerals (FeSe₂, FeMoO₄) and carbonate (MnCO₃) while treating groundwater contaminated with As, Mn, Mo, Se, U, V and Zn by reactive plates made by binding ZVI with aluminosilicate. The solid fraction of a treatment cell was found to consist of ZVI, magnetite (Fe₃O₄), calcite (CaCO₃), goethite (FeOOH) and mixtures of contaminant-bearing phases. The capability of ZVI in removing chromate from groundwater was studied by Puls et al. (1999). The dissolved chromate was reduced from Cr(VI) to Cr(III) through corrosion of the Fe and thus chromate in the groundwater decreased to less than 0.01 mg L⁻¹. As the Fe corroded, pH increased, redox potential decreased, dissolved oxygen was consumed and Fe(II) was generated. Fe corrosion resulted in the mineral phases including ferrous sulphides, various Fe oxides, hydroxides and oxyhydroxides (Puls et al., 1999). Wilkin et al. (2009) assessed the performance of a pilot-scale PRB of dimensions 9.1 m long, 14 m deep, and 1.8–2.4 m, filled up with granular ZVI installed at a former lead smelting facility, located near Helena, Montana (USA). Over a period of 2 years, it removed high concentrations of As(III) and As(V) from above 25 mg L⁻¹ to below 0.5 mg L⁻¹.

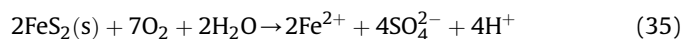
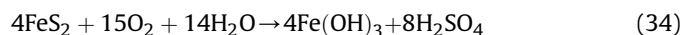
Jun et al. (2009) experimented with two laboratory scale sequenced PRBs, marked as A and B, to treat landfill leachate-polluted groundwater containing various hazardous contaminants including heavy metals such as Cr, Ni, Pb, Mn, Se, Co, Cu, Cd, Zn, Ca, Mg, Sr and Al. The percentage of heavy metals removal in two

reactors varied from 46.7% to 93.2% for reactor A, and 58.7%–99.6% for reactor B. The heavy metals precipitated as sulphides, carbonates and hydroxide compounds with an increment in pH value from 6.9 to 8.2 and 10.4 in A and B reactors. Zeolites removed the precipitates of Zn, Mn, Mg, Cd, Sr, and NH₄⁺ at an efficiency of 97.2%, 99.6%, 95.9%, 90.5% and 97.4%, respectively. With the progress of the process, metal precipitates reduced the ZVI efficiency and it was oxidized to Fe²⁺ and Fe³⁺. A problem regarding the use of ZVI as reactive medium in PRB is the accumulation of precipitates of hydroxides, various Fe corrosion products and different salts such as carbonates, thus clogging the pores of the PRB. The pollutant removal efficiency as well as hydraulic permeability of the barrier gets compromised severely and the performance of the PRB deteriorates over years. This can lead to formation of preferential higher-permeability path of groundwater flow bypassing the barrier (Li et al., 2005, 2006; Liang et al., 2005). A number of researchers tried to solve this problem by mixing ZVI with some porous matrix such as sand (Bartzas and Komnitsas, 2010; Komnitsas et al., 2007) and pumice (Moraci and Calabrò, 2010) in various proportions varying from 50:50 to 30:70 (ZVI : sand/pumice). Jeen et al. (2011) evaluated the long term performance prediction capability of the ZVI PRBs by recently-developed reactive transport model at two field-scale PRBs, containing high concentrations of dissolved carbonate. They suggested that the average groundwater velocity through the PRB could be half or less than the design value.

Some researchers have also examined the generation of reactive sub-surface Fe barriers by remote electrical means (Cundy and Hopkinson, 2005; Faulkner et al., 2005; Hopkinson and Cundy, 2003). This will be discussed under electro-remediation section (3.3.3).

Based on the colloidal carbon particles, a material named Carbo-Iron was developed which combines the sorption properties of the activated carbon carrier and the reactivity of the ZVI deposits. This Carbo-Iron product proved its suitability as a dehalogenation reagent applicable for both plume and source treatment (Mackenzie et al., 2008). This may be experimented for metal removal as well.

3.3.1.2.2. Alkaline complexation agents in PRB. Limestone, lime, or other calcium carbonate or hydroxide materials can be an effective material for use within a PRB system (ITRC, 2005; Roehl et al., 2005). Mixtures of limestone with compost to stimulate microbial action and inert materials such as sand to provide adequate permeability to aquifer was used in PRBs for treating metal-enriched water e.g. in Nickel Rim, Ontario, Canada (www.rtdf.org/public/permbarr). The limestone or alkaline materials usually modify pH conditions of soil to reduce the solubility of certain metals or for bioremediation. It was observed that the weathering of Fe- and sulphur-rich minerals such as pyrite (FeS₂) produce highly acidic and metal-rich water from mine drainage. The following mechanism may be proposed (ITRC, 2005).



Lime barriers may cause an increase in pH up to 12.5 to facilitate the formation of metal hydroxides, which reduce the solubility of certain metals. They were proved to be successful in remediation of anionic and cationic pollutant species in AMD (ITRC, 2005).

The limestone-based PRB for AMD effluent is sometimes called “anoxic limestone drain” (ALD). The Pennsylvania Department of Environmental Protection (www.dep.state.pa.us/dep) described the use of ALDs and provided a generalized method to calculate the amount of limestone required to treat a given flow of AMD effluent.

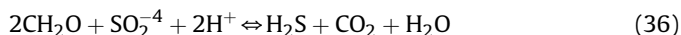
3.3.1.2.3. Atomized slag in PRB. Atomized slag containing composites of CaO, FeO, Fe₂O₃, SiO₂, etc was tested as adsorbent for treating AMD with high arsenic concentrations, by placing it in PRBs. Evaporation cooler dust, basic oxygen furnace slag, oxygen gas sludge and electrostatic precipitator dust reduced both As(V) and As(III) concentration from 25 mg L⁻¹ to <0.5 mg L⁻¹ within 72 h. Blast furnace slag (BFS) was also used for aqueous As(III) remediation. The maximum adsorption capacity of BFS was observed to be 1.40 mg As(III) g⁻¹ of BFS at initial As(III) concentration of 1 mg L⁻¹ (Ahn et al., 2003; Kanel et al., 2006). Various atomized slag based PRB systems were tested and a combination of atomized slag and sand system was found to have a substantial reaction capacity for leachate and organics. Thus it had the potential to be used in the PRBs for a sub-surface remediation. The test results showed that the adsorption capacity increased in the order of pH 7 > pH 5 > pH 9, the heavy metal removal rate increased in the order of Cd > Pb > Cr > Cu and organic removal rate increased in the order of T-P > COD > T-N (Chung et al., 2007).

3.3.1.2.4. Caustic magnesia in PRB. Caustic magnesia which is a mixture of MgO, CaO, SiO₂, Fe₂O₃ and Al₂O₃ can be used in PRBs to remove some heavy metals. Cortina et al. (2003) showed that caustic magnesia reacted with water to form magnesium hydroxide which increased the pH of the water to values higher than 8.5 precipitating Cd as otavite and to a minor amount as a hydroxide. Co and Ni were precipitated as hydroxides forming isostructural solids with brucite. Thus, metal concentrations were depleted down to values below 10 µg L⁻¹ from previous values of 75 mg L⁻¹ in the inflowing water. Earlier, it had been shown that caustic magnesia could retain Zn, Cu, Pb and Mn in permeable reactive barriers (Cortina et al., 2003). Rötting et al. (2006) demonstrated by column experiment that caustic magnesia could immobilize Cd, Ni and Co. It also precipitated Al(III) and Fe(III) at pH 8.5–10. Due to the availability of oxygen, efficiency of precipitating Fe(II) is limited. Once the caustic magnesia gets exhausted, the precipitates of Cd and Co and possibly Ni may dissolve. So, the whole system should be regularly checked and dismantled on the first symptoms of exhaustion (Rötting et al., 2006).

3.3.1.3. Biological barriers in PRB. This technology used engineered passive in-situ bioreactors for microbial transformation of potentially hazardous compounds. Many researchers (Barbaro and Barker, 2000; Fang et al., 2002; Hunkeler et al., 2002; Witt et al., 2002) engineered bioreactive zones for changing redox conditions or provide substrates/nutrient that facilitated the natural biodegradative system. Currently, biological reactive zones rely either on dissolved nutrients or injected nutrients to support the biodegradation of contaminants passing through the barrier. Delivery of nutrients throughout a barrier had been found to be both hydrologically difficult as well as costly. Additionally, it may become necessary to replenish the media periodically (Kalin, 2004). Bioclogging (Seki et al., 2006) and also decreased water saturation during denitrification and associated decrease in hydraulic conductivity can also hamper efficiency of in-situ biobarriers.

3.3.1.3.1. Denitrification and sulphate reduction by organic carbon and biological organism in PRB. Tuttle et al. (1969) suggested the use of sulphate-reducing bacteria (SRB) inside PRBs for the treatment of AMD. Robertson and Cherry (1995) used permeable organic carbon material to stimulate biologically mediated denitrification and sulphate reduction in contaminated groundwater in PRB system. In the presence of organic source, these heterotrophic denitrifying and sulphate-reducing bacteria, already present in the soil, reduces nitrate to nitrogen gas and sulphate to sulphide, in the absence of oxygen (Benner et al., 1999). Processes related to the generation and precipitation of metallic sulphides are responsible

for the removal of divalent metals such as Fe, Cu, Cd, Ni, Zn (Dvorak and Hedin, 1992; Hammack and Edenborn, 1992; Hammack et al., 1994; Waybrant et al., 1998) whereas it seems that removal of trivalent metals (Al, Fe) results from hydroxides and oxyhydroxides precipitation (Dvorak and Hedin, 1992; Thiruvengkatachari et al., 2008). Overall, sulphate reduction process can be represented by the equation (Gibert et al., 2002):



where CH₂O represents an organic compound. The sulphide can precipitate with many of the metals present in an AMD, such as Fe, Zn or Cu:



Metals evaluated in later studies include Fe, Ni, Zn, Al, Mn, Cu, U, Se, As, V (Dvorak and Hedin, 1992; Hammack and Edenborn, 1992; Hammack et al., 1994; Waybrant et al., 1998). Using the SRBs, within the PRBs in most cases resulted in above 95% of metal removal (Gibert et al., 2002).

Hunter and Kuykendall (2005) described in-situ biobarriers containing soyabean oil removing 98% selenite from flowing groundwater. Selenite reduction starts at redox potentials of about 213 mV by abiotic processes though rapid reduction do not occur until 106 mV (Reddy et al., 1995). Also, sulphate-reducing bacteria can reduce selenite to elemental selenium by forming sulphide (Hockin and Gadd, 2003). Microorganisms can detoxify selenite by reducing it to Se⁰ and depositing them as reddish granules in their cytoplasm (Silverberg et al., 1976).

Jarvis et al. (2006) treated AMD of pH < 4 containing [Fe] > 300 mg L⁻¹, [Mn] > 165 mg L⁻¹, [Al] > 100 mg L⁻¹ and [SO₄²⁻] > 6500 mg L⁻¹ in PRB by BSR mechanism for over 2 years. Fe was reduced from 500 mg L⁻¹ to less than 20 mg L⁻¹ whereas sulphate concentrations was reduced by 67%. Acidity was also reduced to some extent. Bio-barrier and reactive zone technologies were tested for bioremediation of Cr(VI) contaminated aquifers employing Cr reducing bacteria. A 10 cm thick biobarrier having an initial biomass concentration of 0.44 mg g⁻¹ of soil completely contained a Cr(VI) plume of 50 mg L⁻¹ concentration, when the Darcy velocity was 0.0196 cm h⁻¹. The reactive zone technology, incorporating a system with four injection wells, each injecting 150 g of bacteria was effective at high Cr(VI) concentration of 250 mg L⁻¹. They also proposed a mathematical model for simulating the bioremediation process by assuming homogeneous conditions (Jeyasingh et al., 2011).

3.3.1.3.2. Mixing biotic components with ZVI in PRB. Some studies indicated that micro-organisms when coupled with Fe⁰, increase the contaminant removal efficiency (Parkin et al., 2000). Coupling of bioaugmentation with the ZVI technology was found to have a symbiotic effect (ARS Technologies Inc., January 2005; Oh and Alvarez, 2002; Till et al., 1998). Till et al. (1998) proved that Fe⁰ can stoichiometrically reduce nitrate to ammonium and that hydrogen produced (during anaerobic Fe⁰ corrosion by water) can sustain microbial denitrification to reduce nitrate to more innocuous products (i.e., N₂O and N₂). Experiments with mixtures of contaminants have also shown that bioaugmentation of PRBs with bacteria offers promise when more than one contaminant is present. Batch experiments with mixtures of carbon-tetrachloride, Cr and nitrate showed that bioaugmentation reduced competition among these pollutants for active sites on the Fe⁰ surface (Parkin et al., 2000). PRBs providing dissolved C, N and P and the plume water entering the barrier providing high concentrations of Fe and other metals promoted the growth and reproduction of micro-organisms (Waybrant et al., 2002).

Van Nooten et al. (2008) also noticed higher trichloroethylene degradation efficiencies of ZVI containing an Fe(III)-reducing *Geobacter sulphurreducens* which formed mineral precipitates of carbonate green rust, aragonite, ferrous hydroxy carbonate, and to some extent goethite. These reactive compounds can be utilized in removing heavy metals as well. Again, Langley et al. (2009) noticed high sorption efficiency of Sr(II) via reversible outer-sphere complexation onto bacteriogenic Fe oxides (BIOS) which were primarily composed of ferrihydrite and microbial cellular debris (Langley et al., 2009).

A 30-month performance evaluation of a pilot PRB consisting of a mixture of leaf compost, zero-valent iron (ZVI), limestone, and pea gravel was conducted at a former phosphate fertilizer manufacturing facility in Charleston, SC. The PRB is designed to remove heavy metals and arsenic from groundwater by promoting microbially-mediated sulphate reduction and sulphide-mineral precipitation and arsenic and heavy metal sorption. Performance monitoring showed effective treatment of As, Pb, Cd, Zn, and Ni from concentrations as high as 206 mg L⁻¹, 2.02 mg L⁻¹, 0.324 mg L⁻¹, 1060 mg L⁻¹, and 2.12 mg L⁻¹, respectively, entering the PRB, to average concentrations of <0.03 mg L⁻¹, <0.003 mg L⁻¹, <0.001 mg L⁻¹, <0.23 mg L⁻¹, and <0.003 mg L⁻¹, respectively, within the PRB. Both As(III) and As(V) were effectively removed from solution. Analysis of core samples indicating the presence of As(V) in oxygen-bound form and As(III) in both oxygen- and sulphur-bound forms (Ludwig et al., 2009).

3.3.2. Adsorption, filtration and absorption mechanisms

Many of the adsorbents and filtration mechanisms described in this section have been frequently used in treating contaminated water or effluent, but had been scarcely used for in-situ groundwater treatment. Most of them are suitable to be used in the PRB technique or in creating a reactive zone.

3.3.2.1. Absorption by using inorganic surfactants. Surfactants initiate some typical desirable processes which help in contaminant removal e.g. solubility enhancement, surface tension reduction, micellar solubilization, wettability and foaming capacity (Mulligan et al., 2001).

Doong et al. (1998) observed the combined effect of complexing agents and surfactants for Cd, Pb and Zn removal from soil. Anionic

(sodium dodecyl sulphate, SDS), cationic (cetyltrimethylammonium bromide, CTAB) and non-ionic (Triton X-100) surfactants were evaluated in combination with complexing agents EDTA and diphenylthiocarbazone (DPC). Anionic and non-ionic surfactants enhanced desorption rates of Cd, Pb and Zn whereas cationic surfactant was most efficient in lower pH. In the surfactant/EDTA mixture system, the heavy metal desorption efficiency was in the order of Cd > Pb > Zn. However, surfactant/DPC system resulted in 2–4 times reduction in extraction efficiency. The results demonstrated that surfactants in combination with complexing agents could be effectively used to flush heavy metal contaminated soil (Doong et al., 1998). Zhang et al. (2007, 2008) also successfully removed Pb from contaminated soil by washing it with EDTA followed by SDS (Zhang et al., 2007, 2008). Torres et al. (in press) washed a soil having heavy metal concentration for As, Cd, Cu, Pb, Ni and Zn of 4019, 14, 35582, 70, 2603, and 261 mg kg⁻¹, respectively, with many different surfactants. High removal efficiency was achieved using Texapon N-40 (83.2%, 82.8% and 86.6% for Cu, Ni and Zn), Tween 80 (85.9, 85.4 and 81.5 for Cd, Zn and Cu), Polafix CAPB (79%, 83.2% and 49.7% for Ni, Zn and As) in a one step washing procedure using 0.5% surfactant solutions (Torres et al., in press).

A pilot scale in-situ surfactant flushing system was designed and tested (Fig. 9). High permeability of soil is required for successful application of this process. To prevent the mobilized contaminants from releasing to the environment, an impermeable barrier can be placed, e.g. a slurry wall around the zone of contamination (Clarke et al., 1994).

3.3.2.2. Membrane and filtration technology. Membrane technology can be used in conjugation to soil washing or flushing techniques for concentrating the contaminants from the wash liquid, so that the raffinate can be treated accordingly. Membranes can be of several types such as electrodialytic membrane liquid membrane, polymer membrane, ultrafiltration membrane, nanofibre membrane and many more. According to Sikdar et al. (1998), an effective membrane method should reduce the volume of contaminated water to be treated while producing clean water that meets the applicable effluent guidelines. Hansen et al. (1997) simultaneously applied cation and anion-exchange membrane barriers in an electrokinetic method to remove Cu, Cr, Hg, Pb, and Zn (concentration several hundred ppm each) from soils

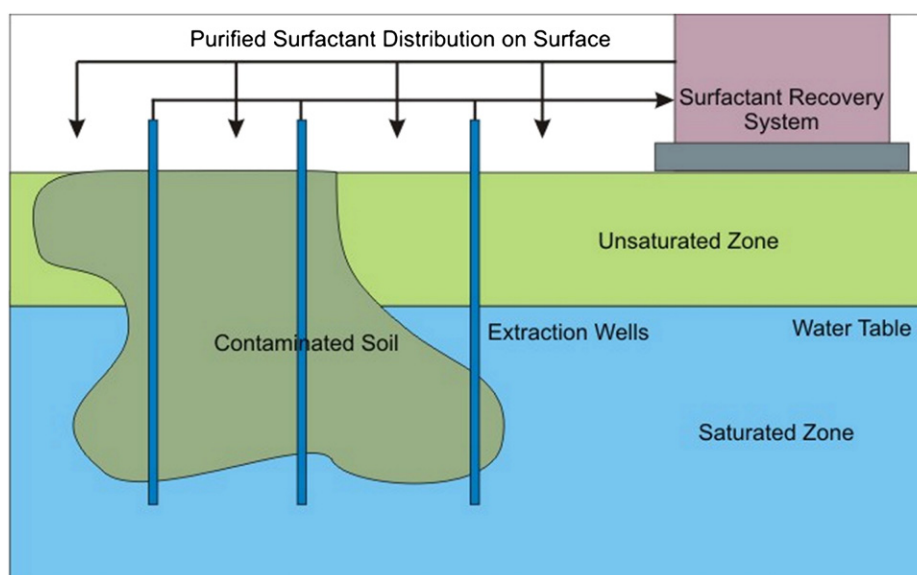


Fig. 9. In-situ surfactant flushing system, adapted from Clarke et al. (1994).

contaminated by wood preserving facilities, chlor-alkali plants, and Cu rolling mills. The anion-exchange membrane showed transport numbers for the anion around 0.95 for NaCl, CaCl₂ and ZnCl₂ solutions for the concentration range investigated. By electro-dialytic desalting experiments, it was revealed that all ions in the simulated soil volume could be removed and the metal content in the different solutions could be controlled in the electro-dialytic decontamination method (Hansen et al., 1997).

Rochem Environmental's (Torrance, CA) high-pressure (1000 psig) Disk Tube™ technology employed reverse osmosis to remove organics and metal contaminants from landfill leachates with an efficiency of more than 98% (Hazardous Waste Consultants, 1995). Also, liquid membranes employing metal-complexing ligands was able to isolate metal ions such as U(VI), Tc(VII), Cr(VI) and nitrates from groundwater in the presence of calcium and magnesium ions (Chiarizia et al., 1992). Heavy metals such as Cu(II), Cr(VI), and As(V) might be removed from the aqueous phase by ultrafiltration, pretreating the phase with a functionalized polymer, such as polyethylene imine or polyacrylic acid which can form complex with metal ions. It was also shown that for low contaminant concentrations below 50 ppm, excellent binding and subsequent removal by polysulfone UF membranes (mol. wt. cut-off 10 or 20 kDa) could be achieved in the presence of sodium salts, if the pH of the solution was controlled within a narrow range (Geckeler and Volchek, 1996).

A microfiltration process was developed to treat heavy metal contaminated groundwater using DuPont's polyolefinic Tyvek filter material best suited for suspended solid concentrations below 5000 ppm. This technology was demonstrated at the Palmerton Zn Superfund site in Palmerton, Pennsylvania where removal of suspended Zn solids was achieved with better than 99% efficiency. An ultrafiltration technique, which employed chelating polymers for capturing dissolved metal ions, could be applied to the filtrate for further cleanup (James and Stacy, 1993). Sirkar (1997) published a review on the developments in membrane separation technologies such as reverse osmosis, ultrafiltration, microfiltration, electrodialysis, dialysis, pervaporation, gas permeation and emulsion liquid membrane. New membrane-based equilibrium separation processes involving gas-liquid and liquid-liquid contacting, distillation and adsorption were also discussed.

Sang et al. (2008b) separated Cu²⁺, Pb²⁺ and Cd²⁺ from the simulated groundwater by a nanofiber membrane, named M-1, having a 3-dimensional network structure with multilayers, wide ranged pore size distribution and large specific surface area. In the micellar enhanced filtration (MEF) process, the surfactant SDBS, above CMC, form micelle which attaches the heavy metal ions to form larger congregations which then get adsorbed in the nanofiber membrane M-1 removing above 73% Cu; 82% Pb and 91% Cd. It could be used for the groundwater treatment with high efficiency. MEF and alumina adsorption were used for achieving 70% removal of groundwater Cu(II) cations, which got attached electrostatically on SDBS micelles and got separated by M-1 nanofiber filter. Then, the positively charged alumina was used for adsorbing the negatively charged SDBS surfactant containing Cu²⁺ (Sang et al., 2008a).

A study was conducted by Hsieh et al. (2008) to examine groundwater arsenic removal efficiency of an electro-ultrafiltration (EUF) system. The initial As(III) to As(V) ratios of two sampled well waters were 1.8 and 0.4. In the absence of electrical voltage, the EUF using 100-kDa membranes removed 1% and 14% of total As respectively, while application of 25 V electrical current reduced the total arsenic concentrations in both groundwater samples by 79%. This was attributed to different charge characteristics of As(V) and As(III) and also a possible association of As(III) species with dissolved organic matter, enhancing the As removal efficiency (Hsieh et al., 2008).

3.3.2.3. Adsorption by commercial and synthetic activated carbon.

Commercial activated carbons was extensively used for As(III) and As(V) adsorption from water (Lorenzen et al., 1995; Navarro and Alguacil, 2002). It was also investigated for As and antimony removal from Cu electro-refining solutions (Navarro and Alguacil, 2002). A high As sorption capacity (2860 mg g⁻¹) was observed on activated carbon (Rajaković, 1992). Among three types of activated carbons with varying ash contents, coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash, the best As(V) removal was observed with the highest ash content (Lorenzen et al., 1995). Gu et al. (2005) came up with iron containing granular activated carbon (GAC) adsorbents for As adsorption from drinking water. GAC provided support for ferric ions that were impregnated on it using aqueous ferrous chloride (FeCl₂) followed by NaOCl oxidation. Gu and Deng (2006) prepared iron containing mesoporous carbon (IMC) from a silica template (MCM-48) and used it for As removal from drinking water. The IMC had a BET (Brunauer, Emmett and Teller) surface area of 401 m² g⁻¹ while mesoporous carbon had 503 m² g⁻¹. The maximum adsorption capacities were 5.96 mg As g⁻¹ for arsenite and 5.15 mg As g⁻¹ for arsenate. Dwivedi et al. (2008) performed column experiments with commercial GAC for Pb(II) removal and found adsorption capacity to be 2.0132 mg g⁻¹ of GAC for 60 mg L⁻¹ feed concentration of Pb(II) at hydraulic loading rate of 12 m³ h⁻¹ and 0.6 m column bed height.

Singh et al. (2008) prepared activated carbon from tamarind wood material by chemical activation with sulphuric acid. The BET surface area of this material was found to be 612 m² g⁻¹ and total pore volume of 0.508 cm³ g⁻¹. It was tested for Pb(II) adsorption from dilute aqueous solution and the maximum removal rate of 97.95% (experimental) and 134.22 mg g⁻¹ (from Langmuir isotherm model) was obtained at initial concentration Pb(II) of 40 mg L⁻¹, adsorbent dose 3 g L⁻¹ and pH 6.5. Tamarind wood activated at pH 5.41 demonstrated high removal rate of Cr(VI) to >89% (Sahu et al., 2009a). High Pb(II) and Cr(VI) rates were also observed by zinc chloride activated carbon prepared from tamarind wood ash (Acharya et al., 2009a, 2009b; Sahu et al., 2010).

Ricordel et al. (2001) used carbon prepared from peanut husks (PHC) for the adsorption of Pb²⁺, Zn²⁺, Ni²⁺ and Cd²⁺. The adsorption mechanism was found to be highly dependent on particle size distribution and on metal/PHC ratio and followed the Langmuir isotherm model. Langmuir constant varied in the order Pb²⁺>Cd²⁺>Ni²⁺>Zn²⁺ signifying that Pb²⁺ had best affinity to PHC than Cd²⁺, Ni²⁺, Zn²⁺ (Ricordel et al., 2001). PHC therefore can be considered for Pb contaminated aquifers in industrial sites.

3.3.2.4. Adsorption in industrial byproducts and wastes.

Lignite, peat charcoals (Allen and Brown, 1995; Allen et al., 1997; Mohan and Chander, 2006), bio-char (Fan et al., 2004; Mohan et al., 2007) and bone-char (Sneddon et al., 2005) were used in wastewater treatment (Allen and Brown, 1995; Allen et al., 1997). They were found to be good substitutes for activated carbons. Bio-char from fast wood/bark pyrolysis were effectively investigated as adsorbents for the heavy metals such as As³⁺, Cd²⁺, Pb²⁺ from water (Mohan et al., 2007). Maple wood ash without any chemical treatment could also be utilized to immobilize As(III) and As(V) from contaminated aqueous streams in low concentrations (Rahman et al., 2004). Static tests removed ≤80% As, while dynamic column experiments reduced the As concentration from 500 ppb to <5 ppb.

3.3.2.5. Use of ferrous materials as adsorbents.

Some researchers proposed the use of Fe oxides, oxyhydroxides and sulphides to sorb or immobilize a range of heavy metals from groundwater and wastes (Contin et al., 2007; Heal et al., 2003; Kumpiene et al., 2006; Mohan and Pittman, 2007; Naveau et al., 2007). Monitored natural

attenuation strategies and passive treatment systems such as constructed wetlands may also include contaminant interaction with Fe-bearing minerals and microbially-mediated reactions involving Fe as an electron acceptor (Kalin, 2004; Schirmer and Butler, 2004).

Notably, a huge amount of literature exists for As removal by different ferrous materials (Bang et al., 2005; Chowdhury and Yanful, 2010; Cundy et al., 2008; Gu and Deng, 2006; Gu et al., 2005; Hartley et al., 2004; Hartley and Lepp, 2008; Kumpiene et al., 2006; Leupin and Hug, 2005; Li et al., 2010; Ludwig et al., 2009; Manning et al., 2002; Park et al., 2009; Ruiping et al., 2009; Saalfeld and Bostick, 2009; Sen Gupta et al., 2009; Su and Puls, 2001, 2003; Sun et al., 2006; Sylvester et al., 2007; Wilkin et al., 2009; Xenidis et al., 2010; Yuan et al., 2002) all of which have been discussed in this review under different sub-sections. The reader may refer to Mohan and Pittman (2007) for a detailed discussion on ferrous and other adsorbents for arsenic removal. Bang et al. (2005) investigated the effect of dissolved oxygen (DO) and pH on arsenic removal with ZVI from water. At higher DO value, more than 99.8% of the As(V) and 82.6% of the As(III) was removed at pH 6 after 9 h of mixing. Simultaneously, Fe⁰ was highly corroded. However, in absence of oxygen, when the solution was purged with N₂, less than 10% of the As(III) and As(V) was removed. The iron hydroxides generated from the corrosion of Fe⁰ actually adsorbed the As. Ahamed et al. (2009) discussed the sorbents used for As removal from groundwater in details. A number of researchers (Mohan and Pittman, 2007; Smedley and Kinniburgh, 2002) have examined As adsorption by Fe oxides, highlighting the tendency of As(III) and As(V) to strongly bind to hydrous Fe oxides as monodentate or bidentate inner-sphere complexes and also the strong geochemical association of As with Fe resulting in As removal by direct adsorption processes (Mohan and Pittman, 2007; Sylvester et al., 2007; Yuan et al., 2002) or coprecipitation, e.g. chemical coprecipitation using ferric chloride (Meng and Korfiatis, 2001). Most iron based treatment methods are more effective in removing pentavalent As rather than the more toxic trivalent. Hence, this may involve oxidation as a pretreatment to oxidize the As(III) to As(V) (Rao and Karthikeyan, 2007).

Fe₃O₄ nanoparticles were coated with 11% by weight of humic acid (HA) by a coprecipitation procedure for enhanced stability against aggregation and pH variation and were subsequently used for the removal of Hg(II), Pb(II), Cd(II), and Cu(II) from water. Maximum adsorption capacity of the heavy metals to HA coated Fe₃O₄ nanoparticles (Fe₃O₄/HA) varied from 46.3 to 97.7 mg g⁻¹ and it removed over 99% of Hg(II) and Pb(II) and over 95% of Cu(II) and Cd(II) in natural and tap water at a pH value of 6. Negligible amount of Fe₃O₄/HA sorbed heavy metals leached back to water over prolonged period of time (Liu et al., 2008).

Ruiping et al. (2009) proposed a process combining ferric and manganese binary oxides (FMBO) adsorption, sand filtration, and ultrafiltration (UF) techniques for arsenic removal. The FMBO demonstrated better efficiency in arsenic removal compared to hydrous ferric oxides (HFO) and hydrous manganese oxides (HMO) due to its combined ability to oxidize As(III) and adsorb As(V). The As(III) level got reduced from 624 µg L⁻¹ to 29.2 µg L⁻¹ with the application of Fe(II) dosage of 3 mg L⁻¹ and the KMnO₄ dosage equivalent to the sum of As(III) and Fe(II). The adsorption of arsenic onto FMBO was fast with the hydraulic retention time (HRT) of 45 s. Sand filtration removed more than 90% of arsenic and UF removed the rest. As leached from sand filter during backwash, but the leaching from FMBO was negligible (Ruiping et al., 2009).

Another promising technique was devised with mixed magnetite and maghemite nanoparticles which can adsorb As and Cr from aqueous solution and fit to use for groundwater treatment. Under acidic pH conditions, 96–99% As and Cr uptake was recorded. For

As(III) & As(V), the maximum adsorption occurred at pH 2 with values of 3.69 mg and 3.71 mg g⁻¹ of adsorbent respectively at the initial concentration of 1.5 mg L⁻¹ solution of both species. Adsorption of Cr(VI) was 2.4 mg g⁻¹ of adsorbent at pH 2 with an initial Cr(VI) concentration of 1 mg L⁻¹. However, the efficiency of the adsorption process suffered in presence of phosphate in the solution. Less than 60% As uptake was achieved from a natural groundwater containing more than 5 mg L⁻¹ phosphate and 1.13 mg L⁻¹ of As. This is a practical problem to be faced in the field application of the technology (Chowdhury and Yanful, 2010).

3.3.2.6. Ferrous salts as in-situ soil amendments. The soil amendments immobilize the contaminants by reducing their leachability and bioavailability through processes such as adsorption to mineral surfaces, surface precipitation, formation of stable complexes with organic ligands and ion exchange. Soil amendments could be applied in field by spreading it over the contaminated land areas or mixing it into the spoils over relatively long treatment periods, e.g. up to six years (Mench et al., 2003, 2006). As mobility was found to be reduced by the formation of amorphous Fe (III) arsenate (FeAsO₄·H₂O) (Carlson et al., 2002) or insoluble secondary oxidation minerals, e.g. scorodite (FeAsO₄·2H₂O) (Sastre et al., 2004). However, using ferrous sulphate to immobilize As may result in acid liberation. Therefore, this is not suitable for soils containing high concentrations of metal contaminants (Warren et al., 2003).

Hartley et al. (2004) failed to immobilize Cu even after using several Fe amendments e.g. goethite, Fe grit (an angular cast steel abrasive of ~ 0.1 mm size containing 97% Fe⁰), Fe (II)/(III) sulphates and lime.

Amorphous Fe(III) hydroxide was shown to be an effective sorbent for both anions and cations (Cornell and Schwertmann, 2003). Macro elements, such as Ca, Mg, P were also immobilized by ZVI (Bleeker et al., 2002).

Some amendments may have detrimental effects on plant growth (Hartley and Lepp, 2008) and may not be equally effective on all contaminants present. In addition, long term monitoring of soil leachate and contaminant bioaccessibility is required following application of the amendments due to possible changes in Fe and contaminant mineralogy and speciation over time (Cundy et al., 2008).

3.3.2.7. Using different mineral derived products for heavy metal adsorption. Hasan et al. (2007) prepared fullers earth based adsorbents i.e. beads and cylinders, using chitosan and sodium silicate for adsorption of cesium, but the sodium silicate binder made the treatment solution alkaline causing cesium to precipitate rather than adsorbed. SEM detected that the beads were porous. The cesium removal capacity of Fullers earth cylinder was found to be higher than that of beads. It was concluded that the alkaline nature of the cylinder precipitated out cesium, thereby increasing its capacity. The maximum cesium removal capacity on chitosan coated Fullers earth beads at a pH of 6.5 and 30 °C temperature was found to be about 26.3 mg g⁻¹ of bead from a solution containing 1000 mg L⁻¹ of CsCl. However, in presence of NaCl and strontium, the capacity of Fullers earth beads decreased by almost 62%.

Large volume of research publication exists on the adsorption of heavy metals by hydrotalcite, a double-layered mixed-metal hydroxide (Layered Double Hydroxide, LDH) belonging to the family of anionic clays. Various types of hydrotalcites were used over the past decade, such as synthetic hydrotalcite calcined at 350–550 °C to remove arsenate, chromate, and vanadate ions from water solutions (Kovanda et al., 1999), uncalcined and calcined Mg–Al–CO₃ hydrotalcite at 500 °C to remove Cd, Pb, Ni (Lazaridis, 2003) as well as Cr (Álvarez-Ayuso and Nugteren, 2005), and also calcined and uncalcined hydrotalcite to remove As, Se and Cr (Carriazo et al., 2007; Xu

et al., 2010; Yang et al., 2005). Mg–Al hydrotalcite was used, sometimes in conjunction with chelating ligand such as EDTA to remove As(III), As(V), Se, Cr, Cu, Cd and Pb (Hu et al., 2005; Kameda et al., 2005; Norihiro et al., 2005; Pérez et al., 2006). Notably, Cr was the most researched heavy metal followed by As and Se. Regelink and Temminghoff (2011) evaluated the efficiency of the processes of Ni–Al LDH precipitation and Ni adsorption to reduce its mobility in a sandy soil aquifer. Both adsorption and Ni–Al LDH precipitation occurred at pH ≥ 7.2 . A long term column experiment revealed the retention of 99% of influent Ni at pH 7.5 due to Ni adsorption ($\sim 34\%$) and Ni–Al LDH precipitation ($\sim 66\%$) based on mechanistic reactive transport modelling. Nevertheless, leaching of the bound Ni occurred at pH 6.5 due to desorption.

Apatite is a group of phosphate minerals, with a general formula of $(\text{Ca}, \text{Sr}, \text{Pb})_5(\text{P}, \text{As}, \text{V}, \text{Si})\text{O}_4)_3(\text{F}, \text{Cl}, \text{OH})$. It has a unique characteristics that it is produced and used by biological micro-environmental systems. Fuller et al. (2003) discussed about using apatite materials within PRB for remediating U(VI) contaminated groundwater (Fuller et al., 2003). Sneddon et al. (2005) tried to remove 4, 10 and 100 mg L⁻¹ concentration of As(V) from aqueous solutions by using 0.2–10 g L⁻¹ of solid mixture of hydroxylapatite and baryte at an initial pH of 5 or 7. It was not much of a success, but the mechanism involved adsorption rather than coprecipitation. Conca and Wright (2006) used Apatite II, a biogenically precipitated apatite material derived from fish bones having general composition $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$, where $x < 1$, along with 30–40% by weight of organic materials, in PRB to treat AMD. Apatite II was proved to have higher metal removal capacity than phosphate rock, cow bone, C-sorb, Fe⁰ filings, compost and activated charcoal (Conca et al., 2000). Sulphate reduction in the PRB occurred microbially resulting in the precipitation of Zn as sphalerite [ZnS]. Apatite II supported the growth of sulphate-reducing bacteria. Pb was most likely to be immobilized by precipitation as pyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH}, \text{Cl})_2]$. Apatite II supplied the PO_4^{3-} required in the process and also maintained the requisite pH. By the same mechanism, U, Ce, Pu, Mn and other metals might be remediated. The PRB with apatite II reduced the concentrations of Cd and Pb to below detection level and reduced Zn to near background in the experimental site, about 100 $\mu\text{g L}^{-1}$. In the PRB, 90% of the immobilization occurred in the first 20% of the Apatite II barrier (Conca and Wright, 2006). So, Apatite II played a versatile role as microbial growth site, phosphate group supplier and also pH regulator.

These may be used in the PRB to evaluate their effectiveness in groundwater treatment.

3.3.3. Electrokinetic remediation of Soil

When a direct current electrical field is applied across a wet mass of contaminated soil, the migration of non-ionic pore fluids by electro-osmosis and the ionic migration of dissolved ions towards the electrodes take place. Combining these two removal mechanisms result in the electrokinetic extraction of metal contaminants from soils (Lestan, 2008). The process has been schematically represented, as in Fig. 10.

Virkutyte et al. (2002) considered electro-remediation to be most effective in treating near saturated, clay soils polluted with metals, whereby removal is $>90\%$. Electromigration rates in the sub-surface is dependent upon the soil pore, density of water current, grain size, ionic mobility, concentration of contaminant and total ionic concentration (Cauwenberghe, 1997; Sims, 1990). In turn, it is governed by advection which is generated by electro-osmotic flow and externally applied hydraulic gradients, diffusion of the acid front to the cathode and the migration of cations and anions towards the respective electrodes (Zelina and Rusling, 1999). Electrolysis of water is the dominant electron transfer reaction occurring at electrodes during the electrokinetic process:

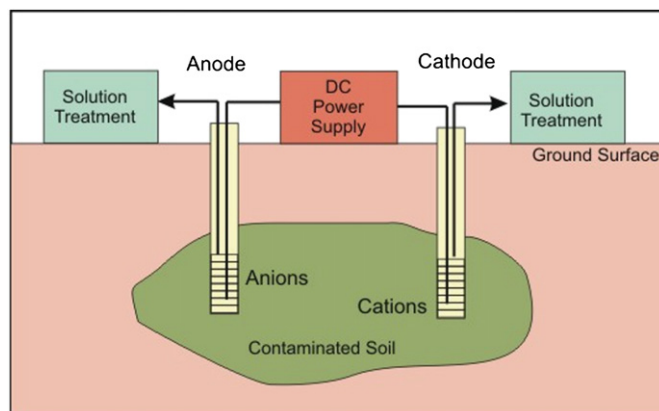


Fig. 10. Electrokinetic treatment of soil contaminants, adapted from <https://portal.navy.mil>.



The hydrogen ions produced in the process decrease the pH near the anode causing desorption of metallic contaminants from the soil solid phases. The dissolved metallic ions are then removed from the soil solution by ionic migration and precipitation at the cathode (Acar and Alshawabkeh, 1993). On the other hand, increase in the hydroxide ion concentration causes an increase of the pH near the cathode. Three phenomena occurring during electrokinesis are electro-osmosis, electromigration and electrophoresis (Virkutyte et al., 2002).

Electrokinetic techniques resembling natural soil/sediment reactions could be used for generating sub-surface reactive Fe barriers in various geometries. This could be done using a low-magnitude of $\sim 2 \text{ V cm}^{-1}$ electrical potential generated between vertical Fe-rich electrodes (Yin and Allen, 1999). Faulkner et al. (2005) experimentally generated a continuous Fe-rich impervious precipitate zone in the sub-surface by electrokinetic method to act as a reactive barrier for contaminant containment. Fe electrodes were placed around the site for introducing Fe in the system. When electric field was applied, these electrodes dissolved and reprecipitated. In a time period of 300–500 h, at voltages of $<5 \text{ V}$ and with electrode separation of 15–30 cm, continuous Fe-rich bands up to 2 cm thick was generated. The thickness of the Fe-rich band increased with the applied voltage. Geotechnical tests indicated that sufficient imperviousness with coefficient of permeability of 10^{-9} ms^{-1} or less and mechanical strength (unconfined compressive strength of 10.8 N mm^{-2}) were required to contain the pollutants. The Fe-rich barrier was found to be composed of amorphous Fe, lepidocrocite, goethite, maghemite and native Fe (Faulkner et al., 2005).

3.3.3.1. Heavy metal removal efficiency from contaminated soils. Electrokinetic remediation techniques demonstrated 85–95% efficiency in removing As, Cd, Cr, Co, Hg, Ni, Mn, Mb, Zn, Sb and Pb from low-permeability soils such as clay, peat, kaolinite, high-purity fine quartz, Na and sand montmorillonite mixtures, as well as from argillaceous sand (Yeung et al., 1997). In addition, kaolinite showed more than 90% removal efficiencies of heavy metals (Pamukcu and Wittle, 1992). However, the removal efficiency of porous, high permeability soils, such as peat and river sediment, was approximately 65% (Chilingar et al., 1997).

If the soil has high buffer capacity, then soil acidification is prevented resulting in the poor performance of the electrokinetic

extraction of toxic metals. In such conditions, chelating agents such as EDTA were suggested to be added to the soil to enhance the process (Yeung et al., 1996). Chelant-enhanced electrokinetic extraction was found to be promising for dealing with fine-grained soils with high clay or organic matter content at moderate depth.

Giannis and Gidarakos (2005) used sodium dodecyl sulphate (SDS), a surfactant as purging solution in the electrode compartment and were able to enhance Cd removal from the soil. Almost 90% Cd was removed. Using electrokinetic process, Reddy and Parupudi (1997) experimented with Ni(II), Cd(II) and Cr(VI) removal from Kaoline with sharp pH gradient from anode to cathode and glacial till alkaline pH. They observed that Cd(II) and Ni(II) precipitated in both Kaolin near cathode and Glacial till due to presence of alkaline conditions. However, Cr(VI) showed low adsorption in high pH. Therefore, its adsorption in alkaline Glacial Till and cathodic portion of Kaoline was found to be low. Cr(VI) became immobile only in acidic regions of Kaoline. Colacicco et al. (2010) also removed heavy metals from marine sediments by using EDTA solution.

Runnells and Wahli (1993) (Runnells and Wahli, 1993) proposed a process of electromigration with a series of metallic or carbon electrodes placed in boreholes around the source of contaminated groundwater or in the downgradient of the groundwater flow. They suggested that the process was effective in in-situ containment or cleanup of heavy metals. An electric potential applied across the electrodes attracted the dissolved heavy metal, sulphate, nitrate and chloride contaminants leading to concentrate them in the boreholes of the electrodes so that they can be pumped out. However, the field application had some difficulties e.g. high current density and extreme pH could corrode the anodes. Also, due to the hydrolysis of water, cost of electricity may be high and high flow rate of groundwater may overwhelm the electromigration towards the anode.

Some researchers performed numerical simulations by a mathematical model for electrokinetic treatment of heavy metal contaminated aquifer. They reported that electromigration was found to be effective for the local removal of heavy metals between the electrodes and heavy metal accumulated at cathode region in the downstream after being removed from the upstream anode region. Also, they found that the hydraulic flow by purge water was essential to carry away the heavy metal from the aquifer (Shiba and Hirata, 2002; Shiba et al., 2005).

3.3.3.2. Coupling of electrokinetic remediation technique with other technologies. Czurda and Haus (2002) suggested coupling of electrokinetic treatment with PRB technique. Electrokinetics could enforce the process of hydraulic flow through the reactive zone or wall of PRB and could help in moving the contaminants in the soil pore water into treatment zones where the contaminants can be captured or decomposed.

Giannis and Gidarakos (2005) combined electrokinetic remediation and soil washing technology for removing Cd from contaminated soil. Soil was saturated with tap water, while acetic acid, hydrochloric acid and EDTA were used as purging solutions resulting in a decrease of Cd concentration near anode, but a significant increase in the middle of the cell, due to the increasing pH. When citric acid, nitric acid and acetic acids were used, there was an 85% reduction of Cd concentration. The soil pH and washing solutions were thus found to be the most important factors in governing the dissolution and/or desorption mechanism of Cd in soil under electrical fields (Giannis and Gidarakos, 2005).

A galvanic cell was used in an electrokinetic process to remove Cu from sediments. Polluted sediments were put between Fe and C rods connected with a conductive wire and was flooded with water, forming a galvanic cell, which ultimately removed the pollutants by

electromigration and/or electro-osmosis. A weak voltage >1 V, decreasing with time, was formed by the galvanic cell. Removal efficiency was improved at lower pH when there was more electrolyte in the sediment and less electrolyte in the supernatant water. Cu was found to desorb from sediment to pore solution and subsequently electromigrated from the anode to the cathode (Yuan et al., 2009).

A hybrid method of EDTA-enhanced bioelectrokinetics effectively removed heavy metals, especially Pb. Active bio-augmentation was performed using *Acidithiobacillus thiooxidans* which enhanced the mobility of heavy metals in the soil improving the final removal efficiencies of Cu and Zn in the hybrid electrokinetics using acid and EDTA. In spite of forming of some $PbSO_4$, the removal efficiency for Pb was about 92.7%, which was superior to that of an abiotic process (Lee and Kim, 2010).

3.3.4. Other physico-chemical soil treatment processes

Some more ex-situ and in-situ physico-chemical treatment processes which were primarily used for soil remediation, not for groundwater treatment are left out of this review. Nevertheless, one can always apply them in combination of some other methods to treat groundwater as well. These methods are Solidification/Stabilization (Complete and partial vitrification) (Abramovitch et al., 2003; Acar and Alshawabkeh, 1993; Anderson and Mitchell, 2003; Dermatas and Meng, 2003; Leist et al., 2003; Moon et al., 2008; Sherwood and Qualls, 2001; Singh and Pant, 2006; Sullivan et al., 2010; USEPA, 1992; Wait and Thomas, 2003), Pyrometallurgical Separation (in-situ and ex-situ) (Hazardous Waste Consultants, 1995; Mulligan et al., 2001; Smith et al., 1995) and Physical Separation Process (screening, gravity, magnetic separations) (Allen and Torres, 1991; Evanko and Dzombak, 1997; Rosetti, 1993; Scullion, 2006).

4. Critical discussion

Heavy metals are extremely toxic for living beings and they are highly persistent pollutants. Once they get into the soil sub-surface or in groundwater, it becomes extremely difficult to handle them due to the complex speciation chemistry coming into play. However, many techniques have been devised over the past few decades to remediate heavy metal contaminated soil and groundwater. In this review, all the existing and promising technologies have been discussed under three broad headings viz. chemical, biological/biochemical/biosorptive and physico-chemical treatment technologies. Many new concepts have also been described, which are yet to be practically applied and are in experimental stages only, but we consider them to be very much upcoming and too much promising to leave out of the discussion.

4.1. Chemical treatment technologies

These technologies are mostly applied for controlling large plumes of contaminants spread over a large area deep in the aquifer. These techniques lack sophistication and resort to chemical leaching processes and stabilization methods. Reductants such as dithionites and gaseous hydrogen sulphide can be injected in the contaminated zone, but alkaline pH and high permeability of soil are pre-requisites. The delivery of gas becomes difficult and nitrogen may be used as a carrier gas. Toxic intermediates are formed during the reduction process and these cannot be properly handled.

Colloidal ZVI is another very strong reductant highly acclaimed for its easy handling. It can be injected deep in the aquifer but it undergoes rapid corrosion and also produces toxic byproducts.

Some ferrous salts are used for mainly chromate reduction, but this process is suitable for only sub-surface regions, not for aquifers.

Chemical washing provides a very effective and direct method of dealing with the heavy metal contamination problem. However, using strong extractants such as acids may destroy the soil texture jeopardising the soil environment. Ex-situ treatment of the contaminated soil is a messy affair and should be avoided due to handling problems. The wash solution emerging from the process poses another hazard and their treatment is indeed a complex issue. Chelate flushing is very effective to extract a large number of heavy metals, but chelates such as EDTA and DTPA are costly and also carcinogenic in nature. They can be regenerated and reused. Solvent impregnated resins are also very efficient, can be 100% regenerated and can be used in PRBs.

4.2. Biological, biochemical and biosorptive treatment technologies

Natural biological activity do not has the ability to remove heavy metals from deeper layers of soil or from aquifers. However, the biological processes such as phytoremediation, phytoextraction and hyperaccumulation can be used for long term remediation purposes in conjugation with some other more intense remediation process. Genetically engineered organisms can be used for more active role in this process.

Enhanced bioremediation is a highly researched area. Immobilization of radionuclides such as U, Tc and Ra by micro-organisms of *Geobacter* species is very novel method. Biobarriers can be used for remediating such radionuclides in flowing groundwaters. However, optimization of applied acetate and also the effect of nitrate are to be considered for success of the technique.

ISBP process immobilizes the heavy metals as sulphide precipitate through BSR process, but stability of the sulphides under changing pH and redox conditions remains to be a questionable issue.

BSR process involves a wide choice of electron donors to boost up activities of SRBs and can be applied in a reactive barrier or in an ex-situ anaerobic bioreactor, which is rather difficult. AMD can be effectively treated by BSR.

In-situ arsenic removal by micro-organisms and ferrous oxides has been proved to be a very effective and sustainable technology in practice. It is a long term process and have long lasting effect on aquifer. No waste is generated and practically no chemical is required to create an oxygenation zone in the aquifer. It maintains a very fine balance between coprecipitation of As(V) with Fe(III) and adsorption of the former into the later. Adsorption is more desirable than coprecipitation and can be achieved by calculated oxygenation process.

Biosorption is a highly practical solution for heavy metal remediation and is a much researched field of study. Biosorption is cost effective, has possibility of metal recovery and also generates minimum sludge.

Biosurfactants are biodegradable and they solubilize the metals by reducing surface tension and increasing their wettability, thus bringing them out of soil or aquifer matrix. However, their field application for heavy metal removal is still limited.

Metal uptake by various organisms is principally a slower natural process that can be used in field for long term remediation measures. This can be applied in fluidized bed reactors also. However, the immobilized metals leach back in the solution under influence of acidic pH.

Agricultural wastes and cellulosic materials have huge potential to be used for biosorption of heavy metals through ion exchange process, surface complexation and electrostatic interactions. Simple pre-treatments with chemical agents may be necessary to increase their sorptive power and stability. Low cost, non-toxicity,

high adsorption rate, easy availability makes this option most lucrative and intense scientific research is going on in this field. These can be used in PRBs for aquifer remediation.

4.3. Physico-chemical treatment technologies

PRBs present the most practical all round solution for remediating flowing groundwater. They incorporate the strength of other technologies such as adsorbents, ZVI, microbial fixations, BSR and electrokinetic remediation. However, they are prone to serious problem regarding clogging and reduction of permeability, leading to bypass of groundwater flow. Exhaustion of reactivity of barriers also hamper their activity and recharging, replacing or replenishing the reactive media poses a challenge in this technology and regular performance monitoring is required. The PRB technology principally depends upon sorption process, precipitation process and biological reduction processes.

Sorption process in the PRBs is achieved by employing the iron based sorbents, activated carbons, zeolite materials as well as biosorbents. Nevertheless, with change in the soil environment e.g. pH and redox potential, the sorbed heavy metals may once again gain mobility. Activated carbon sorbents having surface active groups can adsorb a wide range of heavy metals, can be regenerated and also can be coupled with micro-organisms for enhanced metal immobilization. Red mud can also sorb a large number of heavy metals and have very low leachability, but is very much sensitive to pH variation. Zeolites show high rate of molecular sieving depending on the mineralogy and mineral content of the zeolite. It is a very good choice for selective screening of some heavy metal. Iron sorbents are extremely popular for arresting arsenic from groundwater and the activity depends on oxygen content of the water and aerobic or anaerobic condition of the aquifer. Excessive DO values can precipitate arsenic on the iron sorbents, which can also undergo corrosion.

Chemical precipitation in PRB involves use of various chemical agents such as ZVI, alkaline complexing agents, atomized slags and caustic magnesia to arrest the mobile heavy metals by converting them chemically into their insoluble state. ZVI, as precipitating agent can immobilize a large number of heavy metals e.g. As, Cr, Ni, Pb, Mn, Se, Co, Cu, Cd, Zn, Ca, Mg, V, Sr and Al which coprecipitate with it. However, these precipitation results in corrosion of ZVI and clogging of the PRB which ultimately loses its permeability. Caustic magnesia and alkaline complexing agents such as limestone increase the pH of the flowing contaminated plume e.g. groundwater and AMD thereby precipitating the heavy metals. Sometimes, biocompost can also be used with it to support the growth of metal reducing micro-organisms. Atomized slags from industry are highly pH dependent and under appropriate conditions can treat metal as well as organic contaminants.

The biological barriers shelter micro-organisms capable of bio-precipitating heavy metals. Nutrient delivery along the barrier and bioclogging are two difficulties faced in this technique. BSR and denitrification mechanisms help in removal of Cr, Se, Al, Fe, Fe, Ni, Zn, Al, Mn, Cu, U, As and V. Again, PRBs containing ZVI can be bioaugmented by providing micro-organisms, nutrient and substrates to remove As, Sr, Pb, Cd, Zn, and Ni by BSR process.

The adsorption, absorption and filtration mechanisms provide the widest scope of practical application as well as research options for heavy metal removal from groundwater. Activated carbon (GAC, IMC, PHC), membrane and filter techniques (electrodialytic membrane liquid membrane, polymer membrane, ultrafiltration membrane, nanofibre membrane), surfactants (SDS, SDBS), industrial byproducts and wastes (lignite, bio-char, maple wood ash), different ferrous materials (ZVI, Fe₃O₄, FeCl₃, FMBO) and minerals (Fuller's earth beads, hydrotalcite, apatite) had been researched and

applied over years for heavy metal removal from water, soil and other matrices. These can be similarly used in PRBs or reactive zones to treat groundwater as well.

Electrokinetic treatments sometimes demonstrate high efficiency of heavy metal removal from groundwater depending on the factors such as water content, pH, ionic conductivity, texture, porosity and groundwater flow rate. This treatment process can be combined with other processes such as PRB, membrane filtration, surfactant flushing, bioaugmentation and reactive zone treatment to attain successful remediation goals.

Some other soil remediation techniques e.g. solidification, pyrometallurgical separation, screening, gravity and magnetic separation are never applied to groundwater remediation, but can be researched to utilize by coupling with some other technologies discussed throughout the paper.

5. Conclusion

Groundwater treatment technologies have come a long way since the days of their inception. Much research has been done on numerous technologies ranging from simple ex-situ physical separation techniques to complex in-situ microbiological and adsorption techniques. In modern days, sustainability is the keyword to any process. Instant remedy may provide a temporary solution to a problem but it may not be a permanent one. Therefore, natural processes and biogeochemistry of the soil should be given due consideration before planning remediation processes.

According to Scholz and Schnabel (2006), selection of site specific soil remediation technique can be a challenging task due to the uncertainty in assessment of level of contamination, high costs of remediation and the collateral impacts of the technique on the environment. They came up with some multi-criteria utility functions which used probability density functions, representing contamination for all site coordinates, to select a remediation technique for a particular contaminated site. The multi-criteria-decision making was found to be of non-linear structure and it depended upon the geostatistical uncertainties of the log-normal distributed soil contamination (Scholz and Schnabel, 2006). It can be definitely and positively stated that decision making in case of groundwater contamination is far more difficult due to additional factors such as soil permeability, groundwater flow pattern and complex chemical processes taking place in the aquifer. Nasiri et al. (2007) discussed about the compatibility analysis targeting the interactions between remediation technologies and site characteristics such as the types of active contaminants and their concentrations, soil composition and geological features before implementing groundwater remediation strategies in contaminated areas. They introduced a decision support system for ranking the different remediation plans based on their estimated compatibility index which was calculated by using a multiple-attribute decision-making (MADM) outline (Nasiri et al., 2007).

Soil washing, chelate flushing or physical separation tend to destroy the soil profile and should be performed to recover metals from heavily polluted industrial sites and in case no other methods can be applied. In-situ chemical injection in the aquifer is a very promising technique but the soil chemistry and aquifer may get disrupted in the process of cleaning. Some chemicals are non-biodegradable, even produce toxic intermediates and are carcinogenic. Hence, caution should be taken while introducing chemicals in aquifers.

PRB is a much developed technology and scientific research is still going on for using site and contaminant specific reactive cells ranging from strong chemicals, ion exchange resins, zeolites, iron, surfactants, adsorptive substances, bio-active materials and organisms. Here again, the effect of the reactive cell on the aquifer

should be given good consideration before application. In this review, many adsorbents and separation processes are described which are actually used for heavy metal separation from aqueous solutions. However, these can be used in permeable reactive barriers as well to separate the pollutants from aquifers. Also, civil construction of barriers over vast area may be costly and the reactive media should be removed once it serves its purpose. Detailed sub-surface characterization data that capture geochemical and hydrogeologic variability, including a flux-based analysis, are needed for successful applications of PRB technology for arsenic remediation (Wilkin et al., 2009). Electrokinetic separation is also a promising field and when coupled with iron based technologies and biosorption, has shown very promising results.

The iron based technologies will need a special mention. A range of materials such as ZVI, red mud and ferrous salts are being used as reductants, precipitants, adsorbents and amendments in different types of treatments. They are also being coupled with other techniques such as activated charcoal and electrokinetic treatments for increasing process efficiency. Membrane and filtration technologies along with various adsorbents have very promising future in field application.

However, the most promising field of technology emerging in the last decade is the biological or biochemical techniques employing microbes and nutrients for bioprecipitation, enzymatic oxidations, biosurfactants and sulphate reductions as heavy metal removal tools. Injection of nutrients and electron donors is mostly cheap and non-toxic. Regular monitoring of microbe population and water quality can ensure the success of the ongoing treatment process. Use of aerated groundwater to boost As(III) oxidizing microbe population in the aquifer and to oxidize Fe(II) to Fe(III), thus trapping the As(V) is indeed a simple yet effective technology. In the BSR process, the metal sulphides produced by SRBs are usually very stable. These biochemical processes have long lasting effects on aquifer and are highly sustainable requiring occasional monitoring. These biochemical processes have the advantages of using in PRBs along with iron based technologies. However, presence of a group of heavy metals along with N, P, K, sulphate, nitrate, phosphate, carbonate and other organic radicals in the aquifer, may render the microbes ineffective.

Due to extreme complexity of soil chemistry and, extensive site specific research is necessary to bring out the optimum performance from any of these technologies.

Acknowledgements

We are grateful to Prof Amitava Gangopadhyay, Jadavpur University, Kolkata, India and Prof S. C. Santra, University of Kalyani, West Bengal, India for letting access to their facility and resources for this review work and to University of Malaya, Kuala Lumpur, Malaysia for the financial assistance.

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