

# Ex-Situ Remediation Technologies for Environmental Pollutants: A Critical Perspective

Saranya Kuppusamy, Thavamani Palanisami, Mallavarapu Megharaj,  
Kadiyala Venkateswarlu, and Ravi Naidu

## Contents

|     |  |     |
|-----|--|-----|
| 1   | Introduction.....  | 120 |
| 2   | Ex-Situ vs. In-Situ Remediation .....  | 124 |
| 3   | Existing <i>Ex-Situ</i> Remedial Options for Contaminated Soil and Groundwater:<br>Technology Profile and Recent Advances..... | 124 |
| 3.1 | Dig-and-Dump (Landfills and Engineered Landfills) .....  | 124 |
| 3.2 | Pump-and-Treat .....   | 126 |
| 3.3 | Incineration .....   | 126 |
| 3.4 | Oxidation.....   | 130 |
| 3.5 | Adsorption.....  | 131 |
| 3.6 | Ion-Exchange .....   | 136 |
| 3.7 | Pyrolysis.....   | 140 |
| 3.8 | Soil Washing .....   | 141 |
| 3.9 | Dehalogenation .....   | 144 |

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S. Kuppusamy

CERAR-Centre for Environmental Risk Assessment and Remediation, University of South  
Australia, Mawson Lakes SA5095, Australia

CRC CARE-Cooperative Research Centre for Contamination Assessment and Remediation  
of Environment, PO Box 486, Salisbury South SA5106, Australia

T. Palanisami • M. Megharaj (✉) • R. Naidu

GIER- Global Institute for Environmental Research, Faculty of Science and Information  
Technology, The University of Newcastle, Callaghan, NSW 2308, Australia

CRC CARE-Cooperative Research Centre for Contamination Assessment and Remediation  
of Environment, PO Box 486, Salisbury South SA5106, Australia

e-mail: [megh.mallavarapu@newcastle.edu.au](mailto:megh.mallavarapu@newcastle.edu.au)

K. Venkateswarlu

Formerly Department of Microbiology, Sri Krishnadevaraya University,  
Anantapur 515055, India

|      |   |     |
|------|---|-----|
| 3.10 | Solid-Phase Bioremediation.....                             | 148 |
| 3.11 | Slurry-Phase Bioremediation: Bioreactors.....               | 157 |
| 3.12 | Solidification/Stabilization.....                           | 159 |
| 3.13 | Constructed Wetlands .....                                  | 162 |
| 4    | <i>Ex-Situ</i> Technologies for Air Pollution Control ..... | 164 |
| 5    | Emerging <i>Ex-Situ</i> Remediation Technologies .....      | 168 |
| 5.1  | Ultrasonic Technology .....                                 | 168 |
| 5.2  | Microbial Fuel Cells, Nanoremediation and Others .....      | 170 |
| 6    | Future Research Needs .....                                 | 170 |
| 7    | Summary .....   | 172 |
|      | References.....   | 173 |

## Abbreviations

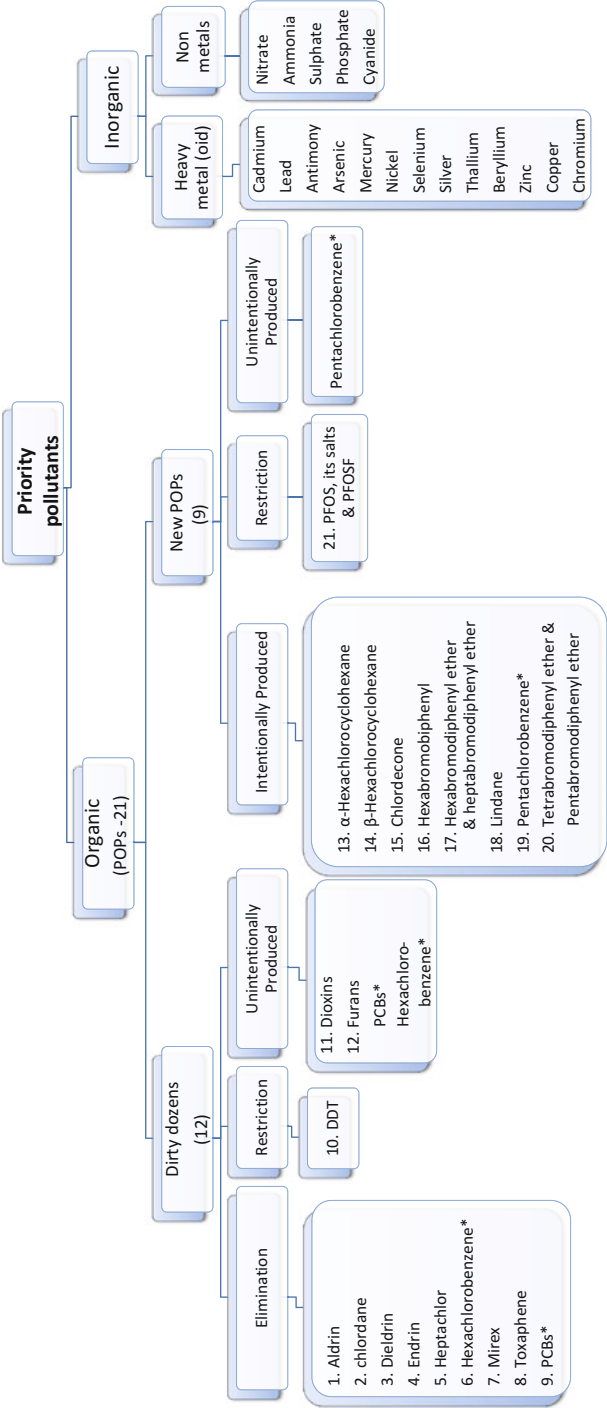
|                  |   |
|------------------|---|
| °C               | Degree celsius                                      |
| \$               | Dollar  |
| >                | Greater than  |
| <                | Less than   |
| %                | Per cent  |
| 2,4-D            | 2,4-Dichlorophenoxyacetic acid                      |
| A                | Australian  |
| Al               | Aluminium   |
| AOP              | Advanced oxidation process                          |
| As               | Arsenic   |
| B                | Boron   |
| Ba               | Barium  |
| BDD              | Boron-doped diamond                                 |
| BTEX             | Benzene toluene ethylbenzene and xylenes            |
| BTF-PCO          | Biotricking filtration and photocatalytic oxidation |
| CCl <sub>4</sub> | Carbon tetrachloride                                |
| Cd               | Cadmium   |
| CH <sub>4</sub>  | Methane   |
| Cl <sub>2</sub>  | Chlorine  |
| cm               | Centimetre  |
| Co               | Cobalt  |
| CO <sub>2</sub>  | Carbon-di-oxide                                     |
| COD              | Chemical oxygen demand                              |
| Cr               | Chromium  |
| CTMAB            | Cetyltrimethyl ammonium bromide                     |
| Cu               | Copper  |
| DDE              | Dichlorodiphenyldichloroethylene                    |
| DDT              | Dichlorodiphenyltrichloroethane                     |
| DNAPL            | Dense non-aqueous phase liquid                      |
| EDTA             | Ethylenediaminetetraacetic acid                     |
| EK               | Enhanced electrokinetics                            |
| EPA              | Environmental Protection Agency                     |
| Fe               | Iron  |

|                               |   |
|-------------------------------|---|
| F-gases                       | Fluorinated gases                           |
| FRTR                          | Federal Remediation Technologies Roundtable |
| g                             | Gram  |
| GDP                           | Gross domestic product                      |
| h                             | Hour  |
| H <sub>2</sub> O <sub>2</sub> | Hydrogen peroxide                           |
| H <sub>2</sub> S              | Hydrogen cyanide                            |
| HCH                           | <a href="#">Hexachlorocyclohexane</a>       |
| Hg                            | Mercury                                     |
| Hz                            | Hertz                                       |
| IEM                           | Ion-exchange membrane                       |
| IrO <sub>2</sub>              | Iridium oxide                               |
| kW                            | Kilowatt                                    |
| L                             | Litre                                       |
| lb                            | Metric pound                                |
| m <sup>2</sup>                | Square metre                                |
| m <sup>3</sup>                | Cubic metre                                 |
| MFC                           | Microbial fuel cells                        |
| mg                            | Milligram                                   |
| min                           | Minute                                      |
| Mo                            | Molybdenum                                  |
| N                             | Nitrogen                                    |
| N <sub>2</sub>                | Atmospheric nitrogen                        |
| NAPL                          | Non-aqueous phase liquid                    |
| NO <sub>2</sub>               | Nitrogen dioxide                            |
| nZVI                          | Nano zero-valent iron                       |
| O <sub>3</sub>                | Ozone                                       |
| OH <sup>•</sup>               | Hydroxyl radical                            |
| P                             | Phosphorous                                 |
| PAHs                          | Polycyclic aromatic hydrocarbons            |
| Pb                            | Palladium                                   |
| Pb                            | Lead  |
| PBDE                          | Polybrominated diphenyl ethers              |
| PCB                           | Polychlorinated biphenyl                    |
| PCDDs                         | Polychlorinated dibenzodioxins              |
| PCDFs                         | Polychlorinated dibenzofurans               |
| PCE                           | <a href="#">Perchloroethylene</a>           |
| PCNs                          | Polychlorinated naphthalenes                |
| PCP                           | Pentachlorophenol                           |
| Pd                            | Palladium                                   |
| PFCs                          | Perfluorochemicals                          |
| PFOA                          | Perfluorooctanoate                          |
| PFOS                          | Perfluorooctane sulfonate                   |
| POP                           | Priority organic pollutant                  |
| QACs                          | Quaternary ammonium compounds               |
| s                             | Second                                      |

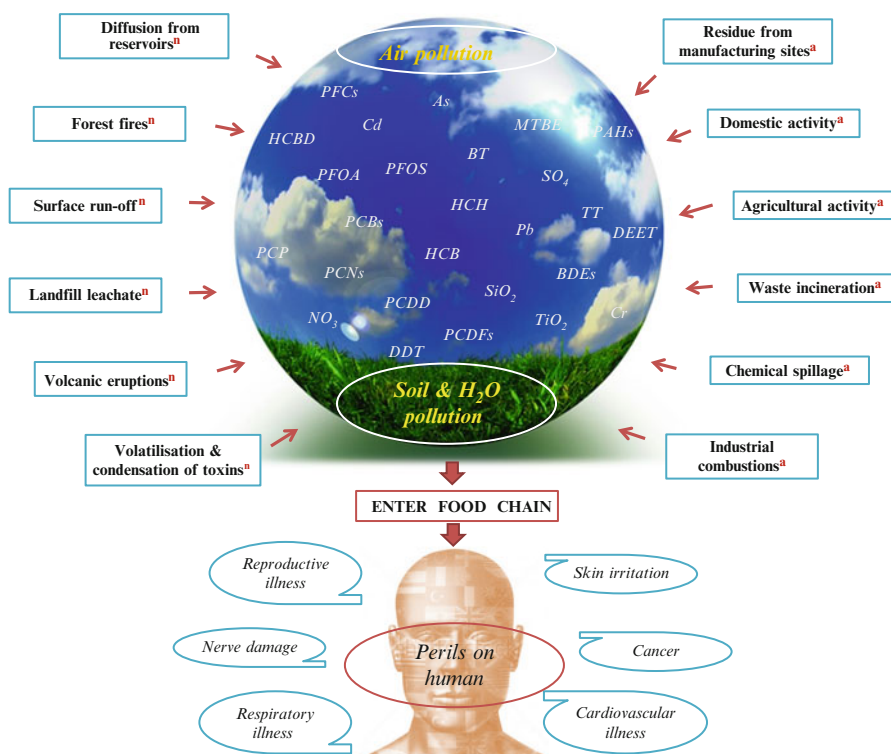
|                                |                                 |
|--------------------------------|---------------------------------|
| S/S                            | Solidification/stabilization    |
| Sb <sub>2</sub> O <sub>5</sub> | Antimony pentoxide              |
| Se                             | Selenium                        |
| SnO <sub>2</sub>               | Tin dioxide                     |
| SO <sub>2</sub>                | Sulfur dioxide                  |
| SVOC                           | Semi-volatile organic compounds |
| t                              | Metric ton                      |
| TCE                            | Trichloroethylene               |
| TCPP                           | Tris(chloroisopropyl)phosphate  |
| Ti                             | Titanium                        |
| TMB                            | Trimethyl benzene               |
| TNT                            | Trinitrotoluene                 |
| TOC                            | Total organic carbon            |
| TPH                            | Total petroleum hydrocarbons    |
| U                              | Uranium                         |
| US                             | United States                   |
| UV                             | Ultra-violet                    |
| VOC                            | Volatile organic compounds      |
| W                              | Watt                            |
| WHO                            | World Health Organization       |
| Zn                             | Zinc                            |

## 1 Introduction

Pollution and the global health impacts from toxic pollutants are presently of great concern. World-wide, one serious problem of half the population is polluted drinking water. Such pollution causes nearly 250 million cases of water-based diseases and 0.005–0.01 billion deaths annually. In US alone, more than 70 % of the cancer risk from exposure to air toxicants is contributed by diesel emissions (WHO 2013). Currently, more than 100 million people are at risk from exposure to a list of toxic organic and inorganic pollutants (Fig. 1) such as pharmaceutical and personal care products, illicit drugs, hormones, steroids, polychlorinated naphthalenes (PCNs), perfluorochemicals (PFCs), synthetic musks, quaternary ammonium compounds (QACs), veterinary products, polychlorinated alkanes, benzothiazoles, polydimethylsiloxanes, bisphenol A, triclosan, industrial compounds/byproducts, food additives, pesticides, heavy metals, chlorinated solvents, polycyclic aromatic hydrocarbons, engineered nanoparticles, etc. Exposure to toxicant pollution can causes immense health impacts (Fig. 2) such as physical and mental disorders, organ dysfunction, neurological disorder, cancer, reduced life expectancy, weakening of the body's immune system, and in some cases death (Godduhn and Duffy 2003; Perera and Herbstman 2011; Mates et al. 2010; Yu et al. 2011; Huang et al. 2012).



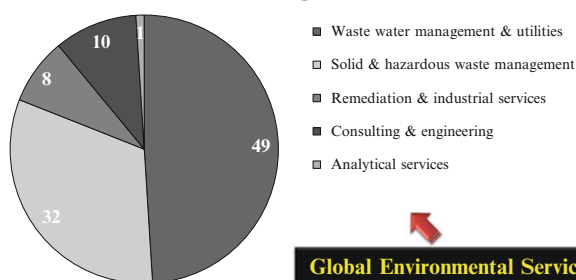
**Fig. 1** Priority organic and inorganic pollutants of global issue: a comprehensive framework. *Source:* Stockholm Convention (2010); US EPA (2012). *POP*s priority organic pollutants, *PCB* pentachlorobenzene, *PFOS* perfluorooctanesulfonic acid, *PFOSF* perfluorooctanesulfonyl fluoride, *asterisk* listed twice under the annexes; *numbers* in parentheses indicate the total number of pollutants



**Fig. 2** Priority noxious wastes in the biosphere: causes and consequences. <sup>n</sup>natural source; <sup>a</sup>anthropogenic source; *PCP* pentachlorophenol, *Cd* cadmium, *As* arsenic, *BT* benzotriazole, *PFOS* perfluorooctanesulfonate, *PFOA* perfluorooctanoate, *HCB* hexachlorobutadiene, *PCBs* pentachlorobenzene, *HCH* hexachlorocyclohexane, *PCBs* pentachlorobenzene, *MTBE*, methyl tertiary butyl ether, *SO<sub>4</sub>* sulfate, *Pb* lead, *TT* tolyltriazole, *PCDFs* polychlorinated dibenzofurans, *PCDD* polychlorinated dibenzo-*p*-dioxins, *DEET* diethyl-meta-toluamide, *PAHs* polyaromatic hydrocarbons, *Cr* chromium, *TiO<sub>2</sub>* titanium di oxide nanoparticles, *SiO<sub>2</sub>* silicon nanoparticles, *BDEs* brominated diphenyl ether, *NO<sub>3</sub>* nitrate, *DDT* dichloro diphenyl trichloroethane, *PCNs* polychlorinated naphthalenes

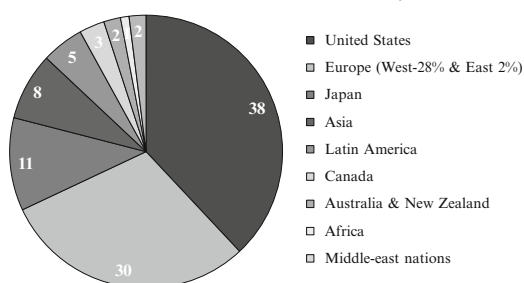
Notably polychlorinated dibenzofurans and dibenzodioxins are highly persistent chemicals, and some of the congeners, mostly those with lateral chlorine substitutions at certain positions, are extremely toxic and carcinogenic to humans. Pesticides are often used in public health and agricultural programs globally. Solvents such as carbon tetrachloride and trichloroethylene (TCE) contaminate the surroundings due to large-scale anthropogenic applications. Pharmaceutical and personal care products and food additives are used in our day-to-day life. Recently, the use of nanoparticles in sunscreen lotions and tooth pastes has increased. In most cases, the negative ecological consequences of the toxic chemicals, when released, have been observed to exceed the benefits of their use and necessitate the need for their removal or mineralization (Landis and Yu 2003).

## Share (%): Environmental remedial products and services



**Global Environmental Service Market: US\$ 505.5 billion**

## Share (%): Global environmental revenue by nations



**Fig. 3** Global remediation market scenario in 2010: per cent contribution by different nations and services. *Source:* EBI online (2013); US ITC (2013)

Remediation of pollutants, whether by physical, chemical, biological means or any combination thereof constitute the only options to remove them. Globally, the remediation sector annually contributes US\$505.5 billion to revenue (Fig. 3), of which 30–50 % of profit is derived from managing solid and hazardous wastes and wastewaters. The major global contributor to environmental income of the sector is the US, followed by Western Europe (EBI 2013; US ITC 2013). This shows that the remedial sector is economically important and contributes significantly to GDP, as does other sectors like agriculture. Many remediating technologies are available, and selecting the most suitable one for any application depends mainly on the site characteristics and the objectives of the task. Since there is a strong demand for developing a promising technology that aids in minimizing treatment cost and maximizing the benefits, current research is focused on developing new remedial measures by integrating the principles of successful existing techniques. This is paving the way for emerging technologies such as ultrasonics, sonophotocatalytic oxidation, etc. Normally, it will be easier to choose the right technology for implementation only when reviews of the existing and emerging ones are available. Moreover, comparing available technologies helps one to understand the merits and demerits of each one.

Several techniques are suited as both *in-situ* and *ex-situ* options and such techniques are well established as *ex-situ* measures, where remedial efficiency is fairly

high. For instance, advanced oxidation processes, incineration, dehalogenation, solidification, ion-exchange, sorption by natural materials (e.g., modified clays), constructed wetlands and bioslurries are suited for the remediation of a broad range of contaminants. It is our goal to present a comprehensive survey of such existing and emerging options that are suited for both *in-situ* and *ex-situ* remediation of contaminated sites. Since off-site remediation is the prime objective of the current review, the major aspects addressed for each technology involved in *ex-situ* applications include (1) technology profile, (2) merits, (3) drawbacks, (4) success stories, (5) recent advancements, and (6) future research directions.

## 2 Ex-Situ vs. In-Situ Remediation

The two main types of remediation are *ex-situ* and *in-situ*. *Ex-situ* involves physically extracting media from a contaminated site and moving it to another location for treatment whereas *in-situ* remediation involves treating contaminants on-site. At an *ex-situ* site, if the pollutant exists only in soil, the soil is excavated. If pollution has reached the groundwater, it is then pumped and both the polluted soil and water are removed. *Ex-situ* and *in-situ* techniques each have specific benefits and costs. The prime benefit of *in-situ* techniques is that contaminated soil need not be removed or transported. The downside of *in-situ* techniques is that they are less efficient at contaminant removal than *ex-situ* remedial options. In addition, *in-situ* remediation techniques are favored over *ex-situ* ones, because the excavation incurs a high cost and individual excavators are exposed to adverse health risks of contaminants. Despite the high cost, *ex-situ* treatment generally requires less time to achieve efficient contaminant cleanup, is easily monitored and achieves more uniformity. After *ex-situ* treatment, decontaminated soils may be used for landscape purposes.

## 3 Existing *Ex-Situ* Remedial Options for Contaminated Soil and Groundwater: Technology Profile and Recent Advances

### 3.1 *Dig-and-Dump (Landfills and Engineered Landfills)*

Dig-and-dump is the most used and conventional *ex-situ* remediation technology. Dig-and-dump/excavation-and-disposal generally targets “hot spots”, in which contaminants at a polluted site exceed pre-set risk levels, and therefore require remediation. In dig-and-dump, contaminated soils are excavated and transported to landfills or environmentally acceptable locations for disposal. Often polluted soils must be moved to secure landfills. A secure ‘landfill’ is a plot or site that is carefully



engineered to receive dumped wastes. Landfill types are quite variable, and include inert waste landfills, solid waste landfills, and hazardous waste landfills, with an assumed annual disposal rate of between 5000 and 230,000 t waste/year. Generally, a secure landfill has four critical elements: a natural hydrogeological setting, a cover or “cap”, a leachate collection system, and a bottom liner. The materials used in bottom liners are made either of plastic or clay or a composite of both; such liners are layered on a bathtub shaped depression in the ground and is designed to prevent waste from escaping into the environment. Covering or capping the landfill helps prevent leachates, and are augmented with a pipe system (leachate system) in the landfill to collect leachate. Any leachate that is pumped is treated at a waste treatment plant (US EPA 2012).

One upgraded form of engineered landfill is called the ‘bioreactor landfill’ — it is a sanitary landfill spot used to transform and stabilize toxins via microbial processes within the first 5–8 years of bioreactor operation. The advantages of bioreactor landfills include an ability to: (a) reduce greenhouse gas emission into the environment, (b) produce end-products that do not require landfilling, (c) steep decline in the landfilling cost, (d) decrease leachate treatment cost (capital and operating), and (e) reduce contaminant concentrations during landfill operation. A bioreactor landfill can either be aerobic or anaerobic or hybrid (aerobic-anaerobic), wherein accelerated degradation of waste is achieved by decreasing the cost of long-term monitoring (Warith 2002; US EPA 2012). The main drawback of landfills, either conventional or bioreactor types, is that they generate greenhouse gases that have a drastic environmental impact. Landfills also pose a risk to humans during their excavation, because the hazardous wastes that are deposited in them are not pre-treated. The final drawback is that the cost of transporting the excavated contaminated material to a final destination is very high (Campbell 2009).

EPA charges landfill operators different levels of license fees, and requires financial assurances from operators, depending on the proposed facility’s location and nature. There is a strict legal liability for unauthorised disposal of wastes that may reach a daily maximum penalty of US\$60,000 per individual. Moreover, damage costs can be assessed by regulators for (a) greenhouse gas emissions, (b) air pollution, (c) leachate releases, and (d) amenity impacts. More recently, governments have increased the cost of waste disposal at existing and new landfills, and have strengthened regulations. For example, the total waste disposal costs at urban and rural landfills in Australia range between A\$42–102 and A\$41–101 per t waste, respectively (BDA Group 2009).

In a field investigation, Osako et al. (2002) observed the mobility of polychlorinated dibenzofurans/polychlorinated dibenzodioxins (PCDFs/PCDDs) in a landfill area replete with municipal solid waste residues. Al-Yaqout and Hamoda (2003) also found that considerable quantities of leachate are formed at a landfill site. Baumann et al. (2006) witnessed heavy metal transport that was in direct contact with groundwater at a landfill site. According to VanGulck and Rowe (2004), when suspended on solids landfill leachate can form bio-rocks (clogs). Some researchers have reported methane emissions from solid waste landfills (Scheutz and Kjeldsen 2004; Kumar et al. 2004). Scheutz et al. (2009) illustrated the need for developing

new technology to mitigate methane emission from a landfill site via improved oxidation processes. In Southern Spain, Zamorano et al. (2008) suggested that the biogas produced from urban landfills could be used to generate electricity (approx. 4,500,000 kW/year). Although landfills have several negative environmental impacts, these may be overcome by applying the results of further investigations and utilizing more advanced technologies.

### 3.2 *Pump-and-Treat*

In pump-and-treat, the groundwater is pumped and then treated using granular activated charcoal. Generally, the pump-and-treat approach requires 50–100 years to reach remedial goals, and in most cases the goals are never achieved (US EPA 1996). Moreover, disposal of contaminants that become bound to activated carbon after treatment becomes a problem (Bau and Mayer 2006). Because of these drawbacks, surfactant-enhanced remediation, metallic iron technology, permeable reactive barriers, etc., have emerged as alternatives to traditional pump-and-treat systems.

Mackay et al. (2000) performed a field experiment at a Dover site in Delaware and observed that pulsed pumping is more advantageous than continuous pumping. Wang and Mulligan (2004) recommended the use of ‘surfactant foam technology’ to improve contaminant removal efficiency and cost-effectiveness of a current pump-and-treat system. At the Dover national test site, Delaware, a surfactant-based flood (sodium dihexyl sulfosuccinate, isopropanol, and calcium chloride) significantly reduced the tetrachloroethylene (TCE) concentrations (80 %) within 800 h in a pump-and-treat system (Childs et al. 2006). Utilizing a pilot-scale pumping system, Wei et al. (2010) successfully demonstrated effective remediation (50–99 %) of groundwater polluted with chlorinated organic mixtures by employing nano-scale zero-valent iron (ZVI). Consequently, the conventional pump-and-treat system no longer operates, and has been amended for integration with recently advanced techniques (nano, or surfactant treatments, reactive barriers, etc.).

### 3.3 *Incineration*

As pump-and-treat techniques have declined, incineration technologies to treat environmental wastes have grown in importance over the past 20 years. Incineration, combustion or thermal oxidation are different terms for a process in which hazardous wastes are subjected to very high temperature (750–1200 °C) treatments to affect their disposal. Incineration is carried out in different experimental units like: infrared combustors (electrically-powered silicon carbide rods are used to heat organic wastes up to temperatures of 1010 °C via infrared energy); fluidized bed combustors (utilizes high-velocity air with infrared as a heat source; incineration occurs at temperatures up to 850 °C); circulating bed combustors (high velocity air

entrains circulating solids and destroys noxious hydrocarbons by creating a highly turbulent combustion zone at temperatures up to 850 °C); and rotary kilns (rotating cylinder that is slightly-inclined and refractory-lined, with an afterburner that burns at temperatures up to 980 °C) (FRTR 2012).

Commercial incinerators are generally designed as closed burning rotary kilns that are equipped with an air pollution control system, a quench unit and an afterburner (Pavel and Gavrilescu 2008). Such incinerators are used to remediate soils that are contaminated with dioxins, PCBs, chlorinated hydrocarbons and explosives. The application of this incineration technology will reduce bulky solids or wastes that are combusted to 5 % of their original volume, and 25 % of their original weight. These reductions are achieved even when the wastes possess high moisture content. It aids in the detoxification of combustible carcinogens, pathogenically-contaminated materials and toxic organic compounds. In addition, the amounts of greenhouse gases (CH<sub>4</sub> and CO<sub>2</sub>) generated by incineration are less than those generated in landfills for the same wastes (Hutton 2009). Incineration is used to treat very large quantities of wastes. One other advantage of incineration is that energy can be recovered from incinerating wastes that will add to the economy (by producing steam, electricity and fuel). The above advantages justified using incineration at more than 150 superfund sites, and using energy generated from combusting wastes at off-site locations described below. Incineration also has disadvantages that limit its effectiveness and usefulness.

Incineration is expensive, both in initial capital costs to construct a facility, and also in operating costs. Incineration equipment requires maintenance and is rather unreliable, requiring practical repairs to routine waste-handling issues. To achieve targeted combustion temperatures, supplementary fuels are often required, and these can be expensive. One prime disadvantage is that incineration practices may cause drastic secondary environmental impacts (Santolieri et al. 2000). For instance, most waste combustion systems have gas or particulate emissions that are highly dispersible by wind (e.g., flue gases composed of noxious fumes, nitrogen gases, carcinogenic hydrocarbons, carbon monoxide, hydrogen chloride, odors and sulfur dioxide). Incineration also may generate leachates (i.e. discharges of residue that may contain abrasive suspended or dissolved solids, heavy metals and pathogenic organisms into soil/groundwater/surface water bodies) that pose health risks (Chandler et al. 1997). Moreover the release of inorganic wastes from incineration processes, such as the heavy metals zinc (Zn), lead (Pb), copper (Cu), arsenic (As), cadmium (Cd), are very difficult to control (Sabbas et al. 2003). Incineration processes have technical risks, i.e., shortfall in performance (higher maintenance expenses, reduced system capacity than expected), and a newly installed incinerator is affected by changes in waste characteristics that are common due to seasonal variations (Niessen 2002).

Despite the above-mentioned technical challenges, incineration has progressed from batch-fed, simple, refractory hearth systems, and as a result now has much wider applicability. Currently, incineration plants in the United States are subject to a series of regulations/federal requirements that are technology-specific as follows: NCA—Noise Control Act (noise), NPDES—National Pollutant Discharge Elimination System (discharge to surface water), RCRA—Resource Conservation

and Recovery Act (generation, treatment, storage and disposal of hazardous wastes), CAA—Clean Air Act (air emissions), and TSCA—Toxic Substances Control Act (treatment and disposal of PCB). These regulations help to reduce the environmental impacts of this system. Also, the incinerated residues need to be subjected to a few treatments before reuse or disposal like thermal treatments (melting, vitrification and sintering), solidification/stabilization (solidification with hydraulic binders, chemical stabilization and ageing/weathering), and separation (crystallization/evaporation, adsorption, ion-exchange, chemical precipitation, immobilization, chemical extraction, washing, eddy-current separation and magnetic separation) (Sabbas et al. 2003). Incineration costs US\$0.74–1.25 per m<sup>3</sup> when it is chosen to remediate a specific contaminated site (US EPA 2012).

McKay (2002) standardized the municipal solid waste incineration system of dioxins, and concluded that effective dioxin reduction with minimized PCDD/PCDF formation could be achieved when incinerators are operated using the following process conditions: combustion residence time of >2 s, chamber turbulence of >50,000, incineration temperature of >1000 °C and post-combustion temperature of 200 °C, and with the use of air pollution control systems like activated carbon injection, bag filters and semi-dry scrubbers. More recently, many experiments were conducted with the objective of electrochemical oxidation/incineration of wastewater containing organics where the organic contaminants were completely oxidized to CO<sub>2</sub>. The electrochemical incineration of chloranilic acid using Si/diamond (Si/BDD), Pb/PbO<sub>2</sub> and Ti/IrO<sub>2</sub> electrodes was studied by Martinez-Huitle et al. (2004). In this context, electrochemical oxidation of many organics was investigated for a few other anodic materials like SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, PbO<sub>2</sub> and IrO<sub>2</sub>.

Chang et al. (2000) stated that the removal of mercury by municipal waste incineration is mostly low varying from 30 to 45 %. Studies have been conducted using anodic materials like Si/BDD and Ti/BDD which are considered to be the boundaries of the novel ‘electrode material technique’ (Polcaro et al. 2002). Rein (2009) reported that the energy inefficient incineration of NAPLs by flaming technology could be replaced by smouldering combustions since smouldering is self-sustaining with no requirement for any energy input after ignition. Grant and Major (2010) evaluated the efficacy of STAR (Self-sustaining Treatment for Active Remediation—Smouldering combustions) technology to treat soils contaminated with coal-tar at a former manufacturing plant in Newark, New Jersey. Ignition was achieved after 25 h of preheating. Maintenance of the peak ignition temperature of 1340 °C for about 9 days completely removed the contaminant mass. Similar studies were conducted by Pironi et al. (2009) and Switzer et al. (2009) where the treatment efficacy of STAR for removing 99.9 % PAHs and TPHs was confirmed. Pironi (2010) also recommended smouldering combustion as a suitable incineration approach to treat soils contaminated with NAPLs. He observed a mass removal of 99.5 % NAPLs when the materials were smouldered to a temperature of 600–1100 °C at pilot-scale.

Remedial studies conducted by implementing incineration at superfund sites are numerous, and were successful in remediating 99.9 % NAPLs (FRTR 2012) as listed in Table 1. However, incineration applications at real contaminated sites are currently scarce compared to those done in the 1990s. It is necessary to search for a

**Table 1** Overview of the selected full-scale incineration studies conducted at superfund sites of US EPA

| Remediation site   | Contaminants of concern  | Volume treated                                  | Target temperature (°C) | Outcome   | Efficiency (%) |
|--|--|---|-------------------------|---|----------------|
| 1. Bayou Bonifouca, slidell, Louisiana <sup>R</sup>                              | PAHs   | 129,204 m <sup>3</sup> sediment                 | 871–982                 | Completed 18 months ahead of schedule <sup>+</sup>  | 99,9           |
| 2. Baird and McGuire, Holbrook, Massachusetts <sup>R</sup>                       | Dioxins, PAHs, pesticides, Pb, As                                    | 210,000 t soil and 1153 m <sup>3</sup> sediment | 871                     | Ability to treat wide range of contaminants like dioxins, PAHs and pesticides in soils/sediments <sup>+</sup>                         | 99,9           |
| 3. Bridgeport refinery and oil services, Logan Township, New Jersey <sup>R</sup> | PCBs, VOCs, benzene, Cd, methylene chloride, Zn, Pb, Ba, Cr, toluene | 172,000 t lagoon, sediment and sludge           | 760                     | Inadequate design caused mechanical problems <sup>-</sup><br>Demulsifying problems<br>complicated dewatering of sediment <sup>-</sup> | 99,9           |
| 4. Celanese, Shelby, North Carolina <sup>R</sup>                                 | VOCs, TCE, Pb, Cr, PAHs, ethylene glycol                             | 4660 t sludge and soil                          | 815–1037                | Remediation was successful as low volume was incinerated <sup>-</sup>   | 99,9           |
| 5. Former Nebraska ordnance works, Nebraska <sup>R</sup>                         | Explosives, propellants  | 10,006 m <sup>3</sup> soil and debris           | 621–982                 | Remedial goals achieved in short time period <sup>+</sup>   | 99,9           |
| 6. Petro processors, Baton Rouge, Louisiana <sup>R</sup>                         | Hydrocarbons, heavy metals, hexachlorobutadiene, hexachlorobenzene   | 810,828 L liquids and fumes                     | 1093–1315               | Best suited groundwater treatment system for liquid organics and air stripper fumes <sup>+</sup>                                      | 99,9           |
| 7. Sikes disposal pits, Crosby, Texas <sup>R</sup>                               | PAHs, BTEX, VC, chlorobenzene, EDC                                   | 496,000 t soil and debris                       | 704–982                 | Complete remediation within the framed time limit in spite of voluminous treatment zone <sup>+</sup>                                  | 99,9           |

<sup>R</sup>Use of rotary Kilns; <sup>+</sup>Significant; <sup>-</sup>Problem

suitable remedial option to combat greenhouse gas emissions resulting from this mechanism as its end product is nothing but CO<sub>2</sub>. Otherwise, suitable *ex-situ* treatment techniques that are listed below could be implemented.

### 3.4 Oxidation

Oxidation is a promising remedial option where the target contaminant is not only destroyed but also the toxicity of the pollutant is considerably reduced either by chemical or biological or advanced processes. Chemical oxidation destroys the target compound and reduces the toxicity associated with it. The most commonly used oxidizing agents are permanganate, chlorine-di-oxide, chlorine, peroxides, hypochlorites and ozone (O<sub>3</sub>) (FRTR 2012).

Recent treatment methodologies termed ‘advanced oxidation processes (AOPs)’ have the potential to treat all types of inorganic and organic pollutants (volatile, semi- and non-volatile). An oxidation system that can produce adequate OH<sup>•</sup> radicals entails complete mineralization, implying that the terminal degradation products are inorganic ions, short-chain organic acids and CO<sub>2</sub> that are typically amenable for biodegradation, and are less toxic. AOP generally uses a combination of oxidation agents, irradiation like UV/ultrasound and catalysts such as TiO<sub>2</sub>, and is more powerful than the conventional chemical oxidation process (Mahamuni and Adewuyi 2010). Of the different types of oxidation processes, Fenton’s (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) oxidation, TiO<sub>2</sub>/UV system and H<sub>2</sub>O<sub>2</sub>/UV system are some of the most powerful ones, and can be used to destroy a wide range of organic contaminants in aqueous ecosystems due to their high oxidative potential and being subject to high scrutiny. Advanced oxidation technique can be either: (a) non-thermal heterogeneous systems with irradiation (solar energy/O<sub>2</sub>/UV/TiO<sub>2</sub>); (b) a non-thermal homogeneous system without irradiation (Fenton’s reagent, O<sub>3</sub>/OH<sup>•</sup>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>); (c) without irradiation (electro-Fenton); (d) hydrothermal or (e) sonochemical (electrochemical/catalytic/photocatalytic) oxidation. There are also supercritical water oxidation and wet-air oxidation types.

Generally, advanced oxidation processes potentially reduce toxicity of organic compounds without producing additional hazardous by-products or sludge which requires further handling. Without much discrimination, the AOP system can be used to react virtually with all types of aqueous pollutants because of the remarkably high reactivity of the OH<sup>•</sup> radicals. In some cases, disinfection could also be achieved when using this method. However, some drawbacks exist like high cost, technical demand and an inability to handle large quantities of pollutants.

Andreottola et al. (2008) found that about 90 % organolead compounds can be removed from the contaminated groundwater by the use of chemical oxidation with Fenton’s reagent followed by filtration on activated carbon. In the treatment of leachate effluent, Abdul et al. (2009) compared the performance of advanced oxidation processes over granular activated carbon bio-sorption and found that Fenton’s oxidation could remove only 80 % TOC; however, biosorption (including adsorption and biodegradation) could remove 85 % of the TOC in a few weeks. According to Rodriguez et al. (2008), catalytic (copper supported on carbon nanofibers) wet-air

oxidation can remove about 74 % TOC in 180 min. Orescanin et al. (2012) developed and adopted an appropriate combined treatment approach for landfill leachate, the use of calcium oxide/electrooxidation, where about 99.7 % of the contaminant was removed.

Advanced oxidation catalyzed with nZVI particles, for example, ferrous iron ( $\text{Fe}^{2+}$ ) successfully removed the organics in wastewater treatment studies (Ershadi et al. 2011). More recently, biological oxidation integrated with solar driven oxidation processes was established at a pilot plant equipped with a photocatalytic system and an immobilized biological reactor for winery wastewater remediation (Souza et al. 2012). Among the AOPs tested ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  and  $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ ), solar photo-Fenton process demonstrated the highest efficiency. Parida and Mohapatra (2012) identified a novel photocatalyst—carbonate intercalated Fe/Zn layered double hydroxide with dissimilar intercalated anions (carbonate, chloride and nitrate)—for enhanced photodegradation of azodyes. In a pilot-scale study, Vargas and Nunez (2010) found that advanced photooxidation ( $\text{TiO}_2/\text{UV}$ ) could mineralize 90 % *p*-nitrophenol, naphthalene and dibenzothiophene in 180 min.

Tsai et al. (2010) demonstrated that iron electrode corrosion-enhanced electrokinetic-Fenton oxidation is a valuable approach for effective and efficient remediation of TPH-contaminated lands. To achieve an environmentally friendly and cost-effective remedial option for tannery sludge containing high Cr levels, Kilic et al. (2011) used biosurfactants as sorbents in comparison with chemical oxidation and observed that oxidation was 3× higher than sorption. Villa et al. (2010) noticed that soil remediation by use of combined processes like photo-Fenton oxidation and soil washing with surfactants could remove 100 % DDT, DDE and diesel.  $\text{TiO}_2$ -based advanced oxidation nanotechnologies are emerging as competitive promising processes for full-scale applications in near future (Choi et al. 2010). Currently, ultrasonolysis with other advanced oxidation process performs better compared to photocatalysis alone (Mohajerani et al. 2010). Many remedial studies have been conducted by employing the latest oxidation processes (Table 2), and this technology is advancing steadily through the introduction of either: firstly, new catalysts (supported noble metal nanoparticles as photo/sono catalysts); secondly, nanoparticles or surfactants; or thirdly, adopting integrated processes with existing remedial measures to achieve 100 % remediation in a very short timespan. However, more emphasis is required on reducing remedial costs by linking this technology to the basic study of its ecotoxicological effects. This is because the recent oxidation methods are expensive, and using extensive chemicals or nanoparticles may damage the ecosystem which is still unexplored.

### 3.5 Adsorption

Adsorption is the most widely used, fastest, inexpensive technology for the treatment of groundwater, industrial wastewater, air emissions, chemical spills, and for removing a series of toxic chemicals such as BTEX, ethylbenzene, xylene, trichloroethene, tetrachloroethene, dichloroethane, PCBs, pesticides, herbicides, explosives, and anions like perchlorate and heavy metals. A process in which molecules

**Table 2** Oxidation: Remedial studies

| Pollutant   | Method   | Remediation (%) | Reference                             |
|---|--|-----------------|---------------------------------------|
| Organolead compounds in groundwater                     | Chemical oxidation with Fenton's reagent   | 90              | Andreottola et al. (2008)             |
| Landfill leachate effluent                              | Advanced oxidation process   | 80              | Abdul et al. (2009)                   |
| Dyes in textile effluent                                | Wet air oxidation  | 70              | Rodriguez et al. (2008)               |
| Landfill leachate                                       | Advanced oxidation combined with electrochemical and microwaves                    | 90              | Orescanin et al. (2012)               |
| TCE   | Oxidation with nano-Pd-Fe <sup>0</sup> particles                                   | 90              | Al-Shamsi et al. (2013)               |
| Chipboard production wastewater                         | Advanced oxidation using solar energy  | 70              | Eduardo da Hora Machado et al. (2004) |
| Dyes in textile effluent                                | Advanced oxidation using TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /sunlight | 100             | Garcia et al. (2009)                  |
| Phenol in water   | Combined biological treatment and photocatalytic oxidation                         | 80              | Suryaman et al. (2006)                |
| Pharmaceutical wastewater                               | Solar photo-Fenton combined with biological treatment                              | 90              | Sirtori et al. (2009)                 |
| <i>p</i> -Nitrophenol, naphthalene and dibenzothiophene | Photodegradation (TiO <sub>2</sub> /UV)  | 90              | Vargas and Nunez (2010)               |
| Phenanthrene and pyrene                                 | Potassium permanganate   | 60              | de Souza e Silva et al. (2009)        |
| PAH-contaminated sediments                              | Chemical oxidation   | 90              | Ferrarese et al. (2008)               |
| Diesel-contaminated soil                                | Electrokinetic-Fenton oxidation  | 90              | Tsai et al. (2010)                    |
| Phenols in agro-industrial wastewater                   | Fenton's oxidation   | 60              | Martins et al. (2010)                 |
| TCE-contaminated groundwater                            | Surfactant-enhanced persulfate/BOF slag oxidation                                  | 90              | Tsai et al. (2010)                    |
| MTBE  | Ferrous-ion activated persulfate oxidation   | 80              | Chen et al. (2009a)                   |
| Chlorinated solvents                                    | Sodium persulfate oxidation  | 80              | Dahmani et al. (2006)                 |
| Chromium in tannery sludge                              | Oxidative remediation  | 70              | Kilic et al. (2011)                   |
| PCB   | Sulfate radical-based advanced oxidation processes                                 | 90              | Rastogi et al. (2009)                 |
| Polyvinyl alcohol                                       | Persulfate activated with heat, Fe <sup>2+</sup> and ZVI                           | 90              | Oh et al. (2009)                      |
| Synthetic dyes  | Electro-Fenton and photo electro-Fenton oxidation                                  | 80              | Peralta-Hernandez et al. (2009)       |
| SVOCs   | Chemical oxidation   | 90              | Wei et al. (2012)                     |
| Phenol  | Catalytic wet peroxide oxidation   | 90              | Valkaj et al. (2011)                  |



of a gas or liquid are attached and then held at a solid surface by electromagnetic forces or chemical bonding is known as 'adsorption'. 'Absorption' is the intraphase distribution of a solute where a solute is absorbed or dissolved into the absorbing phase. When both absorption and adsorption occur simultaneously, and both cannot be distinguished, then it is termed 'sorption'. Adsorption can be categorized into physical, chemical and electrostatic. Chemical adsorption is also referred to as chemisorption (Bhandari et al. 2007). Ion-exchange is a form of adsorption that is detailed in the following section.

Activated carbon is the most common adsorbent which has been used extensively for water and air treatments followed by synthetic ion-exchange resins, activated alumina, sorption clays and forage sponge (open-celled cellulose sponge with an amine containing chelating polymer that selectively adsorbs toxic transition heavy metals). A full-scale system in which the dissolved organic chemicals in groundwater are adsorbed when pumped through a series of columns packed with activated carbon is designated 'liquid-phase carbon adsorption'. The reactor designs available for carbon adsorption systems are moving bed or pulsed and fixed bed. Fixed bed system is the one that is typically utilised. Activated carbon adsorption is effective for remediating sites contaminated even with smaller concentration of pollutants (<10 mg/L), and for polishing the treated water from other remediation systems (FRTR 2012). The carbon adsorption system is a rapidly deployable technique with very high remedial efficiency. However, one of the major problems is the transportation cost and decontamination of the spent carbon.

Shuibo et al. (2009) found that hematite (type of inorganic sorptive medium) can be used to efficiently remove U from aqueous solutions. Choi et al. (2008) developed an innovative remedial strategy employing a series of granular activated carbon composites impregnated with palladium/iron bimetallic nanoparticles which was able to physically adsorb 90 % PCBs in 2 days. Since the emphasis is to select a cost-effective, eco-friendly sorbent for removing environmental contaminants, currently more emphasis is given to biological means of sorption apart from physical or chemical. Gong et al. (2007) proved the advantage of activated carbon adsorption of PAHs. Organoclays performed best on hydrocarbon sorption (Carmody et al. 2007). The effects of different low-cost adsorbents like neem bark, saw dust, fly ash, fuller's earth, activated alumina, rice husk ash and clarified sludge (waste from steel industry) were studied by Bhattacharya et al. (2008). Activated alumina, rice husk and clarified sludge were the most effective tested sorbents for removing Cr(VI) from aqueous solutions. Nano-sized modified ZVI particles are efficient sorbents of As in aqueous solutions (Jegadeesan et al. 2005).

While studying the effect of integrated adsorption, chemical and physical processes for the remediation of landfill leachate, Rivas et al. (2005) found that integrating Fenton's oxidation, wet-air oxidation and adsorption on activated carbon could remove 80–96 % of the COD. Chitosan (a natural amino polysaccharide) was used as a sorbent to remove dye from aqueous solutions (Crini and Badot 2008). Oladoja et al. (2008) discovered that even castor seed shell can be used as a sorbent of dyes in contaminated wastewater. Some of the sorbing materials that have been investigated so far are summarized in Table 3. Studies revealed that several

**Table 3** List of sorptive materials used for pollutant cleanup

| Contaminant  | Sorptive medium   |
|--|---|
| Heavy metals (U, Cr, Zn, Pb, Co, As, Cd, Zn, Ni, Cu) | Hematite<br>Clarified sludge, rice husk and activated alumina<br>Nano-sized modified ZVI particles<br>Granular activated carbon<br>Biogenic manganese oxide<br>Natural Jordanian sorbent (quartz, aluminosilicates, calcite, dolomite)<br>Novel organoclays (ammonium organic derivatives with different chelating functionalities in the interspace of montmorillonite)<br>Maize tassel<br>Rice bran<br>Vermiculite<br>Brown seaweed<br>Zeolite<br>Phosphate-modified kaolinite clay<br>Vegetable compost<br>Polymetallic sea nodule<br>Biogenic magnetic nanoparticles<br>Iron oxide coated sand<br>Manganese oxide coated lead<br>Coconut shell<br>Eucalyptus bark<br>Natural siderite<br>Diatomite<br>Zeolite composite<br>Nano-hydroxyapatite<br>Acrylate-based magnetic beads<br>Fuller's earth<br>nZVI<br>Biochar<br>Nano-sized magnesium oxide powder<br>Modified SBA-15 mesoporous silica<br>Zeolite<br>Red mud<br>Psyllium and acrylic acid based hydrogels<br>Gibbsite<br>Multiwall carbon nanotube/ iron oxide magnetic composites<br>Red algae |
| PCB  | Granular activated carbon composites incorporated with Fe/Pd bimetallic nanoparticles   |
| Phenol   | Organoclays<br>Activated clay<br>Hydrophobic modified clay<br>Almond shell residues   |
| PAHs   | Activated carbon<br>Matrix modified organoclays   |
| TPH  | Organoclays   |

(continued)

**Table 3** (continued)

| Contaminant       | Sorptive medium                  |
|-------------------|----------------------------------|
| Dyes              | Chitosan                         |
|                   | Coniferous pine bark powder      |
|                   | Castor seed shell                |
|                   | Jackfruit leaf powder            |
|                   | Activated carbon                 |
|                   | Cyclodextrin polymer             |
|                   | Bentonite                        |
|                   | Broad bean peel                  |
|                   | Citric acid modified wheat straw |
|                   | Sepiolite, fly ash               |
|                   | Apricot shell activated carbon   |
|                   | Palygorskite-supported ZVI       |
| Tetracycline      | Carbon nanotubes                 |
| Nitrate           | Nano-alumina                     |
| Herbicide (2,4-D) | Organo-palygorskite              |
| Cd                | Red algae                        |

agrowastes such as barks of trees, saw dust, bran (wheat, rice), husks (wheat, rice, blackgram), shells (groundnut, coconut, hazelnut, walnut, cotton seed), waste leaves (tea, *Cassia fistula*), stalk (cotton, grape, sunflower), peels (apple, banana, orange), and others (coffee beans, biochar, water hyacinth, soybean hulls, sugar-cane bagasse, jatropha deoiled cakes, maize corn cob, sugar beet pulp, etc.) can be used as sorbents to remove the contaminants, especially heavy metals (Sud et al. 2008). Cr(VI) was successfully remediated by Sarkar et al. (2010) through adsorption by bentonite-based Arquad® 2HT-75 organoclays. Modified clays are recently being developed for sorption of heavy metals. Shu et al. (2010) developed CTMAB modified bentonite and kaolinite for the sorption of chlorobenzenes. Recently, Beckingham et al. (2012) reported that steam-activated poultry litter biochar (commercial black carbon that is produced from organic wastes by pyrolysis mechanism) could remove >99.7 % Hg over a wide range of pH. They suggested that the biochar amendments are effective for sites contaminated with mixed organic and inorganic chemicals as they could sorb the priority pollutants with the benefit of carbon sequestration. Even nanoparticles are increasing in importance recently as effective sorbents of pollutants. For example, nano-alumina developed by Bhatnagar et al. (2010) was used to remove nitrate from water. Iron oxide nanoparticles were also employed to sorb As from soil (Shipley et al. 2011). Thus, the sorption studies are many, and constitute the most promising and cheap remedial options for remediating contaminated soils and groundwater. However, the combined effects of biosorption with other remedial techniques are not yet much explored, and should be the focus of future research.

### 3.6 Ion-Exchange

Exchange of cations or anions between pollutants and the media is referred to as ion-exchange. Ion-exchangeable materials are generally resins (natural polymers with a variety of ionic functional groups for attachment of exchangeable ions) (FRTR 2012). When liquids are passed over a resin bed, ions in resins (i.e., cations and anions) and contaminated materials are exchanged, and the metallic ions remain in the resins. Resins can be regenerated for reuse when their capacity has been exhausted; sometimes the resins are only adapted for single use. So far both anionic and cationic resins have been used (Alexandros 2008).

Ion-exchange systems can remove dissolved metals, radionuclides, nitrate, ammonia and silicates from liquid media (Vilensky et al. 2002; Rengaraj et al. 2003). This technology is widely adopted for decontaminating the hotspots of concern as the resins are considered to be a rapidly developing twentieth century scientific tool. Their promising applicability to biomolecular separations and catalysis, chromatography, hydrometallurgy, wastewater treatments, environmental remediation and water softening has been confirmed (Harmer and Sun 2001; Mergen et al. 2008). Ion-exchange resins are highly adaptable and environmentally compatible since they are insoluble and the loading/regeneration/reloading mechanisms allow them to be used for many years in most cases. Ion-exchange technology has been in industries from late 1990s and is commercially available.

Typically grease, oil and organic or inorganic biological compounds found in various traces (humic and fulvic acids) in the treated media clog the ion-exchange resin (Beril Gonder et al. 2006). The resin can be damaged by the interference of unfavorable soil factors like high pH, oxidation and suspended solid concentrations. Generally, wastewater is generated during the resin regeneration and requires additional treatment and disposal that increase the cost (Pintar et al. 2001). There are also concerns with respect to the treatment size, odor, noise generation and disposal issues after the use of resins. However, remediation practices by making use of ion-exchange technology mainly for perchlorates and heavy metals are being developed to reduce the risks they pose to the public (Srinivasan and Sorial 2009). The cost involved for operating a typical ion-exchange technology to treat 4000 L of water is nearly US\$0.3–0.8 (FRTR 2012).

Recently, Awual et al. (2012) showed that ‘weak base anion-exchange adsorbents’ (Diaion WA30 and Diaion WA20) are the most effective in removing As(V) from drinking water with faster adsorption rates and excellent adsorption capacity. Similarly, Awual et al. (2011, 2013) reported that ion-exchange resins, polyallylamine fibres and primary amine could selectively take up phosphate and As(V) from contaminated groundwater systems at higher flow rates even in the presence of competing anions such as sulphate, bicarbonate, nitrate and chloride. Kim et al. (2005) studied the effect of ion-exchange membrane (IEM)-enhanced electrokinetic (EK) soil processing on metal removal, and observed that nearly 96 % Cd and Pb was removed by this integrated mechanism within 4 days. One limitation of EK remedial system alone (soil hydroxide is precipitated near the cathodic side of the electrodes) was overcome by the use of IEMs.

Gu et al. (2002) conducted a pilot-test at Edwards's Air Force Base, California, to remove perchlorate from polluted groundwater using bifunctional ion-exchange resin and  $\text{FeCl}_3\text{-HCl}$  for the regeneration of resins. The bifunctional ion-exchange resin bed treated nearly 40,000 empty bed volumes of groundwater, and about 100 % perchlorate was successfully removed in 6 months. Gu et al. (2007) also carried out a field experiment in California, the objective being to treat perchlorate-polluted water using perchlorate destruction and highly regenerable, selective ion-exchange tools which could enhance the treatment efficiency as well as minimize secondary waste production. Bifunctional anion-exchange resin (Purolite A530E) and  $\text{FeCl}_3\text{-HCl}$  (as the resin regeneration system) were used for the full-scale study. In 2 years of treatment, there was no deterioration in the resin performance, and around 92–97 % of perchlorate was destructed in the 3700 empty bed volumes of groundwater with equal resin regeneration. A similar study was conducted by Bae et al. (2010) who successfully removed >95 % perchlorate and nitrate from drinking water with the help of ion-exchangeable resin (IX resin—Purolite A530E, Rohm and Haas PWA2) column system. Though the ion-exchange resin system is considered to be a promising technology for removing perchlorate from waterbodies, it is just a separation mechanism where wastewater solutions containing perchlorate after ion-exchange treatments need further treatment. To overcome this drawback, Batista et al. (2002) proposed a technology combining ion-exchange and biological reduction for perchlorate removal.

Woodberry et al. (2007) conducted a field trial (see Table 4) at Thala Valley tip, Casey Station, Antarctica, and found that iminodiacetic acid chelating ion-exchange resins could help in reducing 92–100 % of heavy metals in the following order of selectivity:  $\text{Cd} \sim \text{Zn} > \text{Ni} \sim \text{Cu} > \text{Fe}$  within 1 year of treatment. Extensive investigation into the remediation of perchlorate-contaminated waterbodies was done successfully by Gu et al. (2007) using ion-exchange technology. Tang et al. (2011) stated that 93 % of  $\text{Cr(VI)}$  could be adsorbed onto the cationic hydrogel when integrated with multiple-pulse flushing system. Dilip et al. (2008) found that chromatographic resins are potent in removing mercury and perchlorates from groundwater. Though ion-exchange technology is well tested and is found to be the most efficient for perchlorate and heavy metal removal from the waterbodies, there are still a few major complications with respect to its full-scale implications.

Future research should focus more on exploring suitable solutions to solve the biggest disposal problem of the used resins which are concentrated in the contaminants. The problem caused by most frequently occurring anions that are at higher levels than the contaminants resulting in the competitive adsorption on the resin should be resolved to improve contaminant recovery. It is possible to disperse nanoparticles in a polymer-like, functionalized ion-exchange resin that would render a feasible hydraulic property as suggested by Alonso et al. (2011). Developing 'ion-exchanger supported nanocomposites' will also open up a new opportunity to control the behavior of hybrid nanocomposites by synergistically altering or enhancing the adsorption competencies for diverse hazardous metal ligands (anionic and cationic).

**Table 4** Performance overview of selected *ex-situ* remedial options at field- and pilot-scale

| Site   | Contaminants       | Remediation (%) | Type | Reference                  |
|--|--------------------|-----------------|------|----------------------------|
| <i>Ion-exchange</i>  |                    |                 |      |                            |
| 1. Edwards air force base, California                                  | Perchlorate        | 100             | P    | Gu et al. (2002)           |
| 2. Thala valley tip, Casey Station, Antarctica                         | Cd, Zn, Ni, Cu, Fe | >91             | F    | Woodberry et al. (2007)    |
| 3. Clearwater bay, Hong Kong   | Cr                 | 93              | P    | Tang et al. (2011)         |
| <i>Pyrolysis</i>   |                    |                 |      |                            |
| 1. Portsmouth DOE facility, Ohio                                       | TCE                | >90             | F    | Heron et al. (2000)        |
| 2. Visalia superfund site, Visalia, California                         | Creosote, PCP      | 99              | F    | US EPA (2012)              |
| 3. Savannah river site 321-M solvent storage tank area, Aiken, Georgia | PCE, TCE           | 90              | F    | FRTR (2012)                |
| <i>Soil washing</i>  |                    |                 |      |                            |
| 1. Out-of-station oil distribution and storage station, Mexico         | Heavy metals       | 93              | F    | Iturbe et al. (2004)       |
| 2. Old wood preservation site, Sweden                                  | As, PAHs           | 60–75           | P    | Elgh-Dalgren et al. (2009) |
| 3. Grand manan island, New Brunswick, Canada                           | Heavy metals       | 95              | F    | US EPA (2012)              |
| 4. Botany industrial park, Australia                                   | Mercury            | >90             | F    | Orica Australia (2010)     |
| <i>Enhanced reductive dehalogenation</i>                               |                    |                 |      |                            |
| 1. LLNL site, San Francisco  | PCE, TCE           | 93–98           | F    | Menab and Ruiz (2000)      |
| 2. US DOE., Gaseous diffusion plant, Piketon, Ohio                     | TCE                | 80–90           | F    | Korte et al. (2000)        |
| 3. Active manufacturing facility site, Trenton, New Jersey             | TCE                | 96              | F    | Elliott and Zhang (2001)   |
| 4. Vinyl chloride plant, Rotterdam Botlek, Netherlands                 | DCA                | >90             | F    | Dyer et al. (2003)         |
| 5. Residential area, Lake Huron, Oscoda, Michigan                      | TCE                | 98              | F    | Ramsburg et al. (2004)     |
| 6. Naval air station, Jacksonville, Florida                            | Chlorinated VOCs   | 65–99           | P    | Henn and Waddill (2006)    |
| 7. Vilvoorde, Belgium  | TCE, DCE           | >90             | F    | Lookman et al. (2007)      |
| 8. LabMet, Ghent university, Belgium                                   | TCE                | 90              | P    | Hennebel et al. (2009)     |
| 9. Former manufacturing facility site, US                              | TCE, PCB           | 98              | F    | He et al. (2010)           |
| 10. Housatonic river, Massachusetts                                    | PCB                | >90             | F    | US EPA (2012)              |



### 3.7 Pyrolysis

Pyrolysis/molten solid processing/plasma arc technology is an emerging soil remediation technology where the chemical decomposition of hazardous materials occurs by thermal energy in the absence of oxygen at an operating temperature above 430 °C under pressure (Venderbosch et al. 2010). Pyrolysis transforms the targeted compounds into a gas or an insignificant amount of solid or liquid residues containing ash and fixed carbon, i.e. it yields char, organic liquids, fuel gas and water (Rofiqul Islam et al. 2008). Though complete oxygen-free atmosphere is not obtained, this process is operated with oxygen level that is less than the stoichiometric quantity. If the targeted waste is composed of volatile or semi-volatile materials, then thermal desorption also occurs. Organic and inorganic contaminants such as SVOCs, pesticides, dioxins, PAHs, PCBs, cyanides, mercury, paint wastes, synthetic rubber processing wastes, refinery wastes, creosote-contaminated soils, mixed wastes (radioactive wastes and others), hydrocarbon-contaminated soils, coal tar wastes as well as wood-treating wastes are generally removed by the pyrolysis process (Mohan et al. 2006; Arvanitoyannis et al. 2007).

High pollutant-cleaning efficiency within a short period of time is achieved by adopting the pyrolysis mechanism. One major advantage is that there is no evolution of CO<sub>2</sub> during the course of pollutant treatment in this technology which helps to combat global warming (Inguanzo et al. 2002). However, combustible off-gases like CO, H<sub>2</sub>, CH<sub>4</sub> and other hydrocarbons are produced during the course of operation which requires further treatment. Equipment that is commercially used for pyrolysis includes rotary kilns, fluidized bed furnaces (high velocity air is used for circulation and suspension of waste particles in a combustion loop operated at 430 °C) and molten salt destructions (use of molten salt incinerator as a reaction medium to destroy hazardous wastes).

Operation of a pyrolysis system is typically stable for a broad range of wastes. It is effective in reducing the volume and weight of the target materials. The emissions from the pyrolysis system are well below the regulatory limit values. There are also efficient material recovery and energy production opportunities emerging from this system. Even the operational cost of pyrolysis mechanism is quite low as it does not require any supplementary fuel for its operation or continuous monitoring or maintenance (US EPA 2012). The system is highly flexible in its design and operation. Furthermore this method can be implemented in small-scale or large-scale at real contaminated sites. Yet, there are a few limitations for the applicability and effectiveness of this system. This method involves drying soil to achieve a low moisture content of <1 % before combustion, and if the soil has high moisture content then it increases the treatment cost. Stabilization is usually required if the treated medium is composed of heavy metals. Damage of the processor unit occurs in the case of high abrasive feed. This technology is promising only in remediating the organic pollutants from oily sludges and soils, and cannot effectively destroy or physically separate inorganics from polluted zones. Moreover, studies available for this technology in the field of remediation are scarce as presented in Table 4. The overall cost is expected to be nearly US\$300 per t of the soil treated (FRTR 2012).



While conducting a field study of steam stripping and hydrous pyrolysis oxidation (SS/HPO) of a TCE DNAPL spill at Portsmouth DOE facility site in Ohio, Heron et al. (2000) observed that within 2 months >90 % of TCE was removed when the TCE DNAPL spill was boiled and vaporized at approximately 72–74 °C. At present, studies are conducted to manage the disposal problems of phytoremediation crops with the help of the pyrolysis process. Stals et al. (2010) tried to destroy the phytoremediating plant that accumulated heavy metals (Pb and Cd) via the pyrolysis process at a temperature of 723 K. Pyrolysis of phytoremediating plant yielded char (as soil amendment) and oil (as source of fuel), and only 35 % of the target element was recovered in the char, indicating that it is both an economical and eco-friendly technique.

Zhang et al. (2009) remediated 99.1 % Cr(VI) from a chromite ore processing residue by mixing the residue with sewage sludge and subjecting it to a pyrolysis temperature of 600 °C in 10 min reaction time. Thuan and Chang (2012) investigated the degradation of PCP from the contaminated soils of Taiwan by low temperature pyrolysis. More than 90 % PCP was removed within 40 min at a pyrolysis temperature of 350 °C. Also, the PCP decay rate was observed to increase constantly from 0.2 to 1.9 per minute in the range of the pyrolysis temperature (200–400 °C). Nkansah et al. (2011) reported that hydrous pyrolysis with Pd/C/naion/formic acid at 300 °C, H<sub>2</sub>O<sub>2</sub> at 380 °C and Nafion-SiO<sub>2</sub> at 300 °C could convert anthracene into derivatives that are easily oxidized or reduced within 1, 6 and 8 h of treatment time, respectively.

Currently, the heterogeneous catalysis system is regarded as an effective tool to mineralize toxic organic compounds, and it constitutes a potential environmental remedial system. Semiconductors like aluminium doped zinc oxide films and zinc oxide that could present efficient photocatalytic property were recently produced using the spray pyrolysis process. Bizarro (2010) observed that zinc oxide films created by spray pyrolysis process could remove 80 % methyl orange dye within 1.25 h by its increased photocatalytic activity. When the contaminated soil was mixed with 5–10 % of woody biomass (sawdust) and subjected to a pyrolysis temperature of 400 °C for 1 h, about 93, 91 and 43 % reduction was observed in the concentrations of Cd, Zn and Pb, respectively (Debela et al. 2012).

### 3.8 Soil Washing

Soil washing is also known as mechanical scrubbing, soil scrubbing, physical separation or attrition scrubbing. This approach can be either *ex-situ* or *in-situ*. It is a water-based approach for treating excavated soils and is extensively practiced in Europe but less so in the USA (US EPA 2012). This technology uses coupled aqueous-based separation unit and physical separation operations to minimize the toxin levels of an age-prone contaminated site to site-specific objectives. Soil washing systems do not significantly alter or detoxify the pollutant; instead they mechanically concentrate the hazardous materials into a much smaller soil mass or transfer

the contaminant from soil into washing fluids for successive treatments (Dermont et al. 2008). On the whole, soil washing involves mechanical screening, crushing, physical processes (soaking, spraying and tumbling attrition scrubbing), treatment of coarse and fine-grained soil fractions (aqueous-based leaching and physical separation), and management of the generated residues. Though it is considered as a stand-alone approach, more frequently it is combined with other remedial systems to complete the off-site treatment process.

Soil washing is highly applicable to treat a diverse array of pollutants like heavy metals, SVOCs, PCBs, PAHs, pesticides and petroleum as well as fuel residues (Park et al. 2002; Juhasz et al. 2003; Isoyama and Wada 2007). Soil washing particularly permits the recovery of metals from coarse soils. If the recovery of metal is not desired, then solubility enhancement along with the adjustment of soil parameters like pH, redox potential, etc. are the only options. Since hydrocarbons tend to sorb smaller soil particles, physical separation/soil washing helps to separate smaller soil fractions (constituting silt and clay particles) from larger ones, and tend to reduce the soil volume which can further be treated by incineration or bioremediation after which it can be disposed in accordance with government guidelines. Large volume of treated soil can then be used as backfills since it is considered to be non-toxic (RAAG 2000; Chu and Chan 2003). Soil washing is considered to be very cheap as it reduces the volume of the contaminated soil requiring further treatment, and the reduction in soil volume minimizes the expenditure involved in post-remedial treatments done before disposal. Also, it is a proven suitable option in sandy or gravel soils (Urum et al. 2003).

On the other hand, this technology fails to treat soils with high silt and clay (>40 %) fractions. This *ex-situ* treatment does not work for soils that are not feasible for homogenization, i.e. in soils with different types and contaminant concentrations. Also, this technique is unsuitable for multicomponent soil mixtures with high clay and humic acid content where access of leaching solutions to contaminants is highly restricted. Even metal contaminants with lower solubility may take a very longer contact time and excessive amounts of reagents to solubilize. It costs around US\$170 per t to decontaminate a site with this technique.

Budianta et al. (2010) proposed a new approach of *in-situ* soil washing by the sedimentation method where soil particles are separated hydraulically based on their particle size and density when high air pressure was injected into mixing water-sandy soil ground. In this method it was advised that there is a probability for the occurrence of both washing and separation processes along with remediation. Kos and Lestan (2003) proposed the use of biodegradable chelates and permeable barriers to induce the phytoextraction of Pb coupled with soil washing. They achieved an approximately 27 % increase in metal removal by the use of biodegradable chelates and permeable barriers. Iturbe et al. (2004) conducted a field experiment to remediate an out-of-service oil distribution and storage station contaminated with PAHs, BTEX, MTBE, diesel and gasoline in Mexico by using biopile and soil washing methods between 1966 and 2000. Washing approximately 1600 m<sup>3</sup> soil using non-ionic surfactant and biopiling (operated for 66 days) removed more than 93 % of the total contaminants in 500 days.

Villa et al. (2010) studied the use of combined processes (photo-Fenton oxidation and soil washing) to remediate soil contaminated with DDT, DDE and diesel. Soil washings using triton X-100 aqueous solution removed nearly 100 % diesel, 80 % DDE and 66 % DDT. Further treatment for 6 h using a solar photo-Fenton system removed around 99, 95 and 100 % DDT, DDE and diesel, respectively. In a pilot-scale experiment conducted in Sweden, Elgh-Dalgren et al. (2009) reported that a combination of biodegradable non-ionic surfactant (AG), chelating agent (MGDA) and elevated pH could remove 60–75 % As and PAH with only 10 min washing at an elevated temperature of 50 °C. Qui et al. (2010) found >95 % removal efficiency of cationic (Cu, Pb and Zn) and anionic (As and Cr) metals that co-exist in the soil within 24 h by the use of soil washing with Na<sub>2</sub>EDTA and oxalate.

Jeon et al. (2010) investigated the TPH removal efficiency from clayey soil (oil reservoirs, Incheon, South Korea) after a soil washing process, using the EK remediation mechanism. It emerged that the surfactant-enhanced EK process with NaOH as electrolyte and isopropyl alcohol as a circulating solution could remove >30 % TPHs from low-permeability soils subjected to soil washing within the first 100 h of treatment by utilising 485 KWh/t energy. A similar study was conducted by Gomez et al. (2010) to evaluate the enhancement in the recovery of phenanthrene from polluted soil using sequential washing with cyclodextrin-enhanced electrochemical treatment. Soil washing with aqueous solution of 1 % hydroxypropyl- $\beta$ -cyclodextrin removed 70 % phenanthrene in 7 days, and the second step of EK separation totally degraded the left-out phenanthrene in a day.

Davezza et al. (2012) confirmed the alkylphenol and benzoate removal efficiencies using surfactant-assisted soil washing and photocatalysis within 1–2 h of treatment. The combined effect of electrochemical treatment and EDTA-based soil washing was also reported by Pocięcha et al. (2011), where 85–95 % removal of Cd, Zn and Pb was achieved in 10 and 30 min of soil washing and EK separation treatment time. Peng et al. (2011) stated that liquid/solid ratio, surfactant concentration, washing time and stirring speed are the critical factors that determine the effectiveness of PAHs removal by means of surfactant-enhanced soil washing.

Many technologies combined with soil washing have successfully remediated the contaminated soils as listed in Table 5. Huang et al. (2010) reported that the combined technique of chemical washing and phytoextraction is highly effective in treating sites contaminated with many metals. They conducted a pot culture experiment using crops like *Sedum alfredii* and *Zea mays* along with soil washing by mixed chelators to remove metals from a contaminated soil, and found that ethylenediaminedisuccinic acid enhanced the metal phytoextraction by both crops. Concerning the removal of 80–85 % of Cd, Zn and Pb, 40 % was contributed by phytoextraction and the remaining 45 % by chemical washing. Jansson et al. (2010) observed 81–85 % dioxin removal from soil with 70 % ethanol washing at 60 °C in 30 min, and concluded that ethanol washing is a cost-effective technique compared to other conventional remediation technologies that are commonly used for removing PCDD/Fs.

**Table 5** Recent coupled soil washing remedial practices

| Year | Researchers           | Technology  | Contaminant              | Remediation (%) |
|------|-----------------------|---|--------------------------|-----------------|
| 2003 | Kos and Lestan        | Phytoextraction coupled with EDTA soil washing along with usage of permeable barriers | Heavy metals             | 55–65           |
| 2004 | Kos and Lestan        | Chelator-induced phytoextraction coupled with <i>in-situ</i> soil washing             | Cu                       | <50             |
| 2003 | Urum et al.           | Biosurfactant-enhanced soil washing   | Crude oil                | 75–85           |
| 2005 | Giannis and Gidarakos | Washing-enhanced electrokinetic remediation   | Cd                       | 85–95           |
| 2009 | Elgh-Dalgren et al.   | Soil washing with chelating agents and surfactants                                    | As, PAHs                 | 75–85           |
| 2010 | Villa et al.          | Soil washing and Fenton oxidation   | Pesticides, hydrocarbons | 85–95           |
| 2010 | Gomez et al.          | Soil washing followed by electrokinetic remediation                                   | Hydrocarbons             | >95             |
| 2010 | Huang et al.          | Phytoextraction and soil washing  | Heavy metals             | 55–65           |
| 2012 | Davezza et al.        | Surfactant-assisted soil washing with photocatalysis                                  | Pesticides               | 85–95           |
| 2011 | Pociecha et al.       | Electrokinetic separation combined with EDTA soil washing                             | Heavy metals             | 85–95           |
| 2011 | Sung et al.           | Combined mild soil washing and compost-assisted phytoremediation                      | Heavy metals             | 65–75           |
| 2012 | Begum et al.          | Biodegradable aminopolycarboxylate chelant soil washing                               | Heavy metals             | 85–95           |

Though the washing technique utilizes surfactants and chelating agents for removing hazardous organic mixtures from contaminated soil media such as sediments/soils, a major issue rests with the proper disposal of the surfactant extractant or chelating solution containing the wastes after washing. To overcome such a limitation, Liu et al. (2011a) integrated nanotechnology with photocatalysis (utilization of La–B co-doped TiO<sub>2</sub> nanoparticle in the photocatalysis of a simulated complex system containing non-ionic surfactant Triton X-100 and PCP under solar and visible light irradiation) and removed the wastes from the washing solutions. More strategies using this technology should be the subject of future studies.

### 3.9 Dehalogenation

This treatment technology is used to dehalogenate (remove halogens) halogenated compounds. The treatment could be either chemical or biological. During chemical dehalogenation, contaminated soils and reagents are mixed, and heated in a

treatment vessel (Soesilo and Wilson 1997). Reagents could be either sodium bicarbonate (base-catalyzed decomposition process—BCD) or polyethylene glycol (alkaline polyethylene glycol or glycolate technology—APEG). Biological dehalogenation involves degradation of halocompounds by microorganisms (van Pee and Unversucht 2003). Dehalogenation was successful in removing PCBs, PCDD/Fs and pesticides from soil. It has been recently reported that the BCD process could treat as high as 45,000 mg/kg PCBs at field-scale and APEG is amenable to small-scale PCB treatments (FRTR 2012). This technique is unsuited for treating chlorinated volatile organic compounds. Some concerns with the chemical dechlorination process are as follows: large volumes of reagent are required to treat soils with elevated concentrations of chlorinated compounds; it is difficult to treat volatile contaminants and dust when the contaminated soil is very moist; pretreatment requirements removing the debris from soils that are greater than 60 mm dia; toxicity and persistence of chemical reagents like glycol ethers are evident; and it is very expensive to treat large volumes of soils that are high in clay and moisture content.

Currently, environmental and economic concerns of chemical dehalogenation are overcome by the alternative use of biological dehalogenation mechanisms (Furukawa 2003; Bedard 2004). Biological dehalogenation includes many classes like reductive dehalogenation, oxidative dehalogenation, dehalogenation by methyltransfer, dehalogenation by hydration, dehydro dehalogenation, intramolecular substitution, thiolytic dehalogenation and hydrolytic dehalogenation (Van Pee and Unversucht 2003). Of these, the most important and widely studied broader class of biological dehalogenation mechanism is reductive dehalogenation. It is mostly done by anaerobic bacteria such as *Dehalococcoides*, *Dehalobacter*, *Anaeromyxobacter*, etc., and is becoming significantly important in remediation research (Smidt and de Vos 2004). In addition to the presence of specific dehalogenators (anaerobic microbes), environmental factors such as available carbon or electron sources strongly affect the rate of contaminant dehalogenation as has been first established for PCBs (Nollet et al. 2005).

In many studies, microbiological reductive dechlorination of chlorinated organic molecules is proved to be important for bioremediation of polluted groundwater (McNab and Ruiz 2000). There exists an electrochemical dehalogenation mechanism where chlorinated hydrocarbons and chlorofluorocarbons are dechlorinated by electrolysis using appropriate solvents. Photo-assisted and irradiation type dehalogenations were also reported (Shih and Wang 2009). Moreover, Guo et al. (2010) had described mechano-chemical (tribochemical reaction) reductive dehalogenation of PCBs, DDT, HCH, TCE and dioxins using ball mills as an innovative reductive dehalogenation technology.

So far, many significant methods that could enhance the efficiency of reductive dehalogenation were explored. The more sophisticated microbial dehalogenation types involve the use of microwave-induced and UV-photolytic process (Li et al. 2012a), nanoparticle iron (Zhuang et al. 2011), and ZVI (Xiu et al. 2010). In most cases, metals as such or in the form of nanoparticles or biocells are used as electron donors in dehalogenation processes as summarized in Table 6. The expenditure

**Table 6** Topical reductive dehalogenation methods

| Electron donor                               | Halogenated waste                | Remedial efficiency (%) | Reference   |
|--|----------------------------------|-------------------------|---|
| Iron powder                                  | PCBs, DDT, Triallate             | 95                      | Lampron et al. (2001); Agrawal et al. (2002); Gander et al. (2002); Clark et al. (2003); Volpe et al. (2004); Aristov and Habekost (2010) |
| ZVI  | PCBs, PBDEs                      | 95                      | Kluyev et al. (2002); Clark et al. (2003); Habekost and Aristov (2012)  |
| Ultrasonically-produced air stable nano iron | Chloroethene                     | 85                      | Tiehm et al. (2009)   |
| Fermenting substrates (formate and lactate)  | TCE                              | 90                      | Azizian et al. (2010)   |
| Subcolloidal Fe/Ag particles                 | Chlorinated benzene              | 90                      | Xu and Zhang (2000)   |
| Rhodium nanoparticles                        | Mono- and polyhalogenated arenes | 90                      | Hubert et al. (2011)  |
| Nanoscale iron                               | TCE                              | 95                      | Elliott and Zhang (2001); Nyer and Vance (2001)   |
| Bimetallic copper-aluminium                  | Halogenated methane              | 75                      | Lien and Zhang (2002)   |
| Palladium iron nanoparticles                 | Chlorohydrocarbons               | 90                      | Hildebrand et al. (2009)  |
| Bioinorganic palladium cells                 | PBDE, TCPP                       | 90                      | Deplanche et al. (2009)   |
| Biogenic palladium nanoparticles             | TCE                              | 90                      | Hennebel et al. (2011)  |
| Bimetallic palladium-iron                    | Chlorophenol                     | 90                      | Graham et al. (2006)  |
| Palladium chloride and triphenylphosphine    | Halopyrazoles                    | 85                      | Chen et al. (2012)  |
| Yeast extract                                | DCB                              | 85                      | Fung et al. (2009)  |

for field-scale treatment ranges between US\$200 and 500 per t for the chemical dehalogenation process (FRTR 2012), but no specific cost estimates for other dehalogenation types exist.

Habekost and Aristov (2012) suggested that reductive dechlorination and debromination of PBDEs and PCBs occurs efficiently with ZVI at reasonably high temperatures (350–600 °C) in a nitrogen atmosphere. Tiehm et al. (2009) produced nano-sized air-stable ZVI particles by passing ultrasound to a Fe(CO) solution in edible corn oil and coating the resulting nano-iron with a non-crystalline carbon cover after dispersing it in a carbon matrix. The nano-sized ZVI particles were able to dehalogenate 80 % chloroethene in 5 days. Since most of the reductively dechlorinating

bacteria such as *Dehalococcoides* and *Desulfuromonas* need molecular hydrogen as an electron donor, hydrogen formed by ZVI increases chloroethene elimination. Formate and propionate are valuable fermenting substrates for reductive dehalogenation (Sleep et al. 2006; Aulenta et al. 2007; Azizian et al. 2010). Elliott and Zhang (2001) and Nyer and Vance (2001) proved the efficiency of nano-iron to dehalogenate more than 95 % halogenated wastes. More than 99 % heterogeneous dehalogenation of PCBs and DDT was achieved with iron powder in a nitrogen atmosphere at 500 °C by Aristov and Habekost (2010).

According to Waller (2010) and Wagner et al. (2012), bioaugmentation of *Dehalococcoides* containing cultures is a successful technique for the clean up of chlorinated ethene and brominated benzene-polluted groundwater. Also, Bunge et al. (2003, 2008) and Fennell et al. (2004) reported the dioxin dehalogenating efficacy of *Dehalococcoides* sp. Hubert et al. (2011) observed that rhodium nanocatalyst either as suspension or supported on silica like particles could effectively decontaminate 87–95 % mono- and polyhalogenated arene like endocrine disruptors in water. Lien and Zhang (2002) demonstrated the effect of bimetallic Cu/Al to degrade 77 % halogenated methanes in groundwater. About 97 % chlorinated herbicide (triallate) was reductively degraded by the contact of electrolytic iron powder in a batch system at 25 °C in the absence of oxygen (Volpe et al. 2004). Even the use of Pd nanoparticles (Windt et al. 2005) or yeast extract (Fung et al. 2009) enhanced the treatability (85–90 %) of reductive dehalogenation. Cupples et al. (2005) demonstrated that *Desulfutobacterium chlororespirans* could dehalogenate bromoxynil-like brominated herbicide and its metabolite. Graham et al. (2006) achieved more than 90 % degradation of chlorophenols using magnetically-stabilized fluidized-bed reactor composed of Fe/Pd media in polluted solid slurry under a nitrogen purge at pH 5.8.

Recently, Chen et al. (2012) paved the way for a new and efficient method for dehalogenating more than 83 % halopyrazoles using PdCl<sub>2</sub> and triphenylphosphine as catalysts. Pd/Fe nanocatalysts were explored for the selective dehalogenation process in wastewater systems by Hildebrand et al. (2009). About 64 % reductive dechlorination of PCB mixture aroclor (50 mg/L) was achieved in 160 days by the natural attenuation and bioaugmentation of *Dehalococcoides* (Bedard et al. 2007). Intrinsic community (natural attenuation) + acetate + hydrogen (biostimulation) aided reductive dechlorination of PCE (80 µM) and helped to achieve 100 % PCE transformation to ethane in 76 days (Himmelheber et al. 2007). Deplanche et al. (2009) demonstrated the effective reductive debromination (>90 %) of flame retardants like PBDE and TCPP by palladized cells (bioPd) of sulphate-reducing bacterium, *Desulfovibrio desulfuricans*, which was five times more effective than using commercial Pd as catalyst. Furthermore, Henebel et al. (2011) attained nearly 93 ± 4 % hydro-dehalogenation of persistent groundwater contaminants like TCE in microbial electrolysis cells with biogenic Pd nanoparticles. Shih and Wang (2009) reported 90 % PBDE degradation with less than 60 min of UV and solar irradiation exposures.

Reductive dehalogenation using nano-scale bimetallic iron and Pd particles (Elliott and Zhang 2001), use of Pd-catalyzed and polymer coated ZVI suspensions (Henn and Waddill 2006), application of palladized iron (Korte et al. 2000), bioPd in



membrane reactor (Hennebel et al. 2009), reductive dehalogenation with Tween 80 (Ramsburg et al. 2004), and dehalogenation by the use of carboxymethyl cellulose-stabilized iron nanoparticle (He et al. 2010)—all revealed that halogenated pollutants could be removed efficiently by enhanced dehalogenation mechanism at field/pilot-scale as listed in Table 4. Thus, the studies concerning dehalogenation are many at bench-scale and this technology is being explored at the molecular level to generate further innovations. Overall, the coupling of promising technologies like nanotechnology, irradiations, bioaugmentation, etc., is innovative and aims to sustainably remove halogenated pollutants. This process needs to be explored more fully at full-scale.

### **3.10 Solid-Phase Bioremediation**

Solid-phase *ex-situ* biological remediation techniques including biopiles, landfarming and composting are described in detail below.

#### **3.10.1 Biopiles**

Biopiles, also identified as biomounds, bioheaps, biocells and static pile composts, combine both landfarming and composting, and this technology is increasingly applied to treat excavated soils contaminated with petroleum products through the use of biodegradation. In biopiling, contaminated soils are piled or heaped, and then the microbiological processes are stimulated by aeration followed by addition of water and nutrient besides controlling heat and pH (US EPA 2012). This technique is similar to landfarming as it also works above ground, and the system uses oxygen (generally from air) to stimulate the population of aerobic microbes that helps in degrading the petroleum compounds adsorbed to the soil fractions. It differs from landfarming in that it provides a control over the maintenance of optimum levels of moisture, temperature, pH, aeration and nutrients favoring microbial survival and activity which promotes rapid biodegradation (McCarthy et al. 2004). While landfarming systems are aerated by plowing or tilling, biopiles are aerated most frequently by forcing air artificially to move by injection or extraction through slotted or perforated pipings placed throughout the pile.

Compared to landfarming or composting, mass transfer efficiency of air, nutrient and water in biopiles potentially offers a better pollutant removal strategy. In biopiles, structural materials like sand, straw, sawdust, woodchips and dry manure are used to enhance the mass transfer efficacy (Mohee and Mudhoo 2012). Generally, biopiles are operated up to a height of 0.9–3.1 m and could be enclosed with an impervious lining to prevent run-off or evaporation or volatilization and to promote soil heating. Efficiency of biopiles is poorer in clayey soils compared to sandy soils as the contaminant mass transfer is quite difficult in clayey soils due to its tendency to form agglomerates that limit the soil permeability (Rezende et al. 2012).



Petroleum products, pesticides, halogenated VOCs/SVOCs and non-halogenated VOCs can be degraded by biopiles. At the time of air injection/air extraction/pile turning itself, lighter petroleum products like gasoline are removed. Heavier petroleum products such as heating oil and lubricating oil are broken down by biodegradation which generally takes more degradation time compared to the lighter ones. The effectiveness of a biopile system depends on soil characteristics, contaminant characteristics, followed by climatic conditions (Giasi and Morelli 2003). Optimal biodegradation occurs between 20 and 40 °C at a pH range of 6–8 with adequate moisture and oxygen levels. This is an easy to implement, simple, cost-effective (US\$30–90 per t of contaminated soil), short-term (6 months to 2 years) as well as full-scale technology that is effective over a series of diverse pollutants. Compared to landfarming it requires less land area for contaminant treatments (Li et al. 2004). It is effective even for organic constituents that have very slow biodegradation rates.

Biopile can be designed as a closed system in order to control vapor emissions. It can also be engineered to be possibly effective for any combination of petrochemical compounds and physical settings. Though biopile is an eco-friendly, cost-effective technology, it does have a few limitations. Biopiling is not effective for very high contaminant concentrations (>50,000 mg/kg), especially with significantly heavy metal concentrations of >2500 mg/kg which will inhibit microbial growth. Though the land area required for implementing this process is quite less compared to landfarming, it is quite high compared to the other *ex-situ* technologies. It is very difficult to achieve more than 95 % degradation in most cases when using this technology. Moreover, volatile constituents are evaporated rather than biodegraded which makes it necessary to treat the generated vapors before their discharge into the atmosphere.

Roldan-Martin et al. (2006) described the utilization of biopile technology for remediating oil sludge with TPH concentration up to 300 mg/kg sludge, where 60 % degradation was achieved after 3 months of treatment. After 1 year, Mohn et al. (2001) observed a reduction in the total petroleum hydrocarbons from 2109 to 195 mg/kg and 196 to <10 mg/kg soil TPH (30–49 % TPH degradation) when the biodegradation was stimulated by the addition of ammonium chloride and sodium phosphate in biopiles assembled at two field sites in the Arctic tundra. Liu et al. (2009) confirmed the usefulness of bioaugmentation combined with biosurfactant (rhamnolipid) and nutrient enhancements to treat diesel-contaminated soils using biopiles. Chien et al. (2009) recommended the application of appropriate substrates like organic amendments (chicken manure) or commercially available microbial inocula to enhance the decay rate of petroleum hydrocarbons to 85 % in *ex-situ* field-scale biopiles.

Humidifying air for the remediation of petroleum hydrocarbon-polluted soil by heated/aerated biopile structure reduced the TPH concentration from 11,000 to 300 mg/kg in 10 months at Kingston, Canada (Sanscartier et al. 2009). A wind-powered biopile unit was used at Savitok Point, North-West Territories, Canada, to remediate approximately 15,000 m<sup>3</sup> TPH-contaminated soil, and a reduction of about 7000 mg/kg TPH over a 2 year time frame (ESG 2001) was observed. Reimer et al. (2003) reported 60 % TPH degradation when the temperature of petroleum

hydrocarbon-contaminated soils in the Arctic was maintained at 15 °C by injecting heated air into the biopile. Filler et al. (2001), on the other hand, used heating cables and blankets for enhancing the contaminant volatilization efficiency in a biopile system. A pilot study was conducted by Genovese et al. (2008) to evaluate the effect of bioaugmentation in a biopile. Augmentation with a 300 L culture containing  $10^8$  cells/mL of *Rhodococcus* sp., *Pseudomonas* sp. and *Acinetobacter* sp., followed by nutrient spray on the biopile, led to the reduction of 90 % BTEX and heavy aliphatic hydrocarbons in 15 days.

Delille et al. (2007) observed the performance of nutrient-enriched biopiles (amended with fish compost) in a pilot study that helped in achieving TPH regulatory standard (100 mg/kg) in diesel oil-contaminated soil in Antarctica in less than 12 months. Wu and Crapper (2009) designed a hydraulic-based approach to stimulate a biopile in the context of its ambient temperature. When a 27 m<sup>3</sup> biopile was operated for 22 weeks, it was able to remove 80 % TPH at full-scale (Iturbe et al. 2007). A 28 m<sup>3</sup> pneumatically-aerated bioreactor set up in static biopile amended with manure oil compost (40 %) and garden waste compost (20 %) successfully removed 68.7 % petroleum hydrocarbons within 3–4 months treatment time (Kriipsalu and Nammari 2010). Seabra et al. (2006) demonstrated that it was possible to remediate even crude oil-contaminated clayey soils (39,442 mg/kg TPH concentration) to acceptable levels by rice hull amendments and periodic pile mixings within 16 weeks. While studying the effect of different strategies like bioaugmentation, biostimulation, and bioaugmentation plus biostimulation to enhance the petroleum hydrocarbon degradation in biopiles, Liu et al. (2011b) recorded >80 % TPH degradation after 140 days operation of a biopile subjected to the bioaugmentation approach (introduction of selected consortium and kitchen waste).

Coulon et al. (2010) conducted a field study at a former dockyard in Scotland to compare the remedial effect of biopile and windrow turning technologies of a bunker C fuel-contaminated soil. It was witnessed that windrowing was most effective for treating the bunker fuel soils because the soil was more friable and biopiling is amenable to treating coarse soil textures. Gallego et al. (2011) performed a field-scale clean up study of a jet fuel-polluted soil using biopiles by adding a slow release fertilizer, a surfactant and an oleophilic fertilizer. They observed a reduction in TPH concentration from 500 to 5000 mg/kg within 5 months when the C:N ratio was maintained at 10:1. In an *ex-situ* field-scale biopile study involving a Siberian soil polluted with mazut (heavy residual fuel oil), Beskoski et al. (2011) observed the biological reduction of about 96, 97, 83 and 55 % of aliphatic, aromatic, asphaltene and isoprenoid fractions, respectively, after 150 days of biostimulation with softwood sawdust and bioaugmentation with microbial consortia (isolated microbes from the polluted soil).

A composting field trial of a soil polluted with lubricating and diesel oil by Jorgensen et al. (2000) showed a reduction of 70 % mineral oil content over a period of 150 days. Wang et al. (2011) observed only 20–44 % TPH removal after 220 days when it was biostimulated with excess quantities of urea which indicated the suppression of microbial activity and diversity by large quantities of nutrient amendments. Lin et al. (2010) showed that biosurfactant addition helped in achieving 90 % TPH removal at field level

in 100 days of biopiling which suggests that hydrocarbon bioavailability, desorption and mass transfer are the limiting factors of *ex-situ* petroleum hydrocarbon degradation. Field studies related to biopiling are copious (see Table 7). The present requirement is to explore the use of more natural waste materials as nutrient amendments in order to enhance the soil and microbial health along with the establishment of field-scale treatment trials of coupled *ex-situ* biological/physical/chemical treatment techniques with biopiling to achieve 100 % degradation in a short time.

**Table 7** Full-scale studies of *ex-situ* solid-phase biological treatment technologies

| Site  | Pollutant | Competence (%) | Effect | Reference                    |
|---|-----------|----------------|--------|------------------------------|
| <i>Biopiles</i>   |           |                |        |                              |
| 1. Military radar sites, Komakuk beach and Cambridge bay, Arctic tundra <sup>F</sup>        | TPH       | 30–49          | ☺      | Mohn et al. (2001)           |
| 2. Savitok point, North West territories, Canada <sup>F</sup>                               | TPH       | 88             | ☺ ☺    | ESG (2001)                   |
| 3. Mexican refinery, Mexico <sup>F</sup>  | TPH       | 80             | ☺ ☺    | Iturbe et al. (2007)         |
| 4. Canadian forces base, Kingston, Canada <sup>F</sup>                                      | TPH       | 97             | ☺ ☺    | Sanscartier et al. (2009)    |
| 5. Renova AB, Klapp, Sweden <sup>P</sup>  | TPH       | 68.7           | ☺      | Kriipsalu and Nammari (2010) |
| 6. Former dockyard, Scotland <sup>F</sup>   | TPH       | 22             | O      | Coulon et al. (2010)         |
| 7. Fire fighting practice (airport) site, Spain <sup>F</sup>                                | TPH       | 90             | ☺ ☺    | Gallego et al. (2011)        |
| 8. Mazut reservoir site, Siberia <sup>F</sup>   | TPH       | 55–96          | ☺ ☺    | Beskoski et al. (2011)       |
| 9. Outdoor oil sludge storage site, Shengli oilfield, Shandong province, China <sup>F</sup> | TPH       | 20–44          | O      | Wang et al. (2011)           |
| 10. Aged fuel spilled site, Taiwan <sup>F</sup>   | TPH       | 90             | ☺ ☺    | Lin et al. (2010)            |
| <i>Landfarming</i>  |           |                |        |                              |
| 1. Petroleum refinery, San Francisco, Argentina <sup>F</sup>                                | TPH       | 84             | ☺ ☺    | Belloso (2001)               |
| 2. Haliburton Pad, Prudhoe Bay field, France <sup>F</sup>                                   | Diesel    | 84             | ☺ ☺    | US EPA (2012)                |
| 3. Territory of Kokuyskoye oil field, Russia <sup>F</sup>                                   | Crude oil | 88             | ☺ ☺    | Kuyukina et al. (2003)       |
| 4. Service city pad, Alaska <sup>F</sup>  | Diesel    | 48–71          | ☺      | US EPA (2012)                |
| 5. Wood treatment site, KwaZulu–Natal, South Africa <sup>P</sup>                            | Creosote  | 68–83          | ☺ ☺    | Atagana (2003)               |

(continued)

**Table 7** (continued)

| Site   | Pollutant   | Competence (%) | Effect | Reference                  |
|--|-------------|----------------|--------|----------------------------|
| 6. Factory site, South Africa <sup>F</sup>                                 | Creosote    | 76–87          | ☺ ☺    | Atagana (2004)             |
| 7. Northeast shore of North Salt Lagoon, Barrow, AK <sup>F</sup>           | BTEX        | >90            | ☺ ☺    | McCarthy et al. (2004)     |
| 8. Oil refinery site, Murica, Spain <sup>F</sup>                           | TPH         | 80             | ☺ ☺    | Martin et al. (2005)       |
| 9. Petroleum development, Oman <sup>F</sup>                                | TPH         | 90             | ☺ ☺    | Al-Mahraki et al. (2006)   |
| 10. Former lindane manufacturing site, Spain <sup>F</sup>                  | HCH         | 82–89          | ☺ ☺    | Rubinos et al. (2007)      |
| 11. Arctic location, Canada <sup>F</sup>                                   | TPH         | >80            | ☺ ☺    | Paudyn et al. (2008)       |
| 12. Site with stormwater sediments, France <sup>P</sup>                    | TPHs, PAHs  | 53–97          | ☺ ☺    | Petavy et al. (2009)       |
| 13. Nigeria delta, Nigeria <sup>F</sup>                                    | TPH         | 14–82.2        | ☺ ☺    | Mmom and Deekor (2010)     |
| 14. Resolution island, Nunavut, Canada <sup>F</sup>                        | TPH         | 64             | ☺      | Chang et al. (2010)        |
| 15. Site polluted with oil, Spain <sup>F</sup>                             | PAHs        | 100            | ☺ ☺    | Silva-Castro et al. (2012) |
| <i>Composting</i>  |             |                |        |                            |
| 1. Former gas-work site, Prague Czech Republic <sup>F</sup>                | PAHs        | 37–80          | ☺ ☺    | Sasek et al. (2003)        |
| 2. Industrial facility site, US <sup>F</sup>                               | Perchlorate | 99             | ☺ ☺    | US EPA (2012)              |
| 3. Shengali oil production plant site, China <sup>F</sup>                  | TPH         | 31             | O      | Ouyang et al. (2005)       |
| 4. South China agricultural university, China <sup>F</sup>                 | PAHs        | 64–94          | ☺ ☺    | Cai et al. (2007)          |
| 5. Stauffer management company superfund site, Tampa, Florida <sup>F</sup> | Pesticides  | 90             | ☺ ☺    | FRTR (2012)                |

<sup>F</sup>Field-scale study, <sup>P</sup>Pilot-scale study, ☺ ☺ successful study, ☺ partially successful study, O unsuccessful study

### 3.10.2 Landfarming

Landfarming is a successful, above-ground remedial technique that has been practiced for more than 100 years. Since the 1980s the petroleum industries worldwide have used it to treat hydrocarbons. Wood preserving wastes, coke wastes, diesel fuels and certain pesticides are also treated by landfarming (Paudyn et al. 2008). In this technology, contaminated soil/sediment/sludge is excavated and spread into lined beds of about 0.46 m thick and biological activity of the soil is triggered through the addition of moisture, nutrients and minerals. Only if the contaminated soils are deeper than 1.5 m is excavation carried out; if not (less than 0.9 m below ground surface), the soil microbial activity is triggered without excavation.

For successful landfarming, it is a prerequisite to maintain a temperature of 20–40 °C, pH of 6.5–7.5, moisture up to 40–85 % and C:N ratio of 9:1 (Khan et al. 2004). Also, bacteria that may potentially successfully degrade hydrocarbons are added regularly in order to aid speedy biodegradation. Aerating the soil is an important aspect of this technology because mixing is performed to aerate the soil. Mixing also increases the contact between organic contaminants and microorganisms thereby accelerating the aerobic microbial degradation at contaminated sites (McCarthy et al. 2004).

Depending on the degradation rate, petroleum-contaminated soils could be applied at regular intervals to the landfarm sites which help to more importantly maintain the soil biological activity and replenish the supply of hydrocarbons. Bulking agents and co-substrates are generally applied (Straube et al. 2003; Maila et al. 2005) to stimulate microbial metabolism. Landfarming is quite similar to biopiles in its characteristics, benefits and shortcomings, but only with little dissimilarity as stated in the previous section. Landfarming system is limited to treat heavier hydrocarbons. The higher the molecular weight of a chlorinated and nitrated compound, then the more difficult it is to degrade contaminants using this technology (Hejazi et al. 2003). Landfarming requires a large land area for treatments and it is difficult to achieve more than 95 % degradation. Moreover, treatment of the generated dust and vapors that evolve during the course of landfarming is required as they are toxic will probably cause air pollution. There is a risk that pollutants will migrate from the treatment zone to uncontaminated areas. However, landfarming is a simple and cost-effective eco-friendly technology like biopile which is also widely implemented at field level in most contaminated sites around the world (Hejazi et al. 2003; Martin et al. 2005). Remediating petroleum-contaminated soil by landfarming, takes about 6 months to 2 years for the decontamination process to be completed, and costs about US\$30–60 per t soil (US EPA 2012).

Petavy et al. (2009) conducted a pilot-scale study to treat stormwater sediments contaminated with total hydrocarbons and PAHs, and obtained 53–97 % total hydrocarbon degradation and 60–95 % PAH degradation. Souza et al. (2009) recommended the amendment of rice hulls to accelerate the biodegradation efficiency of landfarming. Silva-Castro et al. (2012) studied the efficiency of combined bioaugmentation and biostimulation applications to remove hydrocarbons like PAHs through landfarming, and reported that when a consortium of four bacteria (*Bacillus pumilus*, *Alcaligenes faecalis*, *Micrococcus luteus* and *Enterobacter* sp.) is augmented into the PAH-contaminated soil with inorganic fertilizers (NPK), it remediated 100 % PAHs in 7 months. Besalatpour et al. (2011) reported about 57 % hydrocarbon degradation through the landfarming process after 4 months of treatment.

While assessing the potential of enhanced landfarming system to treat diesel oil-contaminated soils in bioreactors, Kuo et al. (2012) discovered that the use of additives (kitchen waste compost), bulking agent (rusk husk), activated sludge, and petroleum hydrocarbon-degrading bacteria could remove 92.4 % TPH in 25 days. Acuna et al. (2010) recommended the use of electro-bioremediation after landfarming treatment for unsaturated soils contaminated with hydrocarbons. Mmom and Deekor (2010) also showed 14.5–82.2 % TPH degradation by landfarming in the

Nigerian Delta at a soil pH of 5.5. Studies conducted at the Fahud petroleum development concession site in Oman revealed the significant improvement in landfarm performance through the use of a proper irrigation schedule, fertilization and weekly tilling (90 % degradation in 12–15 months) (Al-Mahraki et al. 2006). da Silva Souza et al. (2013) demonstrated the clastogenic effect of landfarming soil from petroleum refineries through sugar cane vinasse amendment.

A slurry-phase aerobic biotreatment of seriously polluted crude oil sediments at the Kokuyskoye oil field in Russia resulted in 88 % reduction of the crude oil levels after 2 months when combined with landfarming (Kuyukina et al. 2003). Atagana (2003) conducted a pilot-scale landfarming for creosote-contaminated site and confirmed that microbial supplementation and amendment of 10 % sewage sludge, poultry manure and cow manure could remove 68–83 % creosote in 6 weeks. Chang et al. (2010) evaluated the feasibility of landfarming biotreatment of petroleum-contaminated soils at Arctic regions (1–10 °C) and showed 64 % TPH removal in 60 days when the soil C:N:P ratio was maintained at 100:9:1 for 60 days. Belloso (2001) observed that bioaugmentation is effective in degrading 84 % total hydrocarbons in 12 months. Landfarming of a diesel fuel site at a remote Canadian Arctic region was successfully achieved (>80 %) under various temperature regimes (5, 9.3 and 18 °C) by aerating the contaminated field site by rotatilling for every 4 days over a 3 year period in the summer months (Paudyn et al. 2008).

Rubinos et al. (2007) demonstrated hexachlorocyclohexane (HCH) decontamination (82–89 % removal in 11 months) using landfarming at large-scale with moderate temperature (10–40 °C), and no deficit water and periodic tillage as these parameters reduced the heterogeneity in contaminant distribution and increased bioavailability. Martin et al. (2005) bioremediated (80 %) an oily sludge containing hydrocarbons using landfarming techniques in 11 months in a semi-arid climate. Thus, many field studies had been conducted by utilizing the potential of bioaugmentation and biostimulation to aid landfarming activities as listed in Table 7. However, it is necessary to: firstly, explore the applicability of landfarming for varied volatile contaminants other than hydrocarbons by overcoming the above mentioned limitations; and secondly, develop novel integrated landfarming techniques to sustain environmental remediation.

### 3.10.3 Composting

Composting is an *ex-situ* solid-phase remediation technology where organic contaminants like PAHs are transformed into stabilized, innocuous byproducts by microorganisms (under anaerobic and aerobic conditions). Composting is all about creating a suitable environment for the microorganisms, and it has been at the forefront of diversion and processing of organic wastes due to its relatively simple and robust process. Unlike landfarming, during composting a thermophilic condition (50–65 °C) is required to suitably compost hazardous organic compound-contaminated soils. Also, key parameters that must be monitored in the composting system include oxygen (10–15 %), moisture (50–55 %), C:N ratio (30:1), pH (6–9),

and porosity (1–5 cm) (Semple et al. 2001). During composting, polluted soil is excavated and mixed with organic amendments/bulking agents such as hay, vegetative wastes, wood chips and manure to accelerate the thermophilic microbial activity and porosity of the mixtures to be decomposed (Coker 2006). Maximum remedial efficacy is achieved by maintaining temperature, irrigation and oxygenation control.

Process designs used in composting are: windrow composting (compost is placed in long piles known as windrows and periodically mixed with mobile equipment), mechanically agitated in-vessel composting (compost is placed in a reactor vessel where it is mixed and aerated), and aerated static pile composting (compost is formed into piles and aerated with blowers or vacuum pumps). Windrow composting that uses a sophisticated in-vessel technology is one of the most cost-effective composting alternatives (FRTR 2012). Thermophilic composting is capable of reducing the level of heavy oils, explosives and PAHs. Heavy metals are not treated by this technique though it could be reduced by dilution as higher concentrations of heavy metals become toxic to microbes. However, application of compost helps to remediate metal-contaminated soils. For example, van Herwijnen et al. (2007) remediated 80 % metal (Cd and Zn)-polluted soil with mineral amended composts. Increased Cu, Cd and As removal from the contaminated soils by the use of composts was shown by Cao et al. (2003a) and Gadepalle et al. (2009).

The factors that limit the effectiveness and applicability of the composting system are its need for substantial space and the post-treatment excavation requirement of contaminated soil. Management of odor and leachates that are generated at the time of composting is also a limiting factor. Otherwise, composting is a sustainable, simple technique which reduces pathogens, stabilizes the waste, reduces the mass of the waste and yields a product (van Herwijnen et al. 2007). It generally takes 6–18 months to complete a composting process. Composting cost is about US\$314–458 per m<sup>3</sup> (FRTR 2012).

Ouyang et al. (2005) conducted a field study in China comparing bioaugmentation and composting for remediation of oily sludge, and observed that bioaugmentation could decrease oil contamination in the soil sludge by 45–53 %, while composting was able to remove only 31 % of the total hydrocarbons after 30 days when saw dust was used as an additive, indicating that bioaugmentation of microbial preparations is an effective treatment mechanism for oily sludges. Ceccanti et al. (2006) found significant hydrocarbon reduction in soil treatments using a combination of compost and earthworms (*Eisenia fetida*), both regulating the biochemical equilibrium of the soil. Tandy et al. (2009) recommended co-composting as a sustainable management option for remediating mine soil polluted with metals (Cu, As, Zn and Pb). Cai et al. (2007) investigated the efficacy of four different composting systems to bioremediate sewage sludge contaminated with PAHs. Sewage sludge was mixed with rice straw to obtain a C:N ratio of 13:1 prior to the composting. After 56 days of composting, the total concentration of 16 PAHs increased considerably in the order of intermittent aerated compost < continuous aerated compost < inoculated manual turned compost that indicated removal rates of 94, 85 and 64 %, respectively.

Jiang et al. (2006) indicated that composting with immobilized *Phanerochaete chrysosporium* is potent in that it bioremediated 90 % of PCP in 60 days when



yard waste, straw and bran were used as amendments in aerated compost systems. The parameters (0.8:1.0 soil/green waste, 60 % moisture content, and 38 °C) for controlled in-vessel composting of PAH-contaminated media were standardized by Antizar-Ladislao et al. (2006). Compost-mediated removal of PAHs from a manufactured gas plant soil was undertaken by Sasek et al. (2003) in a thermally insulated composting chamber using mushroom compost consisting of gypsum, chicken manure and wheat straw. The removal of individual PAHs ranged from 37 to 80 % after 154 days of maturation. To treat acid-mine drainage at the former Wheal Jane Tin Mine, Cornwall, in the United Kingdom, Johnson and Hallberg (2005) constructed compost bioreactor (anaerobic cell/anaerobic wetlands—consisting of bulky organic material held in a water-tight membrane buried underground that is totally devoid of macrophytes) components of three composite passive clean up models (lime-diluted, anoxic limestone and lime-free drain) for 16 months. They observed more than 99 % removal of Zn and Fe in the lime-free system amended with 5 % hay, 95 % softwood sawdust and a small amount of cattle manure to act as a microbial inoculum.

In a field experiment conducted in South Korea, Namkoong et al. (2002) standardized the suitable mix ratio of organic amendments to contaminated soil for improving diesel oil degradation by composting as 1:0.5. Suthar and Singh (2008) tested the feasibility of using vermicomposting technology to remediate metals (44 % Zn, 34 % Fe, 46 % Mn and 26 % Cu) from distillery sludge, recommending that earthworms can enhance nutrient profile and mitigate metal toxicity in the sludge which might be useful in sustainable land restoration practices at a low-input basis. Another feasibility study of aerated in-vessel composting was conducted at bench-scale by Godoy-Faundez et al. (2008) as a biodegradation strategy to remediate polluted sawdust (fuel concentration of >225,000 mg/kg) and desert mining soils (fuel concentration of >50,000 mg/kg) in the Atacama region. After 56 days of treatments, about 35 and 50 % removal of pollutants was observed in the contaminated soil reactors and sawdust, respectively.

Joo et al. (2008) evaluated the efficiency of *Candida catenulata* CM1 during composting of a mixture containing diesel-contaminated soil and food waste. After 13 days of composting, 84 % of the original petroleum hydrocarbons were degraded in the composting mixtures compared to 48 % of reduction in control reactor without the inoculum. Lu et al. (2010) conducted a bench-scale trial to enhance the removal of residual toxins after composting in soil contaminated with higher concentrations of petroleum hydrocarbons by combining biodegradation with Fenton-like pretreatment and observed more than 80 % removal and reduction in toxicity of TPH in 577 days. Walter et al. (2005) reported PCP removal by composting in the presence of white-rot fungi. Singh et al. (2010) stated that degradation of 50:50 mixture of cattle dung and biosludge could be attained in 75 days when earthworms (*Eisenia fetida*) were inoculated at 25 g/kg biosludge collected from the beverage industry.

Contreras-Ramos et al. (2006) reported that vermiremediation by *Eisenia fetida* (150 mg/kg soil) along with the autochthonous microorganisms could accelerate the rate of PAH removal (51 % anthracene, 100 % phenanthrene and 47 % benzo[a]anthracene (BaP) in a spiked soil within 15 days. More than 60 % PAH remediation



was observed by Zhang et al. (2011) in 60 days through composting with mixtures of organic wastes (leaves, branches and biowaste consisting of green vegetables such as cabbage, spinach and celery). Unlike biopile and landfarming, composting is not a widely adopted field-scale remedial option at contaminated sites in full-scale; however, a few lab studies involving compost reactors are available. This technique is commercially adopted only to develop end-product out of organic waste that is devoid of pathogens or pollutants which could be used as nutrient-rich additives to enhance agricultural productivity. It is vital to increase the remedial efficiency of composting technology to more than 90 % in most cases at field-scale by utilizing other cost-effective *ex-situ* techniques either before or after the composting process.

### **3.11 Slurry-Phase Bioremediation: Bioreactors**

Slurry bioreactor is one of the best choices for the biological remediation of subsurfaces contaminated by recalcitrant pollutants under controlled environmental conditions. Bioreactor technique is an *ex-situ* biochemical processing system designed to remove pollutants in wastewater or pumped groundwater using microbes (Robles-Gonzalez et al. 2006). In this technique, contaminated solid or liquid material (water, sludge, sediment and soil) is processed through an engineered contamination structure (bioreactor—manufactured or engineered device that supports a biologically active environment) to achieve bioremediation. Generally, bioreactor treatment is performed using microbes attached on a solid growth support medium or in suspension in liquids. In suspended growth systems (sequencing batch reactors or fluidized beds), polluted groundwater is circulated in an aeration basin where a population of microbes aerobically degrade organic matter, and produce CO<sub>2</sub>, biomass and water (Zaiat et al. 2001). The biomass is settled out in a clarifier, which is then either disposed off as sludge or recycled back to the aeration basin. In attached growth structures (trickling filters, rotating biological contractors and upflow fixed film bioreactor), microbes are grown as biofilms on a solid support matrix and the pollutants in the water are removed as they diffuse into the biofilm (Quijano et al. 2010; FRTR 2012). Solid support matrix has a larger surface area for microbial attachment which could serve as an absorptive medium such as activated carbon (having the ability to adsorb pollutants and slowly release them to the microbes for degradation) or plastic or ceramic packing or sand or gravel.

In a bioreactor, the microbial population is either derived from natural selection or from an inoculum of organisms or enrichment from the polluted media with specific pollutant degradation potential (Nano et al. 2003). The biodegradation rate is rapid and remedial goals are achieved in few months. Also, bioslurry systems are technically versatile, simple and more effective than conventional bioremedial approaches. Since it is a closed system, it allows better control of temperature, pH, aeration, nutrient and surfactant additions, control of VOC emissions, monitoring of reactions, and microbial supplementations. Bioslurries are used to treat SVOCs, VOCs, pesticides and PCBs (Kuyukina et al. 2003; Machin-Ramirez et al. 2008). It is more effective

than bioremediation and it works for most petroleum types. However, it has serious handling problems in heterogeneous soils, and dewatering of fine particles after treatment is costly. It also requires extensive site and contaminant characterization along with an effective disposal method for non-recycled wastewaters. Treatment cost using bioslurries ranges from US\$130 to 200 per m<sup>3</sup>. Cost increases in the case of post-gas treatment requirements for volatile contaminants (US EPA 2012).

Villemur et al. (2000) used a three-phase, aerobic slurry system containing 30 % silicone oil and biodegraded 90–98 % chrysene, pyrene and BaP. Wang and Vipulanandar (2001) observed that 96–99 % naphthalene was rapidly degraded by aerobic slurry bioreactors in 4 days. Castaldi (2003) treated petroleum waste sludges containing four-ringed PAHs in continuous multi-stage slurry bioreactors that operated for a short time with insignificant loss of volatile compounds, and observed more than 90 % removal of chrysene, BaP and pyrene. Hudak and Cassidy (2004) treated an aged PCB-polluted soil in bioslurry reactors inoculated with *Pseudomonas aeruginosa* that produced biosurfactant (rhamnolipid), and observed 98 % PCB remediation after 6 days. The removal of 47.9 % phthalate in a contaminated soil was observed by Venkata Mohan et al. (2006) in 40 h when a bioreactor coupled with bioaugmentation was chosen as the remedial tool. Fava et al. (2003) demonstrated the ability of surfactants like cyclodextrin, saponin and triton X-100 to enhance the actual remediation in slurry-phase systems by 30 %.

Marcoux et al. (2000) and Janikowski et al. (2002) indicated the use of solvents such as dodecane, decene, undecanone, hexadecane, limonene, jasmine, corn oil, silicone oil and paraffin oil can enhance PAH biodegradation. Lanthier et al. (2000) had reported augmentation of dehalorespiring strains (*Desulfotobacterium dehalogenans* and *Desulfotobacterium frappieri*) that used organo-chlorinated materials as electron acceptors in slurry bioreactors. Nano et al. (2003) recommended the combined application of slurry and solid phase bioreactor systems to remediate diesel-contaminated soils along with the use of soil additives, sand and surfactants for rapid TPH degradation (>95 %) in a week. In et al. (2008) estimated the effect of co-substrates (molasses and starch) in anaerobic slurry-phase biological degradation of TNT and reported 87–97 % degradation, which was 50–60 % higher than contaminant degradation without co-substrate addition.

Venkata Mohan et al. (2008) studied the *ex-situ* remediation of stimulated pyrene-polluted soil in slurry bioreactors operated in periodic discontinuous batch mode under anoxic-aerobic-anoxic microenvironments with bioaugmentation, and highlighted a pyrene removal rate of 90 % in 5 days. In a two-phase partitioning bioreactor, Robles-Gonzalez et al. (2006) suggested the slurry bioreactor *ad-situ* biodegradation approach as a successful substitute for treating mineral agricultural soils characterized by high contents of organic matter and fine texture contaminated with 2,4-D. The study reported 95 % removal of the herbicide in 14 days with and without sucrose supplementation. In a solid–liquid two-phase partitioning bioreactor system, Rehmann et al. (2008) managed 80 % phenanthrene removal using isopropyl alcohol as the mobilizing agent. About 66–94 % HCH bioremediation in slurry batch bioreactor was achieved by the white-rot fungus (*Bjerkandera adusta*) in 30 days after inoculation (Quintero et al. 2007). Soil slurry augmentation of an

immobilized bacterium (*Burkholderia cepacia*) with molasses achieved highest carbofuran removal of 96.97 % in a soil slurry-phase reactor in 4 days (Plangklang and Reungsang 2010).

Nasseri et al. (2010) noted the efficiency of bioaugmentation in a bioreactor to remove 87–92 % PAHs from contaminated soils. A successful TPH remediation of 95 % in 225 days was observed by the application of a continuously stirred tank bioreactor for remediating industrial wastewater effluents rich in hydrocarbons using a consortium of *Rhodococcus* sp., *Stenotrophomonas maltophilia*, *Ochrobactrum intermedium*, *Bacillus cereus* and *Aeromonas punctata* (Gargouri et al. 2011). Singh and Fulekar (2010) stated the potential of cowdung microflora as a source of biomass for benzene degradation (50 % in 168 h at an initial concentration of 5000 mg/L) in a two-phase partitioning bioreactor. When wheat straw pellets were used as the bulking agent, emerging pollutants like naproxen and carbamazepine were degraded by white-rot fungi (*Trametes versicolor*) to 38 % in 2 days in spiked sludge by solid and slurry-phase systems (Rodriguez-Rodriguez et al. 2010). Like aerobic bioslurry treatments, anaerobic systems have also been proved to remediate >95 % HCH, PCP, TCE, 2,4-D and TNT as presented in Table 8. Thus, many studies on bioreactor technology have proved that it is the most successful bioremediation technology for large-scale implementations.

### 3.12 Solidification/Stabilization

One of the best known waste fixation processes that offer reduction in mobility of pollutants in the environment through chemical and physical means is solidification/stabilization (S/S). It could be either *ex-situ* or *in-situ*. In this method, contaminants are enclosed or physically bound within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and pollutants to reduce their mobility (stabilization). Though mass reduction in contamination does not occur in this technique, reduced mass flux and mobility to receptors effectively removes the pollutant pathway. Distinct *ex-situ* innovative processes that have been developed in this method are vitrification/molten glass, soluble phosphates, sludge stabilization, radioactive waste solidification, portland cement, polyethylene extrusion, modified sulfur cement, emulsified asphalt batching, and bituminization. *Ex-situ* and *in-situ* S/S processes are usually applied to soils polluted by heavy metals and other inorganics. Mostly, this technology has limited effectiveness against pesticides and organics, except for vitrification and asphalt batching.

*Ex-situ* S/S is very effective for inorganics including radionuclides. Compared to biopiles or monitored natural attenuation, it has a short treatment time scale with an ability to remediate a wide range of mixed contaminants. It offers potential structure or geotechnical improvement in soil. Generally, environmental conditions affect the long-term pollutant immobilization. This treatment, however, is site-specific where residual long-term liability (contaminant mass remains) is observed. Inhibitory substances like free-phase solvents and oils limit the success of this system. Some

**Table 8** Remedial effect of aerobic and anaerobic slurry bioreactors

| Augments   | Contaminant                                 | Remediation (%) | Reference                         |
|--|---|-----------------|-----------------------------------|
| <i>Aerobic</i>   |   |                 |                                   |
| 1. Consortia of <i>Corynebacterium aquaticum</i> , <i>Flavobacterium mizutaii</i> , <i>Mycobacterium gastrii</i> , <i>Pseudomonas aeruginosa</i> and <i>Pseudomonas putida</i>   | Pyrene                                      | 93              | Cassidy and Hudak (2001)          |
| 2. Biosurfactant (Brij 30)   | Pyrene                                      | 70              | Schuur and Mattiasson (2003)      |
| 3. <i>P. aeruginosa</i>  | PCB, TPH                                    | 98–99           | Hudak and Cassidy (2004)          |
| 4. Molasses  | TNT, TNB                                    | 90              | Fuller and Manning Jr (2004)      |
| 5. <i>Rhodococcus</i> sp.  | Fluoranthene, anthracene, pyrene            | 98–100          | Dean-Ross (2005)                  |
| 6. <i>P. putida</i>  | Naphthalene                                 | 100             | Piskonen et al. (2005)            |
| 7. <i>Bjerkandera adusta</i>   | HCH   | 94              | Quintero et al. (2007)            |
| 8. Consortia of bacteria ( <i>Mycobacterium</i> sp., <i>Pseudomonas</i> sp., <i>Sphingomonas</i> sp., and <i>Rhodococcus</i> sp.) and fungi ( <i>Phanerochaete chrysosporium</i> , <i>Bjerkandera adusta</i> , <i>Irpex lacteus</i> and <i>Lentinus tigrinus</i> ) | Anthracene, fluoranthene, benz[a]anthracene | 46–85           | Li et al. (2009)                  |
| 9. <i>Pseudomonas</i> sp.  | BTEX  | 99              | Collins and Daugulis (1999)       |
| 10. Isopropyl alcohol  | Phenanthrene                                | 80              | Rehmann et al. (2008)             |
| 11. Cowdung  | Benzene                                     | 50              | Singh and Fulekar (2010)          |
| 12. <i>Trametes versicolor</i> and wheat straw   | Naproxen, carbamazepine                     | 38              | Rodríguez-Rodríguez et al. (2010) |
| 13. Molasses and immobilized <i>Burkholderia cepacia</i>   | Carbofuran                                  | 97              | Plangklang and Reungsang (2009)   |
| 14. <i>Aeromonas punctata</i> , <i>Bacillus cereus</i> , <i>Ochrobactrum intermedium</i> , <i>Stenotrophomonas maltophilia</i> and <i>Rhodococcus</i> sp.  | TPH   | 95              | Gargouri et al. (2011)            |
| <i>Anaerobic</i>   |   |                 |                                   |
| 1. <i>Desulfotobacterium</i> sp. and zero-valent iron  | TCE   | 100             | Lee et al. (2001)                 |
| 2. Anaerobic sludge  | HCH   | 100             | Quintero et al. (2007)            |
| 3. Sucrose   | 2,4-D                                       | 95              | Robles-Gonzalez et al. (2006)     |
| 4. <i>Desulfotobacterium frappieri</i>   | PCP   | 100             | Lanthier et al. (2000)            |
| 5. Molasses and starch   | TNT   | 87–97           | In et al. (2008)                  |

processes result in a significant rise in the contaminant volume (double the initial volume), and there it is necessary to explore the long-term effectiveness of this technology on the contaminants (RAAG 2000). It costs around US\$132–263 to treat per m<sup>3</sup> contaminated site (FRTR 2012).

Bates et al. (2000) recorded a full-scale remediation of 95–99 % PCP at Selma pressure treating site in Selma, California using S/S technology. Alpaslan and Yukselen (2002) conducted a study on bioremediation of Pb-contaminated soils by S/S and achieved 88 and 99 % Pb immobilization with the use of lime and soil (1:21) followed by cement and soil (1:15), respectively. Singh and Pant (2006) concluded that solidification of As waste with cement is suitable for reducing the leachability of As. Dermatas and Meng (2003) observed that fly ash materials (pozzolanic-based S/S) along with quicklime could immobilize more than 90 % trivalent, hexavalent Cr and Pb present in artificially-polluted sandy clay soils. Hwang and Batchelor (2001) studied the effect of Fe(II)-based degradative S/S (modification of conventional S/S that used Fe(II) as a reducing agent for chlorinated organics) at field-scale for immobilizing inorganic contaminants, and found less than 7 % of the initial amount of PCE on a molar basis between 13 and 335 days of treatment.

Many amendments facilitated the stabilization of heavy metals such as As, Cr, Pb and Cu. Several studies (Kim et al. 2003; Moore et al. 2000; Lee et al. 2011; Yoon et al. 2010) demonstrated the effect of Fe(II), limestone+redmud, Portland cement+cement kiln dust and sulphate to effectively reduce the mobility of As. Also, clay minerals, hydroxyapatites, aluminium oxides, organic matter, alkaline materials like lime and fly ash were proved to be effective amendments that facilitate As stabilization (Garcia-Sanchez et al. 2002). Stabilization of Cr was reported in the presence of divalent iron+organic matter (Seaman et al. 2001), and alkaline materials like hydroxyapatite, fly ash and calcium carbonate (Kim and Dixon 2002). More than 75 % immobilization of Cu by the use of clay minerals, palygorskite (Alvarez-Ayuso and Garcia-Sanchez 2003), fly ash stabilized sewage sludge (Su and Wong 2004), sugar foam (Garrido et al. 2005), peat (Balasoiiu et al. 2001), sewage sludge with earthworms (Kizilkaya 2008), and coal fly ash (Ciccu et al. 2003) was documented.

Pb stabilization was successfully performed with the application of P-containing amendments like natural apatites, hydroxyapatites, rock phosphate, phosphoric acid and their combinations (Brown et al. 2005; Cao et al. 2003b; Raicevic et al. 2005; Ownby et al. 2005). Even alkaline compounds, rice husk, ash, biosolids, compost, zeolite, iron as well as manganese oxides were used as soil amendments to stabilize Pb (Castaldi et al. 2005; Brown et al. 2005; Yin et al. 2006). The optimal cement binder content (5 %) to solidify or stabilize more than 85 % As in abandoned mine tailings was suggested by Choi et al. (2009). More than 95 % S/S of hazardous radioactive wastes using alkali activated cements was achieved by Shi and Fernandez-Jimenez (2006). Chen et al. (2009b) reported 100 % immobilization of heavy metals by the application of enhanced carbonation coupled with CO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> in cement-based S/S of heavy metal-bearing sediment.

Scanferla et al. (2009) developed and patented an innovative S/S technology using high performance additive (water reducers and superplasticizers) concrete

technology and observed superior leaching of heavy metals (99 %) at field-scale. Leonard and Stegemann (2010) reported more than 90 % immobilization of hydrocarbons in petroleum drill cuttings using Portland cement along with the addition of high carbon power plant fly ash which act as a novel sorbent for organic pollutants. In stabilization technology, the aim of adding additives is to change the soil physico-chemical properties through ion-exchange, adsorption, precipitation, redox potential and pH control. These will alter the existing forms of inorganics in soil, thereby reducing the mobility and bioavailability of heavy metals. This approach has been one of the most successful technologies in that it is efficient in immobilizing more than 95 % inorganics at large-scale more cheaply (Table 4). The current focus is to enhance the efficacy of the present reagent-based stabilization, vitrification, plastic material stabilization, lime pozzolanic solidification and cement solidification techniques using several biodegradable, natural reagents or additives or bulking agents in combinations with the ones that are outlined in Table 9.

### 3.13 Constructed Wetlands

Constructed wetland treatment for wastewater is a long-term technology that is primarily microbial, and uses natural, geochemical and biological processes inherent in an artificial wetland ecosystem composed of vascular plants, algae, microflora and organic soils to facilitate the accumulation and removal of explosives, metals and other pollutants from influent waters. Though it is a green technology practiced since 1969, the long-term effectiveness of constructed wetlands is not well understood (Vymazal and Kropfelova 2009). Also, wetland aging along with temperature fluctuations causes a problem which contributes to a decrease in pollutant removal rates over time; indeed, constructing a wetland is financially not viable for many sites (US EPA 2012). However, many remediation studies have been conducted with this technology to remove heavy metals from wastewaters. It is estimated that the capital costs of wetland treatment are about 1.36 US\$ per 1000 gal water (over a 10 year period) and US\$0.45/4000 L water (over a 30 year period) (FRTR 2012).

Polomski et al. (2009) observed more than 85 % N and P removal by three floating marine macrophytes (*Eichhornia crassipes*, *Pistia stratiotes* and *Myriophyllum aquaticum*) in greenhouse-based bench-scale subsurface constructed wetlands. Vymazal (2009) reported the extensive application of constructed wetlands with horizontal subsurface flow for treating wastewater from agriculture, airports, highways, greenhouses and plant nurseries. Horne et al. (2000) emphasized the success of phytoremediation by constructed wetlands. Around 70 % Se was removed by constructed wetlands in 2 years from Se laden drainage water collected from Corcoran, California (Lin and Terry 2003). In Czech Republic, three horizontal flow wetlands were constructed between March 2006 and June 2008 for removal of 34 trace elements (Kropfelova et al. 2009). The highest degree of 90 % Al removal followed by 78 % Zn, 50–75 % Gallium, Fe, Ba, Cr, Mo, Pb, Cu, Sb and U, and low retention concentration of 0–25 % for B and Co was noticed by the end of the study.

**Table 9** Bulking agents used for metal immobilization in solidification or stabilization systems

| Bulking agent  | Metal immobilized              | References   |
|--|--------------------------------|--|
| 1. Cement  | Almost all metals              | Chen et al. (2009b); Paria and Yuet (2006)   |
| 2. Rice husk and its ash   | Pb                             | Yin et al. (2006)  |
| 3. Biosolids and compost   | Pb, Cu, Zn, As                 | Brown et al. (2004); Castaldi et al. (2005); Chiu et al. (2006); Kumpiene et al. (2008)    |
| 4. Zeolite   | Pb, Mn, Zn, Hg                 | Kumpiene et al. (2008)   |
| 5. Iron and manganese oxides   | Cd, Cu, Ni, Pb, Zn             | Contin et al. (2007); Garcia et al. (2004)   |
| 6. Peat  | Pb, Cu                         | Kumpiene et al. (2007)   |
| 7. Fly ash and its geopolymers   | Pb, Cu, Cr, Zn, As             | Phair et al. (2004); Chen et al. (2009a, b); Ciccu et al. (2003); Seoane and Leiros (2001) |
| 8. Cyclonic ashes and steel shots  | Zn                             | Brown et al. (2005)  |
| 9. Ferrous sulphate  | As                             | Kim et al. (2003); Hartley et al. (2004)   |
| 10. Red mud  | Pb                             | Ciccu et al. (2003); Brown et al. (2005)   |
| 11. Limonite   | As                             | Garcia-Sanchez et al. (2002)   |
| 12. Palygorskite   | Cu, Zn                         | Kumpiene et al. (2008)   |
| 13. Calcium carbonate  | Zn, Pb, Mn, Cu, Ni, Cd, Co, Sr | Kumpiene et al. (2008)   |
| 14. Aluminium oxide  | As, Cu                         | Garcia-Sanchez et al. (2002)   |
| 15. Alkali silicate minerals   | Zn, Pb, Cd, Cr                 | Shi and Fernandez-Jimenez (2006)   |
| 16. Sewage sludge  | Cu, Zn                         | Sanchez-Monedero et al. (2004); Su and Wong (2004)   |
| 17. Gypsum   | Pb, Cd                         | Lombi et al. (2002); Garrido et al. (2005)   |
| 18. Chitosan type biopolymer   | Zn, Cu                         | Sherman and Randall (2003); Jothiramalingam et al. (2010)                                  |
| 19. Goethite, lepidocrocite, hematite and ferrihydrite   | As                             | Nurmi et al. (2005)  |
| 20. Nano-sized iron  | Cu, Cr, As                     | Kumpiene et al. (2006); Gil-Diaz et al. (2014)   |
| 21. Nanometallic Ca/CaO dispersion mixture   | Pb, Cr                         | Mallampati et al. (2012)   |
| 22. Phosphates (apatites, hydroxyapatites, phosphate rock, diammonium phosphate and phosphoric acid) | Pb, As, Zn                     | Martinez et al. (2014)   |
| 23. Lime   | Pb, Cu, As, Zn                 | Kumpiene et al. (2008)   |
| 24. Egg shell waste  | Cu, Pb, As                     | Lee et al. (2013)  |



Nyquist and Greger (2009) reported 36–57 % decrease in Fe, Cu, Zn and Cd concentration by the use of emergent plants and constructed wetlands at the Kristineberg mine site in Sweden.

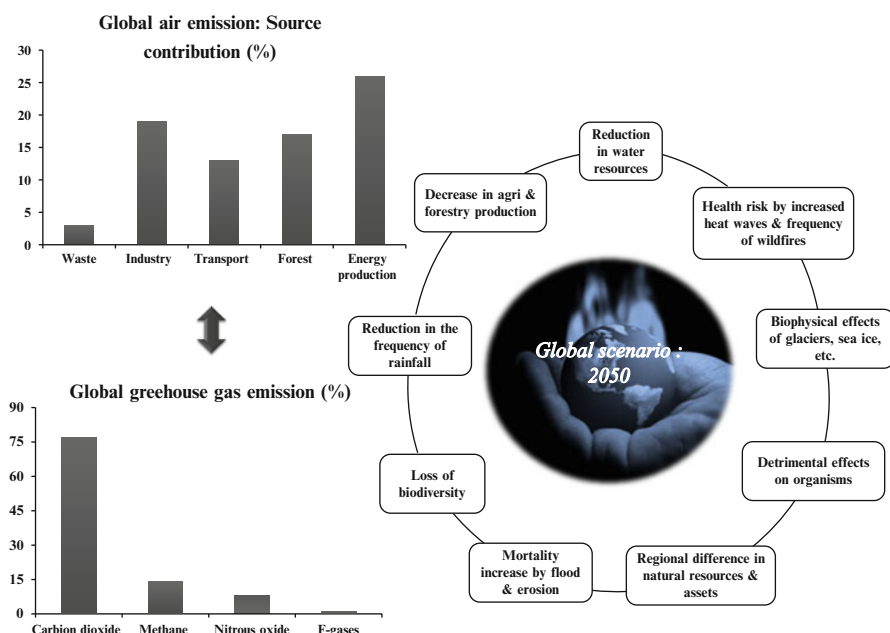
The accumulation of >85 % Cu, Cu and Zn, Al, Fe, Zn and Pb by phytoremediating plants (*Phragmites australis* and *Typha domingensis*) in constructed wetlands was reported by Ye et al. (2003), Ashraf et al. (2011) and Hegazy et al. (2011). Wu et al. (2012) conducted a long-term investigation (2005–2010) in two pilot-scale horizontal flow constructed wetland systems with Fe-rich solid matrix for treating sulphate-rich contaminated groundwater with lower concentration of chlorinated hydrocarbons, and observed 75 % pollutant removal at the SAFIRA research site in Bitterfeld, Germany. Chen et al. (2011) reported up to 70 % PCE dechlorination in two pilot-scale horizontal sub-surface flow constructed wetlands with vegetation (*P. australis*). Shelef et al. (2012) demonstrated 20–60 % salt phytoremediation by *Bassia indica* in a recirculating vertical flow constructed wetland system.

More recently, *Eleocharis macrostachya* used in constructed wetland prototypes showed a higher As mass retention of 87–90 % in 33 week test period (Olmos-Marquez et al. 2012). Zou et al. (2012) recommended employing a new vertical flow constructed wetland structure with drop aeration for treating rural wastewaters. A wetland system that had operated for 11 years in 12,800 m<sup>2</sup> area in the mid-western USA for remediating >90 % chlorinated ethenes rapidly developed into a healthy ecosystem with diverse vegetation, supporting over 60 bird species and several other animal species (Kadleec et al. 2012). Thus, most studies have indicated that planted wetland is a suitable option for treating metal-contaminated water, and long-term establishment of wetlands in a vast area could favor the survival of several micro- and macro-flora over a period of time. However, in high contaminant concentration such a possibility is not applicable, and there is a need to harness the merits of this technology (aesthetic, environmental friendly and sustainable characteristics) for remedial approaches by integrating this technique with several other physico-chemical techniques. They could in turn reduce the initial contaminant concentration and make this method successful.

## 4 *Ex-Situ* Technologies for Air Pollution Control

The recent pollutant release inventories published by environmental organizations and governments demonstrate that emission of atmospheric pollutants is continually rising with a steady increase in global warming leading to more threats to life forms. Of the total global air emissions in 2010, 77 % was CO<sub>2</sub> (US EPA 2012) followed by CH<sub>4</sub> (14 %), NO<sub>2</sub> (8 %) and F-gases (1 %). According to Rice (2007), one of the major contributors to global air emission (26 %) is energy production, distribution and use. Subsequently, road and non-road transport, industrial process, agriculture, accumulation of waste and forestry also contribute to between 3 and 19 % of the ever-increasing air pollution. If the current scenario of air emission is not controlled, by 2020–2050 there would be a drastic decrease in agricultural production, reduction in water





**Fig. 4** Global air emissions and the sources for contribution in 2010 with the projected regional impacts. *Source:* US EPA (2012); Rice (2007)

resources, increased health risks by climate change, elevated detrimental effects on living organisms by the biophysical effects on natural resources, loss of biodiversity and increase in mortality by erosion or flooding or forest fires or volcanoes, etc. (Fig. 4).

One way to control air emissions is to treat the industrial or household waste gases by adopting any of the physico-chemical or biological remedial options such as adsorption or ozonation or incineration or biofiltration or oxidation (UV/photochemical/biocatalytic) or membrane gas separation, etc. before they are let into the atmosphere (Fig. 5). These air pollution control remedial techniques which can be done both *in-situ* and *ex-situ* are just as important as soil and groundwater remediation technologies, and hence are discussed in this review.

Activated carbon is commonly used as adsorbent in waste-gas treatments (Foo and Hameed 2012). Many odorous organics like BTEX, TCE, hydrogen sulphide, SO<sub>2</sub>, acetone, mercaptans, etc. have been successfully removed by adsorption. Though adsorption has been employed for vapor/gas purification systems, it does have numerous drawbacks such as need for desorbate recovery at very low purity, high mechanical energy for pressurization, difficulty in maintenance of complicated set-up and high initial capital cost. Condensation is potentially effective for VOCs (99 % removal) having a boiling point over 40 °C. However, skilled technicians and a rigorous maintenance regime are required to handle the unit efficiently (US EPA 2012). Ozonation is not widely practiced commercially owing to its high cost, and the probability of ozone gas emission and its transformation into toxic intermediates (Li et al. 2012b).

|                                    |                                    |  |
|------------------------------------|------------------------------------|--|
| Adsorption<br><b>1</b>             | Biofiltration<br><b>5</b>          | <b>1</b> ❖ Adsorption of air pollutants onto activated carbon/zeolites, often as filtration post treatment<br>❖ There is a chance of potential risk of pollutant re-emission <sup>x</sup>  |
| Filtration<br><b>2</b>             | Membrane separation<br><b>6</b>    | <b>2</b> ❖ Air passed through a fibrous material often coated with viscous substance<br>❖ Chance of particle re-emission by the accumulation of microbes or blocks in filters <sup>x</sup>   |
| Ozonation<br><b>6</b>              | Enzyme oxidation<br><b>7</b>       | <b>3</b> ❖ Ozone is generated to oxidize pollutants<br>❖ Chance of generation of unhealthy gaseous pollutants and degradation products <sup>x</sup><br>❖ Ozone-based purifiers are not highly recommended for implications in industries <sup>x</sup>  |
| Photo(catalysis/lysis)<br><b>4</b> | Botanical purification<br><b>8</b> | <b>4</b> ❖ High energy UV is used either alone or in combination with a photocatalyst to oxidize air pollutants and kill pathogens<br>❖ Compared to photolysis, photocatalysis is an energy intensive method suited for a broad range of pollutant remediation <sup>x</sup>                      |
|                                    |                                    | <b>5</b> ❖ Air is passed through a packed bed of a solid support colonized by microbes that degrade the volatile organic compounds<br>❖ Eco-friendly and economic remedial option <sup>y</sup>   |
|                                    |                                    | <b>6</b> ❖ Affinity separation technique is applied to remove pollutants by the use of membranes<br>❖ There exist need for post-treatment of the membrane separated off-gases <sup>x</sup><br>❖ Technology is yet to be proven for separating the low volatile organics <sup>x</sup>             |
|                                    |                                    | <b>7</b> ❖ Transfer of air emissions into an aqueous phase where the pollutants are degraded by suitable catalysts or enzymes<br>❖ Only scarce resources are available on the suitable enzymes that can be efficiently used to degrade the air pollutants in commercialised systems <sup>x</sup> |
|                                    |                                    | <b>8</b> ❖ Initially air is passed through soil or directly on the planted vegetation and the contaminants are then degraded by microbes and or plants<br>❖ This technique can be used for interior design purposes and is not completely proven <sup>x</sup>                                    |

*Existing*                      *Emerging*  
Air pollution control remedial options

Principles, notable merits and existing knowledge gaps  
of air pollution control remediation technologies

*Note:*

<sup>x</sup> - Existing knowledge gap; <sup>y</sup> - Merits

**Fig. 5** Existing and emerging air pollution control remedial techniques. *Source:* US EPA (2012)

Membrane processes for gas separation are also gaining a greater acceptance in industries where semi-permeable membranes made of polymers (polydimethylsiloxane/ethylene oxide/polysulfone/polyimides/polycarbonates/polyperfluoro-dioxoles/cellulose acetate) or porous ceramics are used to separate the gas mixtures. Reverse selective membranes (solubility-controlled), carbon hollow fibers, carbon molecular sieve membranes, carbon nanotubes as membranes, mixed matrix membranes, zeolite membranes, facilitated transport membranes are the different types of recent promising membranes used in industries for the separation of  $H_2/N_2$ ,  $H_2/CO_2$ ,  $H_2$ /hydrocarbons,  $O_2/N_2$ ,  $CO_2$ /hydrocarbons,  $H_2S$ /hydrocarbons,  $H_2O$ /hydrocarbons,  $He$ /hydrocarbons,  $He/N_2$  and ethylene/ $N_2$  (Bernardo et al. 2009). Though extensive research is being carried out on improving membrane materials to control air emissions, application of membrane processes coupled with the other separation techniques in hybrid processes may be exploited better in the future.

An emerging purification technique for both air and wastewater due to its high effectiveness and versatility at low temperatures is photocatalytic oxidation (Assadi et al. 2012). Catalytic and thermal oxidations are also used to treat air pollutants present in their environment (Zhou et al. 2012). Bioprocess techniques that are mostly used for air emission control are bioscrubbers, biotrickling filters and biofilters. The biofiltration process is carried out in anaerobic/aerobic bioreactors where a polluted air stream will be allowed to pass through a porous packed media that support the thriving microbial population which help to exhibit a biofilm-like process.

Generally, pollutant diffuses through the biofilm that holds the microbes (Kennes et al. 2009). The treatment efficiency of the biofiltration technique is above 90 %. A diverse range of inorganic and organic chemicals (carboxylic acid, hydrocarbons, aldehydes, alcohols, ketones, hydrogen sulphide and ammonia) have been treated in biofilters (Kennes et al. 2009; Soares et al. 2012). Moreover low capital and operational costs, low energy requirements, and use of less chemicals make biofiltration a feasible biological technology for air emission treatments compared to other techniques. Further, recent technical discoveries and scientific advances have led to the development of novel bioreactor configurations such as continuous-suspended growth bioreactors, foam-emulsion bioreactors, fluidized-bed bioreactors, monolith bioreactors, air-lift bioreactors, and two-liquid-phase biotrickling filters. These have been promising and successful for handling air pollutants with a high remedial potential (Rene et al. 2012).

He et al. (2012) conducted a pilot-scale study integrated with biotrickling filtration and photocatalytic oxidation (BTF-PCO) for treating organic waste gas in a paint plant constituted of ethyltoluene, xylene, ethylbenzene, toluene, ethyl acetate and TMB. Elola et al. (2009)) proposed a new concept of combining adsorption (Pd as adsorbent) and catalytic hydrodechlorination for the treatment of organochlorinated off-gases (92 % conversion). Altomare et al. (2012) were able to remove ammonia (99 %) in nitrogen-containing effluent by photocatalytic treatments. Cai and Sorial (2009) removed 99 % VOCs in a trickling-bed biofilter integrated with cyclic adsorption/desorption beds. Fredenslund et al. (2010) recommended the use of engineered biocovers for the full-scale reduction of greenhouse gas emissions from landfills. The removal efficiency of VOCs by BTF-PCO treatment even after 90 days operation was in the range of 95.8–98.2 %. According to Jiang et al. (2009), graphene sheets with designed subnanometer pores (membrane) can selectively separate  $H_2/CH_4$  mixtures with numerous technological and energy applications including gas sensors, fuel cells and carbon sequestration.

Most recently, electric swing adsorption has been reported as a fruitful second generation technology to capture  $CO_2$  (89.7 % capture) from flue gases of power plants to combat global warming (Thiruvengkatachari et al. 2013). For filtration of air emissions, natural media filtration technology (alternative to conventional gravel, sand and activated carbon filters) was recently adopted (Wanielista et al. 2012). Use of a membrane bioreactor was able to remove 99 % toluene from waste air within 12 h under continuous and intermittent feeding conditions (Alvarez-Hornos et al. 2012). Kumar et al. (2012) investigated the degradation of TCE vapors in a membrane biofilm reactor inoculated with *Burkholderia vietnamiensis*. The primary growth substrate was toluene which was loaded consecutively during 110 days of the system's operation. A supreme TCE volumetric elimination of  $4.2 \times 10^{-3}$  g/m<sup>2</sup>/h was documented and 2–10 times greater than those reported in other gas-phase bio-remediation trials. Biofiltration of methanol in organic biofilter was conducted by Ramirez-Lopez et al. (2010) using peanut shells as the medium which could remove up to 30 kg/m<sup>3</sup> methanol/day. Thus, more available tools that can make use of natural waste materials for remediation require more in-depth research. Overall, advanced adsorption, photocatalytic oxidation, trickling and membrane biofilters

are very critical to aid air pollution control at full-scale, and investigations into the performance of integrated existing and emerging remedial technologies should be encouraged.

## 5 Emerging *Ex-Situ* Remediation Technologies

Contaminated ecosystems constitute a serious environmental problem, and it is difficult to treat pollutants with any one of the existing remedial techniques. For example, owing to the specific properties of the contaminants, remediation efforts devoted at macro-scale like pump-and-treat acquired limited success over time. In some cases, the *ex-situ* treatments become costly and fail to remove the contaminant from the source (Caliman et al. 2011). Under this pressure, some remediation techniques have been developed in the last few years for the decontamination of polluted sites, and many show promise in cleaning up contaminated soil and water.

Many countries have devoted resources to develop advanced and innovative remediation techniques, and as a consequence emerging technologies are finding a suitable platform for environmental clean up and can represent an important tool to overcome environmental risks in the near future. Most of the emerging technologies such as nanoremediation, microbial fuel cells, microbial consortia in photo-heterotroph microbial system, bio/photocatalytic pollution control, and genetic engineering are mostly being applied *in-situ* though they have greater prospects of *ex-situ* application. One recently emerging *ex-situ* remediation technology is ultrasonic technology which is described in more detail below. More efficient and economical *ex-situ* strategies are needed to remediate contaminated groundwater and soil.

### 5.1 Ultrasonic Technology

Ultrasound technology makes use of frequency over 18 kHz that forms the source in developing cavitation bubbles leading to high localized pressures (>50 MPa) and temperatures (>4726 °C), and induce chemical reactions that degrades the pollutants (Adewuyi 2001). Compared to incineration technology, ultrasound remediation of pollutants is worthwhile because of its less space requirement, faster remediation rates, less energy expenses, lower installation and maintenance cost followed by no sludge waste generation (Thangavadivel 2010). Effectiveness of the ultrasound technology in contaminant clean up depends on the transmitting medium characteristics, reactor characteristics, losses and attenuation in the medium as well as the standing wave effect if it is generated. Ultrasonic cleaning has an extensive range of industrial uses. Large-scale clean up of contaminated

soil using audible frequency sonication of 100 Hz and a higher power low frequency ultrasound pilot-scale operation were reported in Canada and Australia, respectively (Mason et al. 2004).

One of the important constraints in this technology is the physical limitation of transducer materials and wave propagation physics where the transmitted power drops with increasing frequency. Also, when intense mechanical energy is applied to the soil particles, clays get dispersed into a stable colloidal suspension, and it becomes difficult to separate organics from it. Desorption efficiency by ultrasonic destruction is slow for finer particles compared to coarse particles, i.e. finer particles demand longer sonication time. However, ultrasonic thermal desorption is an ideal alternative to solvent flushing or conventional soil washing techniques that involve additional costs when trying to solve contaminant accumulation problems in silt and clay particles.

Studies by Kazi et al. (2006) and Abramov et al. (2013) demonstrated the applicability of ultrasonic technology to leach or desorb pollutants from sediments and soils. Mason et al. (2004) reported an enhanced soil washing process with low frequency ultrasound for PCB removal in polluted zones. Low frequency (20 kHz)-assisted economically-viable remediation technology was also reported for PAHs desorption by Meegoda and Veerawat (2002). Ultrasonic thermal desorption can successfully remove chlorinated solvents, petroleum hydrocarbons, heavy metals and pesticides. It costs around US\$31.1 per m<sup>3</sup> when a frequency of 31 kHz is used for on-site remediation.

Thangavadiel et al. (2011) used low frequency, high power ultrasound heated slurries with anionic surfactant (sodium dodecyl sulphate) to enhance DDT desorption from contaminated soils. DDT contaminated soil, prepared as slurry (10 % wt) after the addition of 0.1 % surfactant at pH 6.9 was heated to 40 °C for 30 min. With a frequency of 20 kHz and ultrasonic intensity of 932 W/L, desorption of DDT was found beyond 80 % in 30 s without solvent extraction. He et al. (2011) confirmed the potential of ultrasound and biomass (transgenic *Chlamydomonas reinhardtii*) for *in-situ* mercury removal from contaminated inorganic sediments. Flores et al. (2007) proposed an innovative approach, employing the coupled effect of applying ultrasonic energy with advanced Fenton oxidation processes, for the degradation of hydrocarbons in problematic soils. The coupled effect resulted in 92 and 87 % removal of toluene and xylene, respectively, in 2 days.

Pham et al. (2009) concluded that ultrasonically-enhanced electrokinetics could significantly remove ten times more hexachlorobenzene and phenanthrene than electrokinetics alone. Yazici (2005) removed 25 % cyanides and generated hydrogen peroxide even at an increased alkaline pH of 10.5 when the temperature was high (>30–50 °C). There are many ultrasonic thermal desorption studies summarized in Tables 10 and 11 which ensure that the developing ultrasonic desorption is a reliable remedial technology for emerging priority pollutants. However, this technology's field-scale implications are not documented which emphasizes further applications of this technique are required in the near future.

**Table 10** Ultrasonic-enhanced soil remediation coupled with other technologies—case studies at laboratory-scale

| Contaminant  | Cleanup level (%) | Highlight  | Reference                         |
|--------------|-------------------|--|-----------------------------------|
| Terphenyl    | 99                | Use of 0.1 % octyl-phenyl-ethoxylate—surfactant-enhanced technology              | Meegoda and Veerawat (2002)       |
| PAHs         | 90                | Use of sunflower oil—surfactant-enhanced technology                              | US EPA (2012)                     |
| PAHs         | 90                | Coupled effect of electrokinetic and ultrasonic technology                       | Ik Chung and Kamon (2005)         |
| Alcohols     | 40–80             | Propanol and ethanol were removed with <i>Cladosporium</i> strain as biosorbents | US EPA (2012)                     |
| Phenol       | 15                | NaCl and CCl <sub>4</sub> were used as additives in the solution—biostimulation  | Mahamuni and Pandit (2006)        |
| DDT          | 80                | SDS—surfactant-enhanced technology   | Thangavadivel et al. (2011, 2012) |
| Phenanthrene | 69.5              | Combined application of nanotechnology with soil washing                         | US EPA (2012)                     |

## 5.2 Microbial Fuel Cells, Nanoremediation and Others

Two emerging promising remediation technologies that are mostly applied *in-situ* and can be considered to be successful even in *ex-situ* are microbial fuel cell (MFC) technology and nanoremediation. Another interesting area of research is perhaps the study of photo-heterotroph microbial systems (briefly explained in the other review under *in-situ* remedial techniques). These emerging, innovative approaches are so far not applied *ex-situ*, and thus open interesting possibilities for *ex-situ* field remedial initiatives which require thorough investigation. Cross-disciplinary clean up approaches that are eco-friendly, efficient in that they remove >95 % contaminant in short time, are less energy intensive, and economical should be developed using emerging methods and promising *ex-situ* techniques like advanced photocatalytic oxidation, biocatalysis, etc., and explored under *ex-situ* conditions.

## 6 Future Research Needs

It is evident in this review that many *ex-situ* remedial approaches are available for cleaning up contaminated sites. Although some existing technologies like advanced oxidation processes, sorption, solid and slurry-phase bioremediation are well-established and are potentially suitable for *ex-situ* remediation of contaminated sites, they are not very feasible due to their energy and cost considerations (for example, advanced oxidation processes are expensive). Also, no single technique is applicable for all pollutant types and the diverse physical settings that exist at

**Table 11** Ultrasonic thermal desorption technology for pollutant cleanup

| POP             | Frequency (kHz) | Power (W) | Temperature (°C) | Duration (min) | Cleanup (%) | Reference                  |
|-----------------|-----------------|-----------|------------------|----------------|-------------|----------------------------|
| 1. Chlorophenol | 20–850          | 140–475   | 36–39            | 120            | 100         | Teo et al. (2001)          |
| 2. TCE          | 100             | 140       | 20               | 40             | 90          | Yim et al. (2001)          |
| 3. Phenol       | 20–500          | 50        | 20               | 80             | 100         | Entezari et al. (2003)     |
| 4. Chlorophenol | 1.7             | 35        | 25               | 60             | 20.1        | Hao et al. (2003)          |
| 5. Phenol       | 20–520          | 25–180    | –                | 90             | 60          | Kidak and Ince (2008)      |
| 6. PCP          | 40              | 600       | 20               | 120            | 60          | US EPA (2012)              |
| 7. Phenol       | 22              | 120–240   | 31               | 60             | 50          | Mahamuni and Pandit (2006) |
| 8. Chlorophenol | 20–800          | 30        | 20               | 88             | 50          | Jiang et al. (2006)        |
| 9. Phenol       | 200             | 200       | 20               | 60             | 85          | Melero et al. (2011)       |
| 10. TCE         | 20              | 600       | 10–24            | 10             | 40          | Ayyildiz et al. (2005)     |
| 11. PFOS, PFOA  | 354–612         | 250       | 10               | 140            | 63          | Cheng et al. (2009)        |
| 12. PAHs        | 20–500          | 30        | 20               | 40             | 90          | David (2009)               |
| 13. DDT         | 1.6             | 150       | 24               | 9              | 90          | Thangavadiel (2010)        |
| 14. Cyanide     | 35–130          | 500       | 25               | 90             | 64–74       | Bonyadi et al. (2012)      |

different polluted sites. In most cases, more than one remedial technique is required to address most of the polluted site issues. Apart from the emerging technologies like ultrasonics, several clean up approaches that are both cost-effective and efficient need to be explored as potential methods in a remedial system. Further research and development would bring the emerging technologies to the market for full-scale implementation. Some of the crucial research gaps identified in the field of *ex-situ* remediation are as follows:

- Which combinations of technologies are appropriate for remediating various organic and inorganic pollutants in soil and groundwater ecosystems as well as air emissions?
- After remediation, does the use of some chemically-modified materials, nanoparticles, etc. remain bioavailable and cause a risk to the livings in the biome?
- Can the contaminants be degraded completely or transformed into less toxic forms by making use of microbes in the place of chemically-modified materials, nanoparticles, etc? If so, what is the extent of the metabolic cooperation among the microbial community? What is the structure and function of microbes in contaminated sites and their responses to different stimuli using environmental genomics and community fingerprinting?
- Is it practical to restore, to some extent, the natural functions of some polluted soils (multifunctional remediation) by the use of natural amendments and microbes?
- To what extent can existing and emerging techniques be modified or integrated to develop a feasible function-directed remediation technique that is better able to minimize the risk due to persistence and further spreading of pollutants?
- What are the efficient methods to decontaminate the emerging contaminants like pharmaceutical and personal care products, hormones, antibiotics, engineered nanoparticles, etc?

Answering these questions may lead to the development of new remediation techniques that are more reliable on an economic and environmental basis. This review also suggests the need for research on testing the feasibility of emerging *in-situ* techniques like MFCs, nanoremediation and photo-heterotroph microbial system as *ex-situ* remedial options as well. This is because MFCs have the dual property of remediation+electricity generation, and are most economical. Even nanoparticles can be synthesized by green strategies that will be more environmentally friendly. Large-scale implementation of these emerging technologies can be profitable tools for environmental entrepreneurs while providing options for previously difficult risk-based remediation projects for contaminated ecosystems.

## 7 Summary

Contaminated soil, groundwater and air emissions have been the subject of public concern and research, and the field of remediation has grown and evolved continually spending about US\$505.5 billion/annum globally. To improve decontamination



the remediation industry is continuously developing and adopting new technologies. Clean up of environmental pollutants involves a variety of *in-situ* and *ex-situ* techniques, ranging from physical, chemical, biological to advanced engineering technologies. Clean up activities may also address a wide range of contaminants when they are integrated. This review is an exploration of the *ex-situ* technologies for cleaning-up the contaminated soil, groundwater and air emissions, highlighting their principles, advantages, deficiencies and where gaps in the knowledge exist. Challenges and strategies for removing different types of contaminants, mainly heavy metals and priority organic pollutants, are also described. Included are technologies that are well-established like incineration, soil washing, biopiles, land-farming, bioreactors, oxidation, adsorption, dehalogenation, composting, solidification/stabilization, constructed wetlands, and emerging *ex-situ* technologies such as ultrasonic technology to treat the excavated soils or groundwater or air. It is evident that to attain more remedial efficiency some emerging *in-situ* techniques such as nanoremediation and MFCs may be studied in depth. Even the new technologies can be integrated with existing ones to improve the performance and overcome limitations of the existing remedial options.

Each technology in this review has been discussed as a complete package by starting with its basic principles, highlighting its advantages and disadvantages, field studies that have been conducted so far, recent advancements, and ending with suggestions for further research. This review highlights the fact that excellence in the research and technology process can be attained only when the remedial techniques are effective for a wide range of pollutants under different field conditions. Moreover, knowledge on the toxicological effects of the newly synthesized or modified materials that are used as key components in new and emerging technologies should be made available. The necessity to develop newer cost-effective, environmentally friendly, and reliable remedial techniques is high because contaminants are being discovered on a daily basis, and the load of contaminants in the ecosystem is increasing due to extensive industrialization. Thus, in order to pave the way for a healthy environment for future generations to enjoy, more challenging research focusing on the limitations of the existing as well as emerging remediation technologies during field-scale applications is demanded.

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