Environmental Chemistry for a Sustainable World

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Sustainable Heavy Metal Remediation

Volume 1: Principles and Processes

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Sustainable Heavy Metal Remediation

Volume 1: Principles and Processes

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Preface

Just living is not enough … one must have sunshine, freedom, and a little flower.

Hans Christian Andersen

All of us do not have equal talent. But, all of us have an equal opportunity to develop our talents.

A. P. J. Abdul Kalam

Today, one of the most serious concerns is to make clean water available to all human beings. It is estimated that only 3% of the Earth's water is fresh, which is unfairly distributed on the Earth, and over one billion people worldwide lack access to clean drinking water. As a result of increasing life standards together with demographic expansion, clean water demand is ever-increasing. Approximately 60% of the polluted areas in the world are facing harmful effects of heavy metals (Fig. 1) due to increasing numbers of mining, fertilizer, tannery, paper, batteries, and electroplating industries.

Heavy metals and their adverse effect on human health and the environment have been extensively studied and regulatory bodies such as the World Health Organization (WHO), United States Environmental Protection Agency (US-EPA), European Union (EU), and Occupational Safety and Health Administration (OSHA) have enforced standards and stipulated methods of sampling and analysis for the control of toxic heavy metals in the environment.

Heavy metals are toxic or carcinogenic, and unlike organic contaminants, they are not biodegradable. Heavy metals such as Zn, Cu, Ni, Hg, Cd, Pb, Cr, and As tend to accumulate in organisms, which may lead to a reduction in species diversity. Metal contamination is one of the persistent worldwide environmental problems, and adequate measures should be taken to prevent its exposure to the general population. In recent years, the grades of primary metal ore reserves have decreased due to increasing life standards accompanied with the high metal demand. Therefore, we have to change our perspective to see wastewater as a secondary resource for metal recovery. Hence, today *just end-of-pipe treatment is not enough…. We have to recover water and valuable materials from wastewater.* To meet the global metal

Fig. 1 Acid mine drainage waters at a South African coal mine. (Photos and copyright: Anna Kaksonen)

demand in the market, novel research areas have started to focus on the recovery of metals from metal-contaminated waste streams. In order to conflate both metal removal and recovery, new technologies have been successfully tested, both at the lab and pilot scale.

This book *Sustainable Heavy Metal Remediation* covers the principles, underlying mechanisms, thermodynamic functions, kinetics, and modeling aspects of sustainable technologies, particularly from the standpoint of applying physical, chemical, and biological processes and their combinations as hybrid systems for the treatment of wastewater polluted with heavy metals (Fig. 2). Particular emphasis has been given to technologies that are based on adsorption, electrocoagulation, bioprecipitation, biosolubilization, phytoremediation, and microbial electrolysis. These technologies also allow the utilization of ores of which the extraction would not otherwise be economically feasible through traditional mining methods.

This volume focusing on “principles and processes” reviews the techniques and processes for sustainable heavy metal remediation and recovery of metals from wastewaters. The volume comprises eight different chapters discussing the following topics:

- A general review of industries generating heavy metal pollution (Chaps. 1 and 7)
- Heavy metal removal from wastewater by biosorption and the underlying mechanisms (Chap. 2)

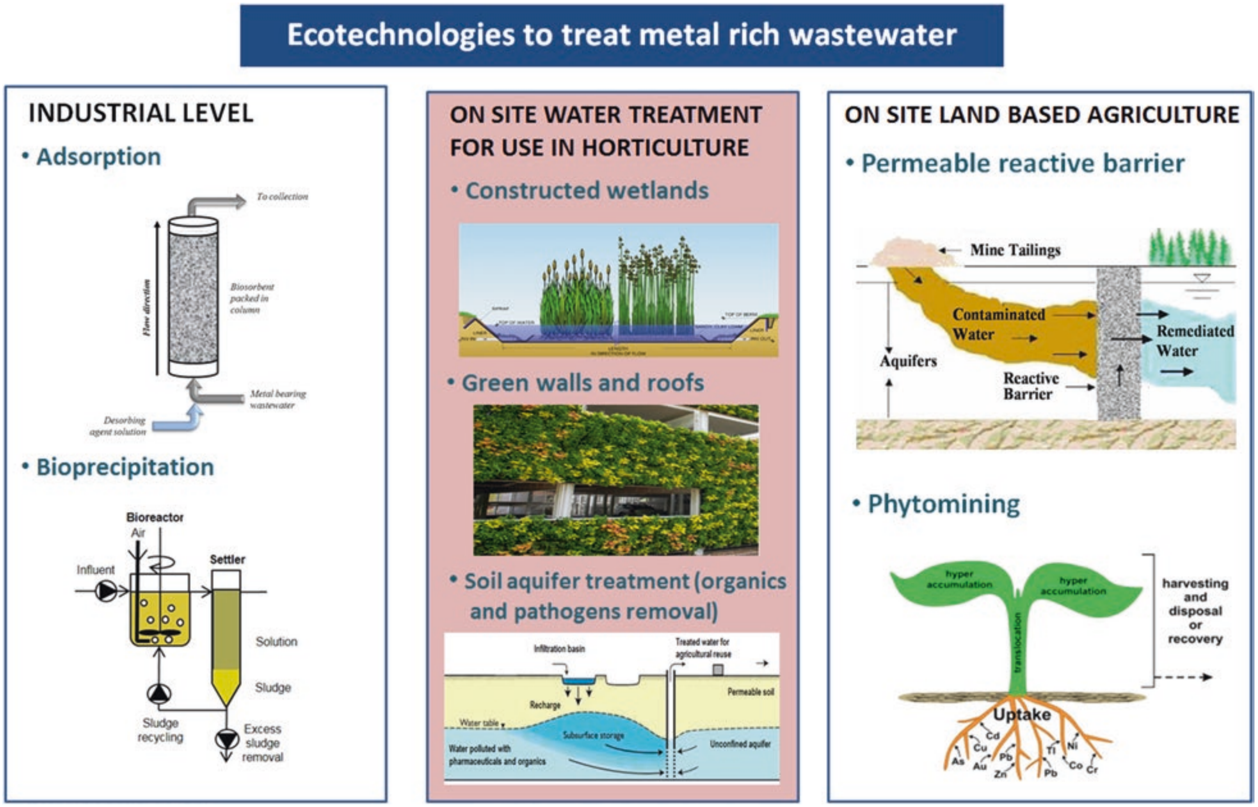

Fig. 2 Technological options for the removal and recovery of heavy metals from wastewater. The treated water can be used for agricultural purposes

- Removal of heavy metals from groundwater using permeable reactive barriers (Chap. 3)
- Thermodynamics and the mechanisms of metal precipitation (Chap. 4)
- Treatment of heavy metal containing leachate using constructed wetlands (Chap. 5)
- Emerging metal recovery concepts based on bioelectrochemical systems (Chap. 6)
- Bioprecipitation of heavy metals together with recovery alternatives (Chap. 7)
- The role of microorganisms in the solubilization of various metals and metalloids, the mechanisms through which biosolubilization occurs, and microbial groups mediating the solubilization (Chap. 8)

All the technologies covered in this book can be commercialized at field scale for the treatment of metal-contaminated wastewater and for the recovery of metals from ores and concentrates. The detailed presentation of the underlying principles and processes behind each technology in this book serves the target audience that primarily comprises researchers, practicing engineers in the field of environmental/chemical technology, and master's and doctoral students.

Finally, we owe a special debt of gratitude to Prof. Eric Lichtfouse (French National Institute for Agricultural Research, INRA, France) for providing many perceptive editorial comments and accepting this book to be a part of the book series *Environmental Chemistry for a Sustainable World*. We thank Ms. Judith Terpos, Springer (the Netherlands), and her production team for supporting us constantly during the editorial process. Further, thanks to the multidisciplinary team of authors for providing high-quality chapters wherein they have blended latest insights from environmental technology with practical scenario prevailing for the remediation of heavy metal-contaminated wastewater. We firmly believe that this book will stimulate the interest within the global research community and would help peers in their research pursuits.

We hope you enjoy reading this book.

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Chapter 1

Techniques for Metal Removal and Recovery from Waste Stream

Suthee Janyasuthiwong, Eldon R. Rene, Giovanni Esposito, and Piet N.L. Lens

Abstract Metal contamination in the environment is one of the persistent global environmental problems and their adverse health effects have been well documented. Heavy metals can be found in various forms, including fine particles, liquid and gas. On the contrary, metal resource depletion also has accelerated dramatically during the twentieth century owing to advances in industrial engineering and sciences, which require large amounts of raw materials. Therefore, researchers have started to focus on developing technologies which can remove metals from the environment and recover them to reuse as material.

In this chapter, the source and characteristics of several metal contaminated waste streams, recent developments and the technical feasibility of applying physico-chemical and biological technologies/processes to the treatment of wastewater polluted with heavy metals are reviewed. The source of metal pollution will be demonstrated from excavation to end of life product (cradle to grave), while particular technologies such as adsorption, electrocoagulation, biological sulphide precipitation and phytoremediation will be focused on as solutions for heavy metal contamination of the environment.

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Contents

1.1 Introduction

The global demand for metals is increasing at a rapid pace as a consequence of both population increase and expansion of industrial infrastructures in developing countries. As a consequence of this demand, metal scarcity and resource depletion have started to gain much attention in recent years. Metals are one of the common global resources used to produce a wide array of items that are aimed to add comfort to the daily life of humans. The source of metals varies from construction materials or electronics to nutrient supplies which help maintain homeostasis in biological systems. The natural occurrence of metals ranges from inorganic rocks and minerals to biochemical compounds like enzymes and protein structures. The contradiction between the utilisation and the production rate started to grow with the industrial revolution, resulting in depletion of metal reservoirs (Blackman and Baumol 2008; Rees and Wackernagel 2008).

With technological advancement, the metal consumption is increasing exponentially, which has directly accelerated reservoir depletion (Roberts 1990; Yellishetty et al. 2011). The demand of metals has increased greatly in the early 2000s and the trend has shown that the demand will still continue to rise. Tcha and Takashina (2002) reported that the imbalance in the consumption pattern of major metals, namely aluminum, copper, lead, nickel, tin and zinc, will affect the availability of these metal stocks. A similar trend in imbalance between the global consumption pattern and demand was also reported by Rauch and Pacyna (2009), who stated that the global metal cycle has changed from minerals and ores to in-use stocks. In these reports, the authors have highlighted that only high grade ore was being consumed and that lower grade ores remain largely unextracted. Moreover, many organisations have come up with metal resource models predicting that several elements will be depleted from the earth surface within several decades and many metals will enter the endangered zone. Rosa and Rosa (2011) reported that Cu production from the Iberian Pyrite belt has passed its peak owing to reservoir depletion. Another report which supports this scenario is from Swart and Dewulf (2013). In that study, the mining data and life cycle assessment results revealed that precious metals, especially Au, Pd and Pt, are in a more critical situation compared to previously reported predictions. Thus, there is an urgent need to ascertain solutions for metal resource management.

1.2 Metal Contaminated Waste Stream

Although metal scarcity is a recent emerging issue, metal contamination in the environment is still a persistent problem in many areas, especially, in industrialized zones. Metal contamination can occur both by natural processes and by anthropogenic activities. In some areas, the geography of rocks and minerals contains high amounts of certain elements which can be leached into surface or groundwater, thus resulting in high levels of a particular metal in the water bodies. Examples of this scenario are As contamination in Vietnam (Berg et al. 2001) and Bangladesh (Alam et al. 2003). These metals in the natural water can cause toxic effects to living organisms if they are exposed to this pollution until the accumulated dose exceeds the tolerate limits. Table 1.1 shows the classification of metal toxicity based on their natural occurrence.

Table 1.1 Toxicity classification of naturally occurring metals

Non toxic metals	Low toxicity metals		Moderate to high toxicity metals		
Aluminum	Barium	Praseodymium	Actinium	Lead	Tantalum
Bismuth	Cerium	Promethium	Antimony	Mercury	Thallium
Calcium	Dysprosium	Rhenium	Beryllium	Nickel	Thorium
Cesium	Erbium	Rhodium	Boron	Niobium	Titanium
Iron	Europium	Samarium	Cadmium	Osmium	Tungsten
Lithium	Gadolinium	Scandium	Chromium	Palladium	Uranium
Magnesium	Gallium	Terbium	Cobalt	Platinum	Vanadium
Manganese	Germanium	Thulium	Copper	Polonium	Zinc
Molybdenum	Gold	Tin	Hafnium	Radium	Zirconium
Potassium	Holmium	Ytterbium	Indium	Ruthenium	
Rubidium	Neodymium	Yttrium	Iridium	Silver	
Sodium					
Strontium					

Goldberg et al. (2012), Jain and Ali (2000), Moore et al. (2012) and Wood (1974)

Although natural processes can generate metal contaminants, anthropogenic activities are the major contributors and are considered to be more powerful towards environmental contamination owing to the excessive amount of heavy metals released within a shorter time frame than that of natural contamination. Table 1.2 shows examples of heavy metals in several environmental media, including living organisms, which results from common industrial activities.

1.2.1 Mining Activity

The ore excavation processes can be considered as the cradle of all anthropogenic metal activities. In order to get the raw materials, the excavation of minerals and rocks from the earth surface is the first step. This resource is crucial in driving nearly all human activities from daily life towards construction of convenience tools and buildings. Tilton (2013) mentioned that the mineral wealth has high affiliation to the economical and political situation of a nation. However, the waste, especially wastewater, generated from these activities contains many hazardous pollutants such as heavy metals, cyanides and metalloids (Johnson and Hallberg 2005; Sheoran and Sheoran 2006). The wastes generated from these activities can adversely affect various media such as soil, surface and groundwater as well as living organisms. Acid mine drainage (AMD) is mainly generated from the oxidation of sulphide ore such as pyrite (FeS_2). AMD is generated through both physico-chemical and biological processes (Neculita et al. 2007). The process starts with sulphide ore oxidation, which yields ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and proton (H^+) (Eq. 1.1). In some cases, the Fe^{2+} will be further oxidised by microbial activity under sufficient oxygen conditions to generate ferric (Fe^{3+}), as shown in Eq. 1.2:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ SO_4^{\ 2-} + 4\ H^+ \tag{1.1}$$

$$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O \tag{1.2}$$

As shown in Eq. 1.3, the ferric can precipitate at pH 2.3–3.5, as hydroxide [$Fe(OH)_3$]:

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \tag{1.3}$$

The overall reaction from Eqs. 1.1, 1.2 and 1.3 is shown in Eq. 1.4 (Akcil and Koldas 2006; Johnson and Hallberg 2005). As the reaction produces protons, the wastewater has usually low pH which is favourable for heavy metal solubilisation.

Table 1.2 Metal concentrations in several media related to anthropogenic activities

Medium	Types of waste	Metal concentration							Notes	References
		Cu	Cd	Co	Cr	Ni	Pb	Zn		
Soil (g/kg)	Abandoned Au-Ag mine	0.75	0.02	–	–	–	50.80	7.54		Lim et al. (2008)
	Industrial estate (tanned leather export)	0.04	–	–	2.65	–	0	0.16	Mean value	Gowd et al. (2010)
Sediment (g/kg)	Print factory	0.037	0.043	–	–	–	0.23	0.15	Sampling point no.6	Peng et al. (2008)
	Zn smelter	4.52	0.64	–	–	–	13.90	1.08	Sampling point no.8	
	WEEE processing	1.07	0.00	0.02	–	0.18	0.23	0.32	Lianjiang River	Wong et al. (2007b)
	Mangrove	0.06	<0.01	–	0.02	0.03	0.08	0.11		Defew et al. (2005)
Receiving surface water (ppb)	Print factory	14.4	4.01	–	–	–	4.01	73.4	Sampling point no.6	Peng et al. (2008)
	Zn smelter	20.5	74.6	–	–	–	10.0	941	Sampling point no.8	
	WEEE processing	7.80	0.09	0.86	2.20	36.6	1.48	30.6	Lianjiang River	Wong et al. (2007a)
Wastewater (mg/l)	Metal plating	0.92	–	–	47.0	28.0	–	239.0	pH 2.2	Kumar et al. (2011)
		1.02	–	–	34.0	190.0	–	24.0	pH 2.8	
		45.0	–	–	44.5	394.0	–	–	pH 3.0	Akbal and Camcı (2011)
	Acid mine drainage	0.20	–	–	–	0.23	0.02	1.28	Al: 47.9 SO_4^{2-}: 665	McCauley et al. (2009)

(continued)

Table 1.2 (continued)

Medium	Types of waste	Metal concentration							Notes	References
		Cu	Cd	Co	Cr	Ni	Pb	Zn		
Landfill leachate (mg/l)	Filter cakes treatment of metal finishing wastes	–	0.17	–	–	–	11.20	4.40	pH 5.9	Zawierucha et al. (2013)
Organisms (g/kg)	*Laguncularia racemosa* leaves	0.00	–	–	–	–	0.01	0.04	Mangrove plants	Defew et al. (2005)
	Common carp's gills (*Cyprinus carpio*)	–	1.88	–	0.790	1.04	1.40	–		Vinodhini and Narayanan (2008)

Note: *WEEE* waste electrical and electronic equipment

$$4\ \mathrm{FeS_2} + 15\ \mathrm{O_2} + 14\ \mathrm{H_2O} \rightarrow 4\ \mathrm{Fe(OH)_3} + 8\ \mathrm{SO_4}^{2-} + 16\ \mathrm{H}^+ \quad (1.4)$$

The major reason for AMD to pose a threat to environmental quality is the treatment cost and complexity of the AMD. The low pH (~2.5–3.6) by nature is considered as an extreme condition (Nordstrom et al. 2000). Moreover, the presence of various heavy metals, including some metalloids such as As (Smedley and Kinniburgh 2013), makes the treatment more complicated. Therefore, conventional treatment technologies are usually inadequate and too expensive in places where the mining activities occur, and most of the AMD is left untreated. As a consequence, AMD has caused severe negative effects on receiving water bodies and groundwater, which have affected plant and animal biota (Equeenuddin et al. 2010; Yesilnacar and Kadiragagil 2013).

1.2.2 Metal Related Production Activities

Industrial processes are the main contributors to metal contamination in the environment. All production processes generate waste. Various types of industrial activities produce different characteristics of wastewater in terms of metal speciation and metal concentration (Table 1.2). Thus it is difficult to achieve the discharge standards and make a treatment technology selection. Some examples of the industries involved with the discharge of highly contaminated wastewater are the fertiliser, tannery, electroplating, pulp and paper, semiconductor and electronics industry (Achoka 2002; Chandra et al. 2009; Chuah et al. 2005; Soloman et al. 2009). There are also several neglected industries which can contribute to metal discharge in the environment, such as textile, pharmaceutical and hospital waste (Suarez et al. 2009), because these industries are usually focused on other (hazardous) pollutants.

1.2.2.1 Electroplating Industry

Electroplating is a process in which the metal ions are moved towards the electrode for surface coating by an electrical field. This process changes the object which is being coated, in terms of its physical, chemical and also mechanical properties. Examples include, among others, corrosion resistance (chemical), appearance of a coating object (physical) and hardness on the work piece surface (mechanical) (Todd et al. 1994). The process connects the anode and cathode to the direct electric supply with the positive terminal connected to the anode, while the cathode is connected to the negative terminal. The material to be coated will be on the cathode side as shown in Fig. 1.1.

The metals and chemicals used in this type of industry depend on the type of work piece, purpose of coating, and the coating process. Even a little difference in these factors may cause the chemicals and metals in the wastewater to be highly

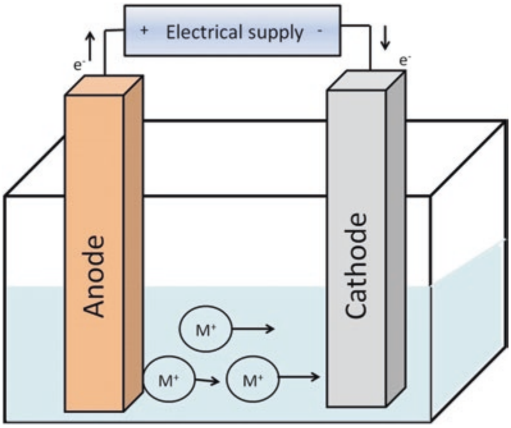

Fig. 1.1 Electroplating process where metal ions (M^+) move from the anode to the cathode resulting in surface coating of the cathode. This process occurs with the movement of electrons (e^-) via the electrical supply

Table 1.3 Characteristics of electroplating wastewater

Wastewater characteristics						
pH	Zn (mg/l)	Ni (mg/l)	Cu (mg/l)	Cr (mg/l)	Other metals (mg/l)	Source
2.0	–	94.2	–	418	–	Chen et al. (2008)
12.5	–	–	27	–	–	Sirianuntapiboon et al. (2008)
1.3	65.5	14.4	200	–	–	Sousa et al. (2009)
3.0	–	394	45	44.5	–	Akbal and Camcı (2011)
11.1	–	–	–	–	Cd: 1,570.0	Sankararamakrishnan et al. (2008)
6.0	232	248	–	–	–	Kabdaşlı et al. (2009)
6.0	217	270	–	–	–	
6.0	236	282	–	–	–	
2.2	239	28	0.92	47	–	Kumar et al. (2011)
2.8	24	190	1.02	34	–	

different. As a consequence, the production management and waste treatment systems should be designed properly for each individual case. Several parameters of environmental importance, like pH and metal species, are shown in Table 1.3.

As shown in Table 1.3, the concentrations and the type of metals have a wide range among each other, which are highly dependent on the type of production and the processes involved in those individual plants. The majority of these plating wastewaters are quite acidic (low pH) although there are some sources which have alkaline pH. Moreover, there are several pollutants which reside along with these metals in the wastewater, such as cyanide and organic solvents. The presence and concentration of these accompanied pollutants varies depending on the type of production, the quantity of usage and the production processes. There are some studies that show the potential of recovery of some metals such as Cr, Cu, Fe, Ni and Zn from this type of wastewater (Ajmal et al. 2001; Huang et al. 2014; Park et al. 2005).

Table 1.4 Semiconductor industries growth in 2009 and 2010

2010 rank	2009 rank	Company	Country of origin	Revenue (million USD)	Market share (%)
1	1	Intel Corporation	USA	40,020	13.2
2	2	Samsung Electronics	South Korea	28,137	9.3
3	3	Toshiba Semiconductors	Japan	13,081	4.3
4	4	Texas Instruments	USA	12,966	4.3
5	9	Renesas Electronics	Japan	11,840	3.9
6	7	Hynix	South Korea	10,577	3.5
7	5	STMicroelectronics	France/Italy	10,290	3.4
8	13	Micron Technology	USA	8,853	2.9
9	6	Qualcomm	USA	7,200	2.4
10	15	Elpida Memory	Japan	6,678	2.3

Source: iSuppli Corporation supplied rankings for 2010

1.2.2.2 Semiconductor Industry

A semiconductor is a material which has the property of electrical conductivity, it is fundamental in modern devices. Computers, radios, televisions, solar cells, diodes and many other devices use this material. Semiconductor materials are commonly known as crystalline solids; the amorphous and liquid phases also exist. The semiconductor industry is the aggregate group of companies that design and fabricate semiconductor devices. The growth of this industry is very high due to modern technological advancements. The countries that dominate the global semiconductor market are the United States, South Korea, Japan and the European Union. Table 1.4 shows the revenue and the share in the market of this business.

According to the growth of these industries, the demand on materials also increases annually along with waste generation. The manufacturing processes of these products involve many metals and chemicals. An improper management plan for production and waste management may cause a huge environmental impact. The characteristics of semiconductor wastewater from some industries are shown in Table 1.5. The major metals which can be found in this industry are Au, Cu, Pb, Ga and W.

1.2.3 Landfills

A landfill is a place where all municipal solid waste is gathered. It has been reported that more than 70% of the generated municipal solid waste is disposed of in a landfill (Slack et al. 2007; Zacarias-Farah and Geyer-Allély 2003) and two-thirds of this waste comes from households. Landfills can be considered as the graves of all end-of-life products. Household waste includes various types of products such as pesticides, pharmaceuticals, cleaning solutions, personal care products and electronic

Table 1.5 Characteristics of semiconductor industrial wastewater

Parameters	Sources	
	Wu and Sun (2005)	Ryu et al. (2008)
pH	5.5–6.5	2.4–4.3
Particle size distribution (μm)	0.07–1.44	–
Total suspended solids (mg/l)	56–440	–
Total chemical oxygen demand	–	221–444
Turbidity (NTU)	37–371	–
Total organic carbon (mg/l)	1.1–2.2	–
Conductivity (μs)	0.5–1.9	–
Zeta potential (mV)	−2.2	–
Indium (mg/l)	2.0–9.0	–
Phosphate (mg/l)	1.0–2.5	5–388
Total Kjeldahl nitrogen (mg/l)	–	106–171
Chloride (mg/l)	~0.04	6.9–9.9
Sulphate (mg/l)	~0.21	3.7–6.4
Sodium (mg/l)	~0.16	6.0–40.1
Potassium (mg/l)	~0.04	9.0–49.0

Note: *NTU* Nephelometric turbidity unit

wastes (Slack and Letcher 2011) which can be regarded as household hazardous waste due to their capability of releasing many toxic compounds (Slack et al. 2005). Some examples of toxic compounds which are released from household hazardous waste are styrene, dioxins, xenobiotic organic compounds and various toxic heavy metals.

Countries with poor solid waste management or those countries lacking waste separation may lead to severe metal contamination in soil and water due to metal leaching. There is evidence in Guiyu, China (e-waste recycling site), where the area and its neighbourhood are heavily contaminated with heavy metals. The human population living in the vicinity of this contaminated site is constantly exposed to Cd, Cr, Ni and Pb (Guo et al. 2010), while the vegetation grown in the nearby fields, such as rice (*Oryza sativa* L.), also shows high heavy metal concentrations (Fu et al. 2008). One of the reasons which makes landfills become one of the possible sources of heavy metals contamination, especially soil and groundwater, is the pH. The landfill is mostly in acidic conditions which are generated from the degradation of organic compounds, and results in the generation of volatile organic acids. These acidic conditions are highly favourable for metal leaching from the solid phase. The site contamination may become more severe if there is rainfall which facilitates the metals, for instance Pb, to reach deeper layers of soil or even the groundwater (Kjeldsen et al. 2002). There are many studies that have supported the fact that the prevailing pH conditions inside a landfill have a great impact on pollution transportation, especially heavy metals like Cr (VI) (Haijun 2010).

Landfills are not only polluted by toxic metals but also by metals with economical value. Morf et al. (2013) reported that incinerator residues of municipal solid waste in Switzerland contained various metals, including precious metals (Au, Ag and Pt) and rare earth elements such as La and Ce. Although the input concentration of these metals before thermal treatment in their study was still quite low, it indicates that we may lose some valuable resources during this treatment and disposal phase.

1.3 Metal Removal and Recovery Technologies

The effluent of industries or other sources containing high levels of heavy metals needs to be treated before it is discharged into the receiving surface water because heavy metals are toxic, carcinogenic and bio-accumulative in organisms. For instance, Pb is considered as a highly toxic metal in any measurable concentration (Needleman 2004). There are various wastewater treatment technologies available for treating heavy metals contaminated wastewater prior to ultimate discharge in natural water bodies, for example chemical precipitation, evaporative recovery, oxidation/reduction, filtration, ion exchange, membrane technologies and electrochemical treatment technologies are commonly used for practical applications (Fu and Wang 2011; Liang et al. 2010). These technologies can be divided into two main categories, viz., physico-chemical and biological processes. Table 1.6 shows examples of metal removal efficiencies from various technologies.

1.3.1 Physico-chemical Treatment

Physico-chemical technologies are effective and rapid methods in dealing with metal contaminated wastewater. They involve the change of physical and/or chemical properties such as size, charge and solubility. However, they have disadvantages due to the harsh conditions used during the processes, e.g. high pressure, high temperature or the addition of hazardous chemicals. Some examples of these technologies are adsorption, electrocoagulation, precipitation and membrane filtration. In this chapter, adsorption and electrocoagulation are the main focus.

1.3.1.1 Adsorption

Adsorption is an effective physico-chemical process for removing heavy metals from wastewater, especially for treating wastewaters with a low metal concentration. This process is very effective and relatively cheap if low cost adsorbents are used. There are many adsorbents available, varying from natural materials (clay balls) to agricultural waste and waste materials (sludges). The advantage of using agricultural waste as heavy metal adsorbent is the reduction of the solid waste problems and an increase in economic value and incentive of several by-products from

Table 1.6 Metal removal efficiencies from waste streams using various methods

Methods	Metals removal efficiency (%)							Reference
	Cd	Cr	Cu	Ni	Pb	Zn	Notes	
Adsorption using natural material	–	–	–	41.0	–	–	Ball clays (dosage 20 g/l) pH 6.0	Chantawong et al. (2003)
	98.0	–	99.0	–	–	–	Kaolinite (dosage 20 g/l) pH 6.0	Ulmanu et al. (2003)
	–	–	66.1	–	–	46.0	Zeolites	Erdem et al. (2004)
Adsorption using biomaterial	–	–	–	96.0	–	–	Orange peel (*Citrus reticulata*) pH 6.0	Ajmal et al. (2000)
Adsorption using industrial waste materials	62.2	–	–	–	–	–	Sewage sludge (dosage 10 g/l) pH 5.5–6.0	Zhai et al. (2004)
	–	–	–	78.0	–	–	Fry ash pH 6.5	Gupta et al. (2003)
	–	–	88.5	–	95.4	–	Iron slag pH 3.5–8.5	Feng et al. (2004)
Electrocoagulation	–	~100	~100	~100	–	–	Fe-Al pair electrode pH 3.0	Akbal and Camcı (2011)
	–	~100	99.0	98.0	–	99.0	Carbon steel electrode	Al-Shannag et al. (2015)
	–	99.8	–	85.6	–	99.0	Iron electrode pH 5.4	Kobya et al. (2014)
Precipitation	97.9	–	98.4	–	96.0	96.5	Sulphide precipitation SRB bioreactor	Villa-Gomez et al. (2011)
	–	–	~100	–	92.0	94.0	Sulphide precipitation	Alvarez et al. (2007)
	–	–	91.5	85.0			Sulphide precipitation	Xie et al. (2005)

agricultural materials. Rice husk, coconut shell, banana peel, sawdust, orange peel and groundnut shell are some examples of adsorbents from agricultural materials which have been studied over the past years (Demirbas 2008; Janyasuthiwong et al. 2015a; Mohan and Singh 2002; Sud et al. 2008).

Since the cost of an adsorbent depends on its abundance, availability and effectiveness, agricultural wastes have been extensively studied. In addition, these agricultural wastes are another global environmental problem as burning of these wastes contributes to CO_2 emissions (Wan Ngah and Hanafiah 2008). Thus, their use as adsorbents for wastewater treatment will reduce disposal problems (Khan et al. 2004; Lasheen et al. 2012).

Besides removing metals from the wastewater, regenerating the adsorbent as well as recovering and recycling of the metals is possible using adsorption based techniques (Barrera et al. 2006; Dakiky et al. 2002). Adsorption is a method well known for its cost effectiveness in metal removal. It is widely used in many countries, especially in developing and transition countries, where expensive, advanced technologies cannot be afforded. Studying the use of low cost adsorbents for heavy metal removal is one of the major fields of research in adsorption. One example of such low cost adsorbents is silk sericin and chitosan which were used to absorb and recover gold (Chen et al. 2011).

1.3.1.2 Electrocoagulation

Electrocoagulation uses the fundamental principle of an electrochemical oxidation process. The formation of metal hydroxide flocks in the wastewater by electrodissolution is the theory behind this treatment (Akbal and Camcı 2011). In this treatment process, the anode, where the metallic cations are generated, is mainly made of aluminum or iron, while H_2 is generated at the cathode (Arroyo et al. 2009). One of the advantages of this process is that the anions or salt concentration of the treated water will not increase, compared to other methods which add chemicals for metal removal, e.g. precipitation (Meunier et al. 2006).

Electrocoagulation is not only applicable to wastewater contaminated with metals, but includes oil and grease and suspended solids as well (Noling 2004). This technology is quite successful in real wastewater applications, such as electroplating (Adhoum et al. 2004; Akbal and Camcı 2011), tannery (Feng et al. 2007), chemical polishing (Drouiche et al. 2007; Lai and Lin 2004) and pulp and paper (Khansorthong and Hunsom 2009; Sridhar et al. 2011) wastewater. Therefore, this technology has been used for industrial wastewater in many places such as the United States, South America and Europe (Rodriguez et al. 2007).

In terms of metal removal, there are many studies that have focused on understanding the effects of operational parameters and optimisation of the processes. Examples of process parameters are pH, electrode material and distance between the electrodes, initial metal concentration, coagulation time and current density (Bhagawan et al. 2014; Senturk 2013; Shafaei et al. 2011). Heidmann and Calmano (2008) reported that higher initial concentrations of Cr (VI) showed higher removal rates for Cr (VI), while the removal rate of Au, Cu, Ni and Zn was not affected by this parameter. Lai and Lin (2003) demonstrated that the Al and Fe electrode pair yielded the highest performance among all of the selected pairs of electrodes during treatment of semiconductor fabrication wastewater. In that study, the Cu removal efficiency was 99%, while the turbidity reduction was 96.5%. Moreover, the effluent COD was less than 100 mg/l, and the overall effluent quality was good enough for reuse. Although the quality of the treated water is good, the operational cost is still high, especially from the electricity consumption.

Table 1.7 Comparison of phytoremediation and microbiological treatment

	Phytoremediation	Microbiological treatment
Land availability requirement	Large area required	Not required large space
Load of pollutant	Medium to high	Medium to high
Maintenance by manpower	Hard	Easy
Manpower needed	High	Low
Effectiveness	Medium to high	High
Ecological view	Low impact	Varied
Material recovery	Need specialize	Easy

1.3.2 Biological Treatment

Table 1.6 shows that biological methods give nearly the same level of removal efficiency as physico-chemical methods although they are usually operated at milder conditions. The major disadvantages of these biological technologies are the time, suitability of microbial or plant species, fluctuations in the performance and environmental conditions, since the process is mainly based on an organism's metabolic activity. The fundamental theory governing the biological treatment of heavy metals concerns the generation of alkalinity and immobilization of the heavy metals via both physical and chemical mechanisms by the organisms (Johnson and Hallberg 2005). This technology can be divided into two main categories: phytoremediation and microbiological treatment (Table 1.7).

1.3.2.1 Phytoremediation

Phytoremediation is one of the biological technologies used for the treatment of pollutants present in wastewater, including heavy metals. This technology not only offers advantages during wastewater treatment, but also provides other advantages in terms of ecology, green area, reduced carbon footprint and aesthetics. Phytoremediation is the method in which selected plant species that are used to mitigate the environmental problems or pollutants (metals, pesticides, solvents, crude oils and theirs derivatives) from soil, air, or water. There are many plant species that are commonly used in this field: *Vetiveria sp.*, *Typha sp.* and *Cyperus sp.* are examples of those plants (Fig. 1.2). Maine et al. (2006) reported that the constructed wetlands which were planted with several plant species for example *Pistia stratiotes, Cyperus alternifolius* and *Typha domingensis*, showed a high percentage of Cr and Ni removals and the Zn concentration was below 50 μg/l. However, this technology still has several drawbacks such as high land requirement, manpower needed and fluctuations in efficiency caused by variations in the stage on the plant growth. Park et al. (2008) reported that two wetlands, an *Acorus* and a *Typha* pond, did not achieve high enough metals and metalloids removal efficiencies. They suggested that the fluctuations of iron and manganese concentrations were primarily due to the microbial activities under anoxic conditions.

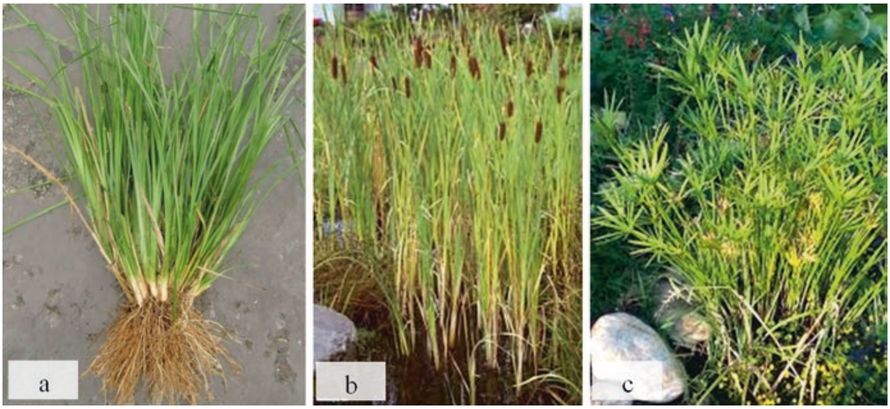

Fig. 1.2 Common plant species used in phytoremediation of heavy metals polluted wastewater: (**a**) *Vetiveria sp.*, (**b**) *Typha sp.* and (**c**) *Cyperus sp.*

1.3.2.2 Sulphate Reducing Bioprocesses

Many microbiological processes generate alkalinity from the reduction of electron donors (mainly carbon source); for example, sulphate reduction, denitrification, methanogenesis, iron and manganese reduction. This chapter will focus mainly on sulphate reduction.

Sulphate reducing bacteria (SRB) are a group of bacteria which have the ability to reduce sulphate to sulphide under anaerobic conditions. In anaerobic respiration, sulphate acts as an electron acceptor instead of oxygen in aerobic respiration, which generates bioenergy in the form of adenosine triphosphate (ATP). Moreover, SRB have been found to play a major role in the S cycle (Fig. 1.3), especially in sulphate reduction where SO_4^{2-} is reduced to S^{2-}. The most common genus mentioned in many studies is *Desulfovibrio*, which are gram negative, rod shaped, flagellate and strictly anaerobes. The classification of the SRB is based on several factors such as organic substrate which can be completely or incompletely degraded (Rzeczycka and Blaszczyk 2005). For example, *Desulfovibrio desulfuricans* uses carbon dioxide (CO_2) as its carbon source and hydrogen (H_2) as its electron donor. In cases where CO_2 is insufficient to complete their metabolism, other organic sources can be used (Widdel 1988). Equation 1.5 is an example of the sulphate reduction process using methane as e^- donor (Holler et al. 2011):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \tag{1.5}$$

Wastewater treatment technologies using SRB are an attractive method for the treatment of wastewater contaminated with heavy metals (Bijmans et al. 2011; Janyasuthiwong et al. 2015b). The metal sulphide precipitation is a very fast and effective reaction. Figure 1.4 shows the metal (Cu) sulphide precipitation in which the reaction occurs immediately after injecting the Cu solution. Moreover, it gives

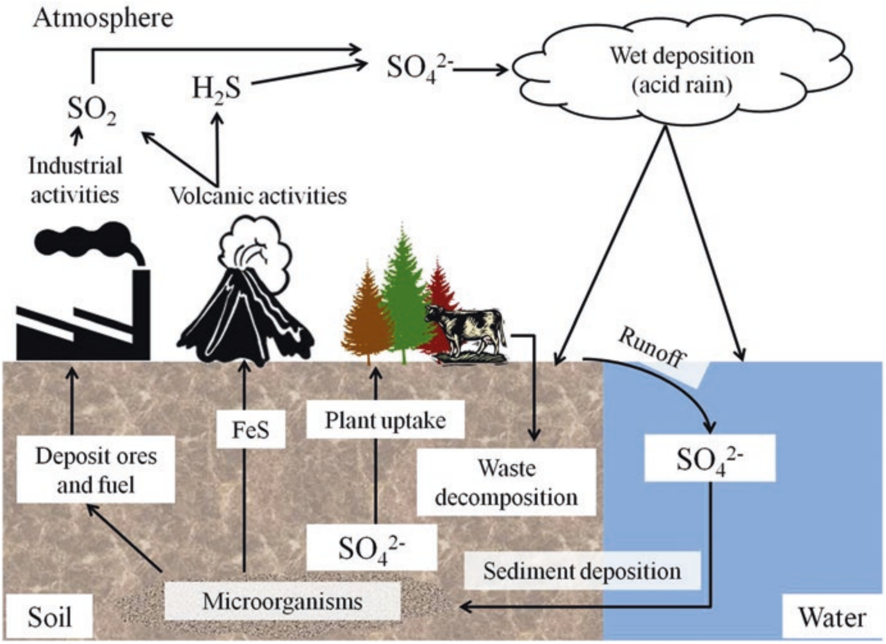

Fig. 1.3 The sulphur cycle in various media, which involves both organic and inorganic factors in the ecosystem

Fig. 1.4 Cu precipitation in a sulphate reducing bacterial culture bottle to which Cu (10 mg/l) was added into the *left* bottle, while no Cu was added into the *right* bottle

advantages in terms of selective metal precipitation since the formation of each metal sulphide is pH specific and the metal sulphide can tolerate a wider pH range than hydroxide and carbonate precipitation (Lewis 2010). Another reason which makes this technology to gain more attention is the low cost of the chemicals used as sulphide source. SRB do not only generate sulphide which is the main component for metal removal, but they also utilise the organic compounds present in wastewater.

There are many factors involved with sulphate reducing activity, but pH is one of the key factors which does not only limit the sulphate reducing activity but also the sulphide speciation (H_2S, HS^- and S^{2-}). Costa et al. (2008) reported that the growth of SRB is observed at around pH 5.0–7.0 and no sulphate reducing activity was observed at pH 2.0. Like other living organisms, bacterial growth is affected by many process conditions, either directly or indirectly. SRB require specific conditions in order to grow and reduce sulphate to sulphide: SRB grow at an optimum pH ranging between 5.0 and 8.0. However, there are some strains that can tolerate harsher conditions, like acidophiles, which can survive in acid mine drainage at a pH as low as 2.0 (Neculita et al. 2007).

Many studies showed that this technology is capable of metal recovery, for instance, Janyasuthiwong et al. (2015c) reported that the mixture of Cu, Ni and Zn at 25 mg/l each can be removed more than 90% within less than 5 min using the fluid withdrawn from the SRB bioreactor. Although SRB based biotechnological approaches yield high metal removal efficiencies, there are still some issues which needed to be considered. For example, toxic sulphide coupled with a low pH by nature of metal contaminated wastewater tends to shift the speciation of sulphide into hydrogen sulphide gas (Cohen 2006). Moreover, metal sulphides in certain conditions precipitate as fine particles, which make the settleability difficult and will thus affect the dewatering and recovery steps (Villa-Gomez et al. 2011).

1.4 Conclusions

The global metal consumption rate is increasing rapidly in accordance with the exponential population growth and the advancement of production technologies. Metal contamination owing to anthropogenic sources is a persistent global issue, having environmental, political and medical implications. Heavy metals are toxic and carcinogenic and have shown to cause serious health effects on humans and the fauna and flora. As a consequence, various treatment methods have been developed for the treatment of metal contaminated waste streams and some processes can also recover the metals. Among the commonly used physico-chemical and biological technologies for heavy metal removal and recovery, cost effectiveness, technical feasibility, plant simplicity and longevity of the process are the factors that govern the selection of an appropriate technology.

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Chapter 2
Heavy Metal Removal from Wastewaters by Biosorption: Mechanisms and Modeling

Stefano Papirio, Luigi Frunzo, Maria Rosaria Mattei, Alberto Ferraro, Marco Race, Berardino D'Acunto, Francesco Pirozzi, and Giovanni Esposito

Abstract Many industrial activities result in heavy metal dispersion in the environment worldwide. Heavy metals are persistent contaminants, which get into contact with living organisms and humans creating serious environmental disorders. Metals are commonly removed from wastewaters by means of physical-chemical processes, but often microbes are also enrolled to control metal fate. When microorganisms are used as biosorbents for metal entrapment, a process called "biosorption" occurs. Biosorption efficiency is significantly influenced by many parameters such as environmental factors, the sorbing material and the metal species to be removed, and highly depends on whether microbial cultures are alive or dead. Moreover, the presence of biofilm agglomerates is of major importance for metal uptake onto extracellular polymeric substances. In this chapter, the effect of the above mentioned variables on biosorption performance was reviewed. Among the environmental factors, pH rules metal mobility and speciation. Temperature has a lower influence with an optimal value ranging between 20 and 35 °C. The co-presence of

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more metals usually decreases the biosorption efficiency of each single metal. Biosorption efficiency can be enhanced by using living microorganisms due to the interaction with active functional groups and the occurrence of transport phenomena into the cells. The existing mathematical modeling approaches used for heavy metal biosorption were overviewed. Several isotherms, obtained in batch conditions, are available for modeling biosorption equilibria and kinetics. In continuous systems, most of the models are used to predict the breakthrough curves. However, the modeling of complex continuous-flow reactors requires further research efforts for better incorporating the effect of the operating parameters and hydrodynamics.

Keywords Mathematical modeling • Heavy metal biosorption • Active biomass • Inert biomass • EPS

Contents

Abbreviations

a, a_i	Langmuir isotherm parameter
a_{mdr},b_{mdr}	Modified dose-response model constants
A_R	1st Redlich-Peterson constant
a_t	1st Toth parameter
B	Constant relating to the energy of interaction with the surface
b, b_i	Langmuir parameter
B_R	2nd Redlich-Peterson constant
b_t	Temkin parameter
C	Solute concentration
C_0	Initial metal concentration
C_{break}	Breakthrough concentration

C_i	Non-adsorbed concentration of each component at equilibrium
$>C_{>e}$	Solute concentration at equilibrium
C_s	Solute saturation constant
EPS	Extracellular polymeric substances
F	Volumetric flow rate
F_{RP}	Radke-Praunsit parameter
K	1st Freundlich constant
k	Boltzmann constant
k_{AB}	Adams-Bohart kinetic constant
k_I	Rate constant of first-order sorption
k_I	Rate constant of the first-order adsorption
k_{II}	Rate constant of pseudo-second order sorption
K_{RP}	Radke-Praunsit parameter
k_t	2nd Toth parameter
K_t	3rd Toth parameter
K_T	Temkin isotherm equilibrium binding constant
k_{TH}	Thomas rate constant
k_{WM}	Weber and Morris intraparticle diffusion rate
k_x	Rate constant with an inverse unit of time
k_{YN}	Yoon-Nelson rate velocity constant
M	Biomass weight
m_R	Redlich-Peterson parameter
n	2nd Freundlich constant
N_0	Saturation concentration
N_{RP}	Radke-Praunsit parameter
Q	Moles of solute sorbed per unit of sorbent weight forming a complete monolayer on the surface
Q_0	Maximum amount of metal adsorbed onto the biomass
q_e	Adsorbed quantity at equilibrium
q_i	Adsorbed quantity of each component at equilibrium
q_i^0	Concentration of each adsorbed component in the equations with C_i^0
q_m	Maximum adsorption capacity
q_{mi}	Maximum adsorption capacity of each component
q_t	Quantity adsorbed at time “t”
r	Clark adsorption rate
R	Gas constant (or biosorbent particle radius)
T	Absolute temperature
t	Time
t_{break}	Breakthrough time
U_0	Linear flow rate
V_{eff}	Throughput volume
W	Adsorbed volume
W_0	Micropore volume
x	Biosorption reaction order with regard to the effective concentration of the adsorption sites available on the surface of biosorbent

Y_i	Solute concentration of the generic component "i" in the solid phase
Z	Column depth
α	Initial sorption rate in Elovich equation
β	Polanyi scaling factor in Polanyi models
β_a	Kinetic coefficient of external mass transfer
β_e	Desorption constant in Elovich equation
ε	Column bed porosity; Polanyi's adsorption potential
λ_t	Effective number of the adsorption sites on the surface of biosorbent available for biosorption at time "t"
τ	Time required for 50% adsorbate breakthrough

2.1 Introduction

Wastewaters from mineral processing and industrial activities are often characterized by high metal concentrations. Heavy metals are toxic and non-biodegradable compounds that can result in serious health disorders for human beings if over-discharged in the hydrosphere (Zhuang et al. 2009). Several physical-chemical processes, such as adsorption, coagulation, flocculation, ion exchange, membrane separation or precipitation can be used to treat heavy-metal containing wastewaters (Fu and Wang 2011). However, the use of microbes to rule metal mobility in the environment has recently gained increasing attention by the scientific community.

Among the bioremediation technologies used for metal immobilization and sequestration, biosorption has shown promising removal efficiencies with several heavy metals, e.g. Cd, Cu, Ni, Pb and Zn (Tsezos 2001; Pardo et al. 2003; Wang et al. 2006; Lakzian et al. 2008). Biosorption is a complex combination of processes aimed at the entrapment of a substance onto the surface of a living/dead organism or extracellular polymeric substances (EPS). Many mechanisms contribute to the overall process, such as adsorption, precipitation and intracellular accumulation of metal compounds, with each mechanism significantly depending on (*i*) the biosorbent used, (*ii*) the substance to be sorbed, (*iii*) pH and temperature, (*iv*) presence of competing metals and ions and (*v*) the possible presence of metabolic activity (Gadd 2009).

Many biological materials are suitable for maintaining biosorption due to high efficiency, cost effectiveness and particular affinity with metals, metalloids and other pollutants (Gadd 1990; Bailey et al. 1999). The potential of archaea, bacteria, fungi, algae, yeasts and agricultural wastes as biosorbents has been largely studied and reviewed (Fourest and Roux 1992; Wang and Chen 2009). Moreover, since most microorganisms live in the form of biofilms, the different nature of the cell agglomerates and the presence/composition of EPS further contribute to biosorption (Flemming 1995; Comte et al. 2008).

Besides metal removal, biosorption has also been used in metal recovery applications (Simmons and Singleton 1996; Mata et al. 2009). The high market price of some precious metals, e.g. gold, silver, platinum and palladium, implies the use of

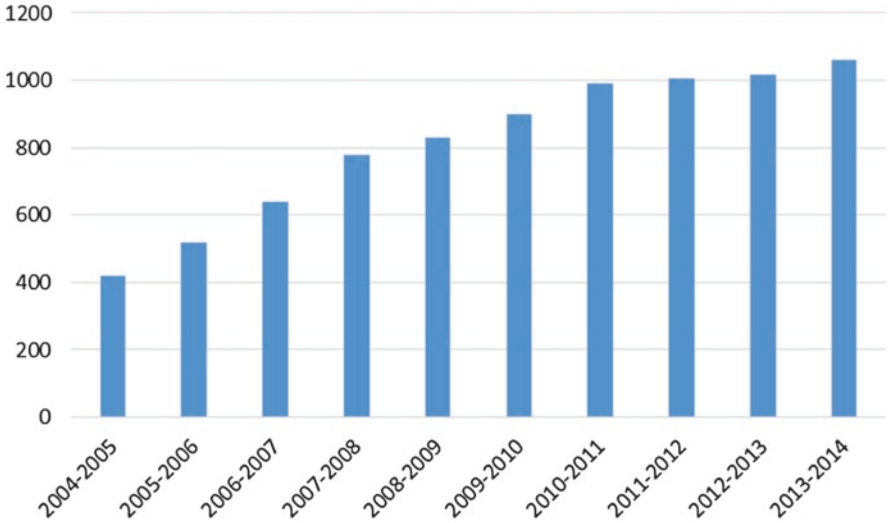


Fig. 2.1 Publication trend of the papers reporting the word "biosorption" in the title according to the Web of Science database from 2004 to 2014 (Adapted from Gadd 2009). A constant increase of the number of publications on biosorption can be easily noticed

cheap technologies in order to maintain the operating costs low and reduce the amount of chemicals that other technologies require (Das 2010). Although the potential of biosorption in this direction appears to be enormous, the control of the operating parameters for the development of a selective metal biorecovery strategy in multi-metal systems needs further investigation.

There is a growing interest of the scientific community in biosorption, as reported by the increasing number of scientific publications in Fig. 2.1. In the first part of this chapter, the biological sorption mechanisms occurring onto microbial biomass (living and dead) and EPS are described. More specifically, the mechanisms involved in biosorption have been classified depending on the microbial metabolism and the location of occurrence. Furthermore, the existing relations between biosorption mechanisms have been individuated. The second part of the chapter focuses on the classification of the most used mathematical models for heavy metal biosorption on microbial biomass. Mathematical models are classified in two main categories: models for (*i*) batch and (*ii*) continuous systems. The first category is further subdivided in sorption equilibrium models and kinetics batch models and summarizes the main modeling approaches introduced to reproduce the behavior of batch systems in terms of maximum sorption capacity and kinetics. Continuous models are aimed at reproducing the dynamic behavior of column bioreactors. Finally, a short analysis of further research directions and biosorption future perspectives are given.

The application of biosorption at the industrial scale has not been yet exploited, mainly due to the complexity of the mechanisms involved for both metal removal and recovery. Therefore, a mathematical model appears as a support tool to gain essential information for the identification of the key factors affecting biosorption efficiency and stability. At the current state, mathematical tools have been developed to simulate biosorption by using isotherm models. Langmuir and Freundlich isotherms are the best known models but their application has been mainly addressed to simple batch systems (Liu and Liu 2008). The modeling of a complex system, such as a continuous-flow bioreactor, requires the use of more powerful mathematical tools. Thus, dynamic models, capable of simulating the biosorption mechanisms and the interaction between substances and biofilm agglomerates, are more appropriate.

2.2 Biochemical Processes at the Biofilm Matrix-Liquid Interface

Biosorption can be performed by many mechanisms occurring under different operating and environmental conditions. Due to the complexity of the biological materials used as biosorbents and the wide range of parameters affecting biosorption, the specific mechanisms involved are usually hard to determine (Gadd 2009). However, biosorption can occur through a single mechanism or a combination of several processes such as adsorption, chelation, complexation, electrostatic interaction, ion exchange and microprecipitation (Veglio and Beolchini 1997; Volesky 2001; Wang and Chen 2006; Vijayaraghavan and Yun 2008).

2.2.1 Parameters Affecting Biosorption

For each biosorbent, many factors can influence metal uptake onto biomass at different rates determining the overall biosorption performance (Park et al. 2010). The influence of some important parameters affecting biosorption is described in the following sections and reported in Table 2.1.

2.2.1.1 pH

pH highly influences metal biosorption and is probably the most important parameter controlling biosorption extent. Indeed, pH plays a crucial role in defining the chemical properties of metals, the availability of biomass functional groups and the competition among metallic ions for adsorption sites (Friis and Myers-Keith 1986; Galun et al. 1987; Comte et al. 2008).

Generally, low pH keeps metals in solution, represses microbial activity and increases the competition between cations for binding sites resulting in lower biosorption efficiencies (Gadd and White 1985). However, biosorption of anionic metal species (e.g. CrO_4^{2-} and SeO_4^{2-}) is often enhanced under acidic conditions. As pH rises, the biosorptive removal efficiency of cationic metals increases albeit may induce metal precipitation at a pH above 7.0 (Park et al. 2010). In some cases, biosorption is pH independent. For instance, Ag^+, Hg^{2+} and $AuCl_4^-$ form strong covalent complexes with the biosorbent resulting in a negligible effect of pH (Gadd 2009).

Table 2.1 Effect of pH, temperature, metal initial concentration, biosorbent dosage and contact time on biosorption extent in batch experiments

Metal	Microbial species	pH	T [°C]	C_0^a [mg/g]	B^a [g/l]	t^a [min]	q^a [mg/kg]	References
Cd (II)	*Geobacillus thermoleovorans* sub.sp. *Stromboliensis*	4	70	50	0.5	60	35	Özdemir et al. (2009)
	Geobacillus toebii sub.sp. *Decanicus*	6	70	50	0.5	60	23	
	Glebionis coronaria L.	6.5	25	100	2	120	30	Tounsadi et al. (2015)
	Diplotaxis harra	6.8	25	100	2	120	22	
	Aspergillus niger	7	25	10	2	60	9	Hajahmadi et al. (2015)
	Bacillus thuringiensis strain OSM29	7	30	100	1	30	25	Oves et al. (2013)
Co (II)	*Glebionis coronaria L.*	6.3	25	100	2	120	13.5	Tounsadi et al. (2015)
	Diplotaxis harra	6.8	25	100	2	120	12	
	Aspergillus niger	7	25	10	2	60	8	Hajahmadi et al. (2015)
Cr (VI)	*Bacillus thuringiensis strain OSM29*	7	30	100	1	30	26	Oves et al. (2013)
	Streptomyces rimosus	5	25	100	3	150	22	Chergui et al. (2007)
Cu (II)	*Geobacillus toebii* sub.sp. *Decanicus*	4	60	50	0.5	60	14	Özdemir et al. (2009)
	Geobacillus thermoleovorans sub.sp. *Stromboliensis*	4	60	50	0.5	60	19	
	Streptomyces rimosus	5	25	100	3	15	27	Chergui et al. (2007)
	Bacillus thuringiensis strain OSM29	7	30	100	1	30	30	Oves et al. (2013)
Hg (II)	*Bacillus* sp.	6	25	5	0.8	90	2	Green-Ruiz (2006)
Mn (II)	*Geobacillus toebii* sub.sp. *Decanicus*	4	80	50	0.5	60	14	Özdemir et al. (2009)
	Geobacillus thermoleovorans sub.sp. *Stromboliensis*	5	70	50	0.5	60	22	
Ni (II)	*Geobacillus toebii* sub.sp. *Decanicus*	4	70	50	0.5	60	15	Özdemir et al. (2009)
	Geobacillus thermoleovorans sub.sp. *Stromboliensis*	4	80	50	0.5	60	11	
	Bacillus thuringiensis strain OSM29	7	30	100	1	30	38	Oves et al. (2013)

(continued)

Table 2.1 (continued)

Metal	Microbial species	pH	T [°C]	$C_0{}^a$ [mg/g]	B^a [g/l]	t^a [min]	q^a [mg/kg]	References
Pb (II)	*Bacillus cereus*	1	25	75	1	80	4–22	Çolak et al. (2011)
		6	25	75	1	100	24	
	Bacillus pumilus	1	25	75	1	80	5	
		6	25	75	1	80	28	
		6	25	75	1	100	30	
	Myriophyllum spicatum	5	25	100	0.18	30	40	Yan et al. (2010)
	Bacillus thuringiensis strain OSM29	7	30	100	1	30	27	Oves et al. (2013)
Zn (II)	*Acinetobacter* sp.	2	25	100	0.5	120	13	Tabaraki et al. (2013)
		6	20	100	0.5	90	26	
		6	40	100	0.5	90	38	
		6	25	100	0.5	120	32	
		6	25	100	0.5	10	10	
		6	25	100	0.5	60	30	
		6	25	100	0.5	120	32	
	Botrytis cinerea	4	25	100	2	30	13	Tunali and Akar (2006)
	Geobacillus thermoleovorans sub.sp. *Stromboliensis*	4	70	50	0.5	60	24	Özdemir et al. (2009)
	Geobacillus toebii sub.sp. *Decanicus*	5	80	50	0.5	60	18	
	Streptomyces rimosus	5	25	100	3	150	23	Chergui et al. (2007)
	Aspergillus niger	7	25	10	2	60	8	Hajahmadi et al. (2015)

[a] C_0 – Initial metal concentration, B – Biosorbent dosage, t – Contact time, q – Biosorption capacity

2.2.1.2 Temperature

In contrast with the effect of pH, influence of temperature on biosorption is observed in the range 20–35 °C (Aksu et al. 1992). A better uptake can however be achieved by increasing the operating temperatures up to 50 °C (Tsezos and Volesky 1981), although high temperatures have shown contrasting effects on biosorption system behavior. For instance, a high temperature determines an increase in surface activity and kinetic energy of the adsorbate, although the biosorbent structural integrity can be irreversibly damaged (Park et al. 2010). Moreover, the effect of temperature on the biosorption efficiency depends on whether living or dead cells are used. A higher temperature normally results in a higher number of cells and an enhanced biosorption efficiency. However, the impact of other parameters (i.e. pH) has to be simultaneously evaluated (Congeevaram et al. 2007).

2.2.1.3 Biosorbent Dosage and Size

The concentration of the biomass used as sorbent is also an important parameter to take into account for evaluating biosorption performance. A high biomass content increases the overall biosorption efficiency but also causes interference between the binding sites with a consequently lower specific uptake (Gadd et al. 1988; Park et al. 2010). With regard to the size of the biosorbent, small particle sizes are desirable in batch assays in order to increase the surface area and enhance the contact between metals and sorbent. On the other hand, in continuous-flow applications the use of small bio-particles results in channeling and clogging of the systems affecting biosorption efficiency (Park et al. 2010).

2.2.1.4 Metal Ions Coexistence and Metal Speciation

The removal of ionic metal species can be affected by the coexistence of further metal ions or other anions. Many studies are contradictory and not all biosorption mechanisms are well understood. This is because the presence of more metals only plays an indirect role on the biosorption of a particular species as the influence of pH or other parameters is often more relevant. Generally, the concomitant presence of several metals affects the biosorption efficiency of single metals, whilst no influence is observed on the total metal binding capacity (Akthar et al. 1996).

For instance, uranium uptake onto *Rhizophus arrhizus* cells is particularly affected by the presence of Fe^{2+} and Zn^{2+} (Tsezos and Volesky 1982). Similarly, inhibition of cobalt uptake has been observed in the presence of uranium, lead, mercury and copper whereas no effect on uranium uptake has been revealed in the presence of the same metals (Sakaguchi and Nakajima 1991).

The solubility, mobility and bioavailability of metals also change depending on metal speciation. Anions like chloride or carbonate can influence metal speciation promoting the formation of complexes and affecting the extent of biosorption. Furthermore, the concomitant presence of other ions hinders biosorption yields. Phosphate may affect biosorption since PO_4^{3-} has been reported to compete with some metals (such as As(V)) for binding sites or form insoluble metal precipitates (Darland and Inskeep 1997; Gadd 2009; Papirio et al. 2014).

2.2.2 *Biosorption Mechanisms*

Besides the factors described above, biosorption mechanisms strongly depend on the metabolism of microbial cells and the location of metal removal (Ahalya et al. 2003; Abbas et al. 2014). Biosorption can be (i) metabolism dependent or (ii) non-metabolism dependent according to the activity of biomass. Depending on the location of the metal removal, biosorption can occur via the mechanisms proposed by Ahalya et al. (2003):

(a) Extra cellular accumulation/precipitation;
(b) Cell surface sorption/precipitation;
(c) Intracellular accumulation.

Figures 2.2 and 2.3 report a flow diagram and a schematic illustration, respectively, of the biosorption mechanisms depending on the presence/absence of metabolism and the location of the metals sorbed.

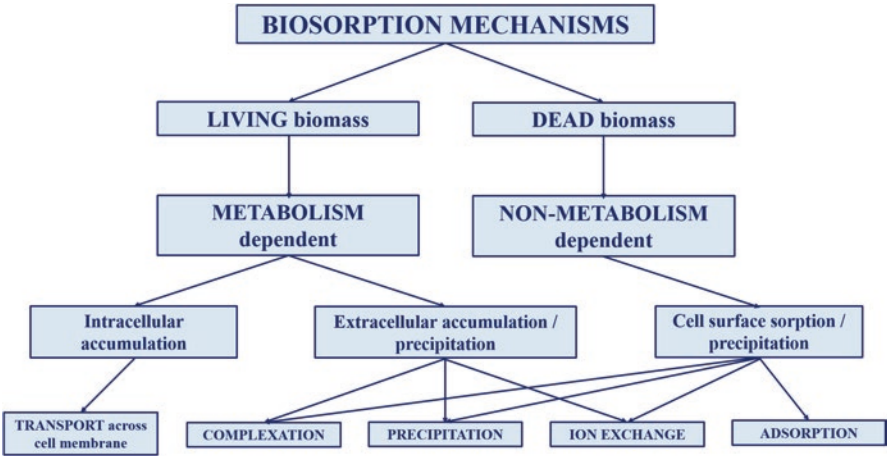


Fig. 2.2 Biosorption mechanisms correlation according to metabolism and metal removal location. Note the complexity of the process and the high number of the concomitant mechanisms contributing to the extent of biosorption

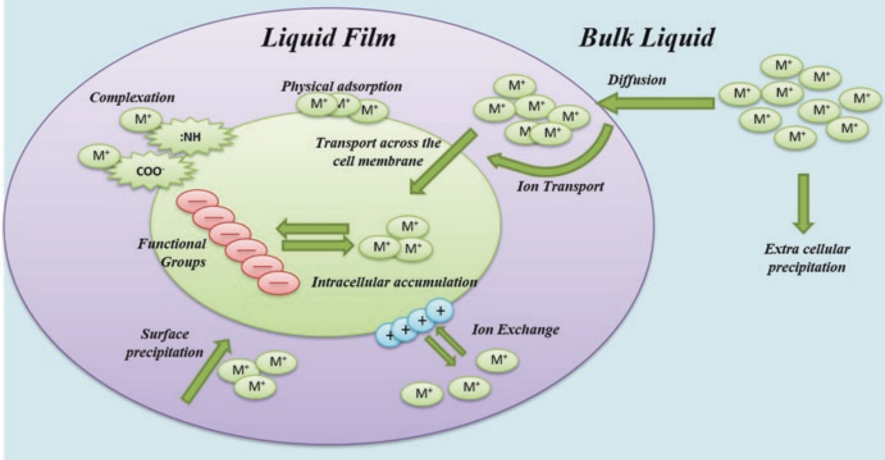


Fig. 2.3 Schematic illustration of the main mechanisms involved in biosorption. Metabolism-dependent mechanisms include the transport across the cell membrane and intracellular accumulation by reacting with active functional groups. In contrast, ion exchange, physical adsorption and complexation also occur in the absence of cellular metabolism

Despite the different classification, all biosorption mechanisms are strictly related to each other and can occur with both metabolic and non-metabolic microbial activity.

Non-metabolism dependent mechanisms are mainly rapid and reversible physical-chemical interactions between metals and the functional groups on the cell surface (Kuyucak and Volesky 1988). On the contrary, intracellular uptake phenomena (bioaccumulation) are ruled by cellular metabolism and occur at lower rates (Goyal et al. 2003). Metal precipitation can be either affected by microbial metabolism, when performed with compounds produced by microorganisms (Sag and Kutsal 2001), or not when a simple chemical interaction between metals and cell surface takes place (Scott and Palmer 1990).

The mode and characteristics of metal binding to biomass also depend on the presence of other substances and the condition of the biomass itself. Besides the cellular wall, metal binding can also occur onto extracellular polysaccharides (McLean et al. 1992) and is different when related to living or dead biomass (Das et al. 2008).

In the next subsections, the interactions between metals and microorganisms will be deepened. In particular, the attention will be focused on the differences between metal sorption onto cell walls and EPS. Since biosorption primarily occurs on the microbial surface, it is of major importance to know whether microbes are present as single cells or complex agglomerates, e.g. flocs, granules or biofilms, held together by EPS. Moreover, some important differences between metal removal occurring onto living and dead biomass will be outlined.

2.2.3 Metal: Cell Wall Interaction

Bacterial cell wall is fundamental for cell integrity and is characterized by the presence of *N*-acetylmuramic acid (peptidoglycan) and poly-*N*-acetylglucosamine right out of the cytoplasmic membrane (Rogers et al. 1980). 10 to 20% and 90% of the cell wall of Gram-negative and Gram-positive bacteria, respectively, is made by peptidoglycan (Kolenbrander and Ensign 1968; Vijayaraghavan and Yun 2008). The remaining part of the outer membrane consists of phospholipids and lipopolysaccharides (Sheu and Freese 1973). The membranes are made of anionic functional groups which are the main elements determining the capability of cell walls to bind metals (Beveridge and Murray 1976; Sherbert 1978). Hard metals preferentially bind with oxygen-containing ligands, whereas soft metals bind with nitrogen- or sulfur-containing ligands (Avery and Tobin 1993). As an example, carboxylic groups observed on the *Streptomyces pilosus* cell walls clearly affect Cu and Pb removal as reported by Golab et al. (1995). Similarly, Cd reduction and Pb uptake can be efficiently performed by dried *Sargassum* species characterized by a high amount of carboxylic groups (Fourest and Volesky 1996). Besides COOH groups, the presence of Cu on the microbial cell surface is due to the interaction with phosphoryl groups (Mullen et al. 1989). Amine groups also contribute to metal biosorption, especially the binding of Cr ions by using *Pseudomonas aeruginosa* (Kang et al. 2007). The chemical modification of lipids, carboxylic and amino functional groups affects Pb, Cu and Cd biosorption (Mashitah et al. 1999). After the esterification of carboxyl and methylation of amine groups, a lower metal biosorption is observed (Kapoor and Viraraghavan 1997).

Different binding groups are involved in Cd biosorption depending on pH (Boyanov et al. 2003). Cd is mainly adsorbed onto phosphoryl sites at a pH of 3.4, whereas Cd interaction with carboxyl groups prevails at a pH ranging from 5.0 to 7.8. The biosorption efficiency also depends on the microbial culture and metal used. For instance, *B. subtilis* and *B. licheniformis* cell walls bind approximately 30 times more Cu^{2+} than *E. coli* (Beveridge and Fyfe 1985). Regarding the different metals used, *Staphylococcus aureus* cell walls have a higher affinity with Ce^{3+} than Cu^{2+}. In conclusion, the role of the cell wall functional groups, the particular microbial species and the metallic contaminant used are fundamental for metal binding. A careful selection of the most appropriate biosorbent is thus essential for achieving a proper process efficiency.

2.2.4 Metal Interaction with Living and Dead Biomass

The extent of metal removal is substantially different when biosorption is performed with living or dead biomass. Metal uptake onto dead cells is mainly carried out through the interaction between the cell wall and contaminant (Veglio and Beolchini 1997). In contrast, biosorption with living cells is a more complex combination of processes. Biosorption can occur through the interaction with active amine and sulfhydryl functional groups, denatured in dead biomass, onto the cell wall and/or through different transport phenomena for intracellular accumulation (Gadd 2001, 2009). Furthermore, the biosorption performance can be positively or negatively affected by metabolic activities (e.g. respiration, nutrient uptake and metabolite release) which specifically modify the cell surrounding environment. The predominant biosorption mechanism and efficiency also depend on the operating conditions, metal type and concentration as well as the microbial culture used as reported in Table 2.2.

Living cells perform Cu uptake better than dead cells mainly through intracellular accumulation (Golab et al. 1995). Cu accumulation has been observed in the cytoplasmic fraction of algae (Nakajima et al. 1979) and yeasts (Naiki and Yamagata 1976). Strontium biosorption is more effective with living biomass as covalent bonds are formed instead of weaker ionic bonds with denatured biomass (Avery and Tobin 1992).

The use of living cells, however, results in lower metal sorption efficiencies in non-buffered systems under acidic conditions. For instance, a higher Cr^{6+} biosorption by dead cells of two *Bacillus sphaericus* strains (OT4b31 and IV(4)10) has been reported at a stable pH of 4.0 (Srinath et al. 2002; Velásquez and Dussan 2009), mainly owing to the good interaction between metal and biomass under acidic conditions. Cr^{6+} uptake is indeed driven by acid adsorption for the higher concentration of H^+ involved in the anion exchange (Sharma and Forster 1993; Kratochvil et al. 1998). The metabolic activity of cells usually leads to an increase of pH that decreases the biosorption efficiency.

Besides Cr^{6+}, the enhancement of metal uptake when using dead cells of *Myxococcus xanthus* and *Saccharomyces cerevisiae* has been reported for other metals such as La^{3+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Cr^{3+} and Ba^{2+} (Omar et al. 1997).

With regard to metal recovery, the use of living and dead cells results in a different heavy metal desorption efficiency. It is generally reported that the metals intracellularly entrapped cannot be extracted from biomass, unless microbial cells are disrupted (Wong et al. 1993; Costley and Wallis 2001). Therefore, a lower metal recovery has been observed with living biomass, as intracellular accumulation is the main mechanism for metal biosorption. For instance, the desorption efficiency of Cu^{2+} and Zn^{2+} from dead cells of *Pseudomonas putida* CZ1 was 95.3 (±2.6)% and 83.8 (±4.3)%, respectively. Conversely, desorption only reached 72.5 (±1.8)% and 45.6 (±1.2)% for Cu^{2+} and Zn^{2+}, respectively, by using living cells (Chen et al. 2005). Similarly, a higher desorption efficiency was also observed for Cd^{2+} by using dead (91.2%) than living (70.2%) *Bacillus cereus* RC-1 cells (Huang et al. 2013).

Table 2.2 Efficiency of biosorption of several heavy metals with living and dead microbial cultures under different operating conditions

Metal	Living cells sorption efficiency	Dead cells sorption efficiency	Operational conditions	Microbial species	Reference
Cd(II)	≃0.14 mmol Cd/g of cells (brewer's yeast)	Not reported	Cd equilibrium concentration ≃1.7 mM	*S. cerevisiae*	Volesky and May-Phillips (1995)
	≃0.16 mmol Cd/g of cells (baker's yeast)				
	8.46 mg Cd/g biomass	8.36 mg Cd/g biomass	Cd initial concentration = 10 mg/l	*Mucor rouxii*	Yan and Viraraghavan (2003)
			Initial pH 5		
	39–60%	45–86%	Cd initial concentration 5–60 mg/l	*Bacillus cereus* RC-1	Huang et al. (2013)
Cr(VI)	23.8 mg Cr/g dry biomass	39.9 mg Cr/g dry biomass	Cr initial concentration = 100 mg/l	*B. coagulans*	Srinath et al. (2002)
			Initial pH 2.5 – final pH 3.5 (living cells)		
			Initial pH 2.5 – final pH 2.7 (dead cells)		
	15.7 mg Cr/g dry biomass	30.7 mg Cr/g dry biomass	Cr initial concentration = 100 mg/l	*B. megaterium*	
			Initial pH 2.5 – final pH 3.3 (living cells)		
			Initial pH 2.5 – final pH 2.6 (dead cells)		
	25.0%	44.5%	Incubation T = 30 °C	*B. sphaericus* OT4b31	Velásquez and Dussan (2009)
			Cr initial concentration = 39.10 mg/l (living cells)		
			Cr initial concentration = 33.38 mg/l (dead cells)		
	32%	45%	Incubation T = 30 °C	*B. sphaericus* IV(4)10	
			Cr initial concentration = 40.05 mg/l (living cells)		
			Cr initial concentration = 33.60 mg/l (dead cells)		

Cr(VI)	≃16% (lag phase)	≃21%	Incubation T = 27 °C	*C. metallidurans* CH34	Fan et al. (2014)
	≃11% (stationary phase)	≃7%	Gyratory speed 80 rpm	O. *intermedium LBr*	
	≃21% (lag phase)				
	≃15% (stationary phase)		Cr initial concentration = 100 mg/l		
Cu(II)	≃30 mg Cu/g dry biomass	≃15 mg Cu/g dry biomass	Cu initial conc. = $1\cdot10^{-5}$ – $1\cdot10^{-2}$ M as $Cu(NO_3)_2$	*Streptomyces pilosus*	Golab et al. (1995)
			Initial pH 3		
	≃0.16 mmol Cu/g of cells (living brewer's yeast)	≃0.07 mmol Cu/g (dry brewer's yeast)	Cu equilibrium concentrations	*S. cerevisiae*	Volesky and May-Phillips (1995)
			≃3.0 mM (dry brewer's yeast)		
	≃0.20 mmol Cu/g of cells (living baker's yeast)	≃0.32 mmol Cu/g (Fisher dry baker's yeast)	≃2.7 mM (Fisher dry baker's yeast)		
			≃3.0 mM (baker's active dry yeast)		
		≃0.07 mmol Cu/g cells (baker's active dry yeast)	≃2.8 mM (living brewer's yeast)		
			≃2.8 mM (living baker's yeast)		
	28%	55%	Incubation T = 30 °C	*Chlamydomonas reinhardtii*	Flouty and Estephane (2012)
			Gyratory speed 150 rpm		
			Cu initial concentration = $5\cdot10^{-7}$ M		
			Initial pH 6		
			Biomass concentration = 0.2 g/L		
	≃11% (lag phase)	≃8%	Incubation T = 27 °C	*C. metallidurans* CH34	Fan et al. (2014)
	≃7% (stationary phase)	≃12%	Gyratory speed 80 rpm	O. *intermedium LBr*	
	≃11% (lag phase)		Cu initial concentration = 100 mg/l		
	≃7% (stationary phase)				

(continued)

Table 2.2 (continued)

Metal	Living cells sorption efficiency	Dead cells sorption efficiency	Operational conditions	Microbial species	Reference
Ni(II)	11.09 mg Ni/g biomass	6.34 mgNi/g biomass	Ni initial concentration = 10 mg/l	*Mucor rouxii*	Yan and Viraraghavan (2003)
			Initial pH 5		
Pb(II)	≃90 mg Pb/g dry biomass	≃120 mgPb/g dry biomass	Pb initial concentration = $1{\cdot}10^{-2}$ M as $Pb(NO_3)_2$	*Streptomyces pilosus*	Golab et al. (1995)
			Initial pH 3		
	35.69 mg Pb/g biomass	25.22 mgPb/g biomass	Pb initial concentration = 10 mg/l	*Mucor rouxii*	Yan and Viraraghavan (2003)
			Initial pH 5		
	8%	40%	Incubation T = 30 °C	*Chlamydomonas reinhardtii*	Flouty and Estephane (2012)
			Gyratory speed 150 rpm		
			Pb initial concentration = $5{\cdot}10^{-7}$ M		
			Initial pH 6		
			Biomass concentration = 0.2 g/L		
U(V)	0.234 mmol U/g of cells (living brewer's yeast)	0.592 mmol U/g of cells (dry brewer's yeast)	U equilibrium concentrations:	*S. cerevisiae*	Volesky and May-Phillips (1995)
			≃0.8 mM (dry brewer's yeast)		
	≃0.150 mmol U/g of cells (living baker's yeast)	≃0.430 mmol U/g of cells (Fisher dry baker's yeast)	≃0.7 mM (Fisher dry baker's yeast)		
			≃0.6 mM (baker's active dry yeast)		
		0.200 mmol U/g of cells (baker's active dry yeast)	≃0.6 mM (living brewer's yeast)		
			≃0.7 mM (living baker's yeast)		

Zn(II)	$\simeq$0.18 mmol Zn/g of cells (living brewer's yeast)	$\simeq$0.27 mmol Zn/g (dry brewer's yeast)	Zn equilibrium concentrations:	*S. cerevisiae*	Volesky and May-Phillips (1995)
			$\simeq$2.8 mM (dry brewer's yeast)		
	$\simeq$0.23 mmol Zn/g of cells (living baker's yeast)	$\simeq$0.15 mmol Zn/g (Fisher dry baker's yeast)	$\simeq$2.5 mM (Fisher dry baker's yeast)		
			$\simeq$2.6 mM (baker's active dry yeast)		
		0.47 mmol Zn/g cells (baker's active dry yeast)	$\simeq$3.0 mM (living brewer's yeast)		
			$\simeq$3.0 mM (living baker's yeast)		
	7.75 mg Zn/g biomass	16.62 mg Zn/g biomass	Zn initial concentration = 10 mg/l	*Mucor rouxii*	Yan and Viraraghavan (2003)
			Initial pH 5		
	58–87%	72–90%	Zn initial concentration 1–150 mg/l	*S. ciscaucasicus* strain CCNWHX 72–14	Li et al. (2010)
	8–3 0%	5–15%	Incubation T = 40 °C	*Fusarium* spp.	Velmurugan et al. (2010)
			Gyratory speed 150 rpm		
			Zn initial concentration 10–320 mg/l		
			Initial pH 6		
			Biomass concentration = 4.5 g/l		

2.2.5 Interaction Between Metals and Extracellular Polymeric Substances

The presence of EPS results in increasing biosorption yields, especially in systems involving bacterial colonies forming biofilms. EPS are biopolymers produced by cell activities such as active bacterial secretion, shedding of cell surface and cell lysis materials. Moreover, EPS can derive from organics adsorption from the environment (Wingender et al. 1999). The composition of EPS is made of organic substances with a higher amount of carbohydrates and proteins and a smaller fraction of humic, uronic and nucleic acids (Sponza 2002). EPS have an abundance of negatively charged functional groups that make them a potent biosorbent to be used for metal sorption (Ledin 2000; Flemming and Wingender 2003; Wang et al. 2014).

EPS can be divided into two main groups: bound and soluble. The bound EPS mainly consist of organic matter produced by microbes and attached to the microbial aggregates (Nielsen et al. 1997). Soluble EPS are composed by hydrolyzed products from attached organic matter, organic molecules released by cell lysis and soluble polymers produced by microbes (Comte et al. 2006). Besides different characteristics, the two groups have different metal biosorption efficiency: Cu^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+} removal is higher with soluble EPS than bound EPS (Comte et al. 2006). A better protonic ion exchange of soluble EPS results in more dissociated sites for metal entrapment and thus a higher biosorption efficiency. In contrast, a higher biosorbed Pb(II) and Cu(II) percentage for attached compared to suspended biomass can be obtained at various metal concentrations (Black et al. 2014). This mainly occurs when a higher EPS content is in the attached than suspended biomass. Similarly, a higher biosorption efficiency for Cu(II) can be observed in the bound (subdivided in loosely and tightly bound EPS) than soluble EPS for both wild-type and mutant type strains (Hou et al. 2013).

The interaction of EPS with heavy metals also depends on pH. Besides modifying the chemical properties of metals, the pH affects the activity of functional groups in biopolymers and the competition of heavy metals for the biosorbent sites (Salehizadeh and Shojaosadati 2003). An increase of Pb and Hg uptake can be achieved at acidic pH by EPS of *Azotobacter chroococcum XU1* (Rasulov et al. 2013). On the contrary, a lower metal biosorption at alkaline pH is mainly attributed to metal precipitation as hydroxide (Salehizadeh and Shojaosadati 2003).

Feed metal concentration and the coexistence of other metals also affect biosorption onto EPS (Rasulov et al. 2013). Pb and Hg biosorption increases at increasing metal concentrations although the saturation of the binding sites occurs more quickly (Lakzian et al. 2008). But, the simultaneous supplementation of Ni and Zn highly affects the adsorption of Pb and Hg onto EPS of *Ensifer meliloti* MS-125 (Lakzian et al. 2008).

Depending on the environmental conditions the bacterial strains are isolated from, biosorption of a particular metal is preferred. For instance, the EPS of

Rhizobium etli, isolated from a manganese rich environment, show a preferential uptake of Mn^{2+} compared to Zn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} (Foster et al. 2000).

Metal biosorption by EPS can occur through a set of processes such as complexation, ion exchange and surface precipitation (Li and Yu 2014). Metal removal by ion attraction significantly depends on pH (Pardo et al. 2003). Alkaline conditions generally favor ion exchange due to the lower presence of protons competing with metals for the binding sites (Lopez et al. 2000). However, high pH leads to the transformation of soluble metals into hydroxylated monomeric and polymeric species and then into crystalline oxides that precipitate, resulting in lower amounts of metal sorbed (Kushwaha et al. 2012). Regarding metal complexation, metal binding occurs due to the deprotonated form of the reactive sites (Morlay 2000). Metal-EPS complexation can be related to the concepts of hard and soft acids and bases, assuming that inner and outer-sphere complexes are those produced during the metal binding with EPS (Avery and Tobin 1993). Complexes and bond typology can be different according to the metals and the functional groups involved. Nitrogen in the amino-sugar and oxygen in the hydroxyl and carboxyl groups mainly bind metals with strong covalent characteristics (e.g. Pb^{2+}, Cu^{2+} and Zn^{2+}) forming inner-sphere complexes (Ha et al. 2010; Fang et al. 2011). On the contrary, metals such as Cd^{2+} and Ni^{2+} form weak covalent bonds with EPS showing low adsorption affinity (Joshi and Juwarkar 2009).

EPS composition and related functional groups significantly depend on various parameters, such as cell cultivation time, presence of organic substrates (e.g. volatile fatty acids), salt concentration (e.g. NaCl and $CaCl_2$), and C/N ratio (Sheng et al. 2006). A different EPS composition results in a variable binding capacity of EPS towards metals (d'Abzac et al. 2013). The metal species to be biosorbed also influences the EPS composition in terms of proteins/carbohydrates ratio (Sheng et al. 2005). Therefore, all the operating conditions adopted in a particular study case affect the chemical nature of EPS and the extent of heavy metal biosorption.

Desorption of metals previously entrapped onto EPS can decrease biosorption performance. A study on Hg^{2+} and Sb^{5+} adsorption/desorption has shown that pH, temperature and the coexistence of chelating agents and competitive cations affect the process efficiency (Zhang et al. 2013). A pH shock highly affects Hg desorption under acidic conditions, whereas no effect has been observed in alkaline systems. In the same way, Hg desorption can occur in the presence of complexing agents (e.g. ethylenediaminetetraacetic acid) or cations competing for the binding sites (e.g. Ca^{2+}). Unlike pH, a temperature range from 10 to 30 °C does not affect Hg and Sb entrapment, indicating insignificant effects of temperature on biosorption (Zhang et al. 2013).

Metal biosorption by EPS cannot be considered as a reversible process as metals can form stable complexes with EPS. This results in a less efficient metal biorecovery. But, on the other hand, the irreversibility of heavy metal biosorption generally leads to a lower metal release in the environment (Malik 2004). A hysteresis trend in the sorption/desorption of Cd and Pb from EPS has been observed after a significant variation of pH (from 11.8 to 2.1) resulting in about 30% of metals irreversibly sorbed onto EPS (Guibaud et al. 2008). Despite the possibility of stable metal-EPS complexes formation, metal desorption occurs and has to be taken into account besides the influence of several operational parameters.

2.3 Modeling Heavy Metal Biosorption in Batch and Continuous Systems

Parallel to the extensive experimental activity carried out during the last decades on heavy metal biosorption, several mathematical models, most in the form of empirical correlations, have been developed to elucidate and represent the heavy metal adsorption on biomass binding sites (Volesky 2003). Mathematical modeling represents a useful tool to describe the complex mechanisms characterizing the biosorbent and the solute interactions and assists in the optimization and design of biosorption processes. Figure 2.4 shows the biosorption models classified into two main categories based on the mode of operation (batch and continuous) used to conduct the process:

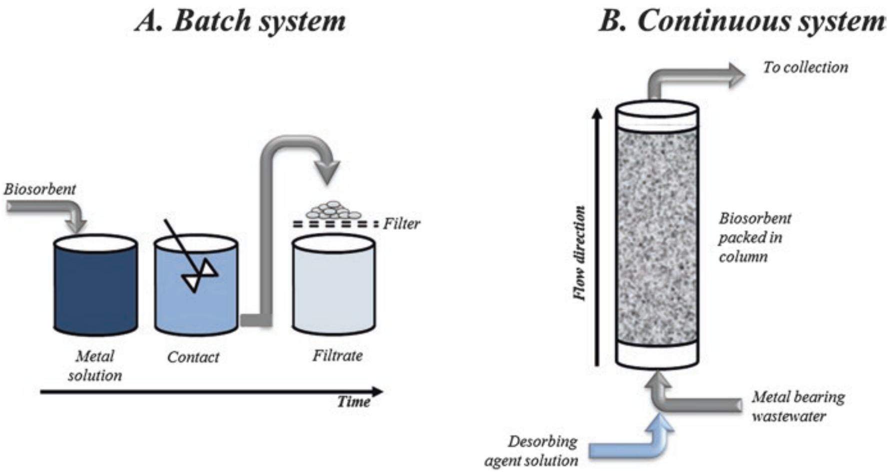


Fig. 2.4 Schematic illustration of batch (**a**) and continuous (**b**) experimental biosorption systems. Under batch conditions, a biosorbent is mixed with a metal-containing solution within a simple reactor operated till the thermodynamic equilibrium. In a continuous-flow system (i.e. a packed bed configuration), a synthetic wastewater is continuously fed to a biosorbent column with an upward or downward stream. The biosorbent regeneration for the sorption/desorption cycle is performed by switching the wastewater flow to an appropriate desorbing agent flow

2.3.1 Modeling of Batch Systems

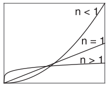
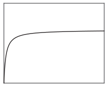
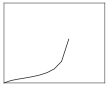
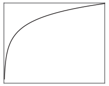
Batch experiments have been mostly devoted to the collection of fundamental information, such as biosorption efficiency or rate, which plays a crucial role in designing biosorption systems (Aksu 2005). In this case, the experimental protocol is quite simple: a suitable mass of biosorbent is immersed in a solution containing single or multiple heavy metals until a thermodynamic equilibrium is reached between the metal concentrations on the solid sorbent and in the liquid phase. At this point, the biosorbent is separated from the liquid phase to be regenerated or disposed (Fig. 2.4a).

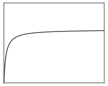
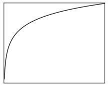
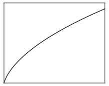
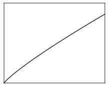
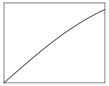
2.3.1.1 Modeling Sorption Equilibrium

The concept of biosorption isotherm is of major importance for the evaluation of the performance of any given sorption system. Any isotherm is related to the solute uptake and is obtained by plotting the solute uptake versus the equilibrium solute concentration in the liquid phase. In general, the solute uptake increases at increasing solute concentration until saturation. The batch equilibrium isotherm curves have usually been modeled by using empirical correlations or mechanistic equations (Park et al. 2010). The empirical models are not able to reproduce the mechanisms of solute uptake, but have widely been recognized as efficient tools for providing a suitable description of the experimental behavior (Volesky 2003). These models can be classified based on the number of parameters involved (n-parameter models) and components included. In the last case, the models are obtained by extending the single component isotherm models to multi-metal systems and taking into account the interferences and competition phenomena for adsorption sites. Such models can be only related to the individual isotherm parameters or can include some correction factors (Aksu 2005). Table 2.3 summarizes the main features, including the equations and the relative degree of freedom, of the most used isotherm models. Among them, the Langmuir and Freundlich isotherms have widely and successfully been applied, as proved by the extensive application present in literature (Liu et al. 2001; Tokunaga and Hakuta 2002; Aksu 2002; Ozdemir et al. 2003; Wang et al. 2006; Luo et al. 2006; Parvathi and Nagendran 2007; Lakzian et al. 2008). The isotherm parameter values can be assessed by a linearization of the equation (two-parameter models), a trial and error procedure for higher order models or by using a non-linear optimization (for all the isotherms).

Parallel to the adoption of empirical equations, more complex mechanistic models have been suggested to effectively elucidate the sorption mechanisms. These models are based on specific hypotheses concerning the reactions between functional groups and heavy metals, and require a biomass characterization. Among them, the surface complexation model (SCM) and the ideal adsorbed solution theory (IAST) have successfully been applied to investigate the metal adsorption process (Daughney and Fein 1998; Fowle and Fein 1999; Volesky 2003; Vijayaraghavan and Yun 2008). The SCM was conceived as reported by Kurbatov et al. (1951) with

Table 2.3 Frequently used equilibrium sorption models

System	Isotherm	Equation	Assumptions	Limitations	Degrees of freedom	Commonly reported trends (q_e vs C_e)
Single component	Freundlich (Freundlich and Hatfield 1926)	$q_e = KC_e^{1/n}$	Unlimited number of available sorption sites, multilayer adsorption; the stronger binding sites occupied first with binding strength decreasing with the increasing degree of site occupation	Empirical; applicable only in the low-intermediate concentration ranges; constant values vary with temperature	2	
	Langmuir (1918)	$q_e = \frac{q_m b C_e}{1 + bC_e}$	Sorption considered as a chemical phenomenon; monolayer adsorption; finite number of identical sites; constant released amount of heat energy	Monolayer adsorption; homogeneous surface; no interactions between adsorbate molecules; no insights into the mechanism aspects	2	
	Brunauer (BET)	$q_e = \frac{BQC_e}{(C_s - C_e)\left[1 + (B-1)(C_e / C_s)\right]}$	Multilayer adsorption, no interactions between each adsorption layer; Langmuir theory applied to each adsorption layer	Inflection point; very restrictive validity; lateral interaction neglected; no "total capacity" equivalent	2	
	Temkin (Temkin and Pyzhev 1940)	$q_e = \frac{RT}{b_T} \ln(K_T C_e)$	Heat of adsorption decreases linearly with the increase of coverage of absorbent	Not suitable for complex adsorption systems and at extremely low and large value of concentrations	2	

	Dubinin-Radushkevich (1947)	$\frac{W}{W_0} = \exp\left[-k\left(\frac{\varepsilon}{\beta}\right)^2\right]$	Accounts for the effect of the porous structure of an adsorbent; Gaussian energy distribution onto a heterogeneous surface	Valid within the domain of conditions imposed on the Langmuir isotherm; temperature dependent	2	
	Langmuir-Freundlich (Sips 1948)	$q_e = \frac{bq_m C_e^{1/n}}{1 + bC_e^{1/n}}$	Combination of Langmuir and Freundlich; derivation from an equilibrium or thermodynamic approach	Not reported	3	
	Redlich-Peterson (1959)	$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$	Comprises the features of the Langmuir and the Freundlich isotherms	Hybrid; does not follow ideal monolayer adsorption	3	
Single component	Toth (1971)	$q_e = \frac{K_t C_e}{\left(a_t + C_e\right)^{1/k_t}}$	Derived from the potential theory; asymmetrical quasi-Gaussian energy distribution with a widened left-hand side	Best suited to multilayer adsorption; similarly to BET very restrictive validity; it cannot reflect the feature of the Freundlich-type biosorption	3	
	Radke and Prausnitz (1972a)	$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1\ N_{RP}}}$	Empirical	Not reported	3	

(continued)

Table 2.3 (continued)

System	Isotherm	Equation	Assumptions	Limitations	Degrees of freedom	Commonly reported trends (q_e vs C_e)
Multi component	Langmuir (multicomponent) (1918)	$q_i = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{i=1}^{N} b_i C_{e,k}}$	Homogeneous surface with respect to the energy of adsorption; no interaction between adsorbed species; all adsorption sites are equally available to all adsorbed species	Constants have physical meaning; isotherm levels off at max saturation; not a "structured" model	1 + N	Langmuir trend for each component
	Combination Langmuir and Freundlich (Sips 1948)	$q_i = \frac{a_i C_i^{1/n_i}}{1 + \sum_{i=1}^{N} b_i C_i^{1/n_i}}$	Homogeneous surface; biosorption is a cooperative process due to sorbate-sorbate interactions	Additional parameters used	1 + 2 N	Freundlich trend for each component
	Redlich-Peterson (1959)	$q_i = \frac{a_i C_i}{1 + \sum_{i=1}^{N} b_i C_i^{n_i}}$	Hybrid isotherm featuring both Langmuir and Freundlich	Not reported	1 + 2 N	Redlich-Peterson trend for each component
	IAST: Ideal Adsorbed Solution Theory (Radke and Prausnitz 1972b)	$\frac{1}{q_t} = \sum \frac{Y_i}{q_i^0}$	Thermodynamic basis, adsorbent is thermodynamically inert, available surface area is identical for all solutes, the liquid phase concentration is low, adsorbed phase forms an ideal solution	Mathematical complexity of the procedure; it depends on the quality of the fit of single-component parameters	Case study specific	Combination of the previous trends

	SCM: surface complexation model (group) (Kurbatov et al. 1951; Davis and Leckie 1978)	$q \sim f(C_e)$	Adsorption of ions based on thermodynamic concepts of complexation in solution; adsorption reactions described quantitatively by mass law equations; electrostatic double layer	Equilibrium constants have to be established for different types of binding	Case study specific	Based on the dependence of q on C_e

The reported trends have been obtained by plotting q_e (or W/W_0 for the Dubinin-Radushkevich model) on the y axis versus $C_{e.}$ on the x axis. q_e and C_e are the sorbed and free metal concentration at equilibrium, respectively

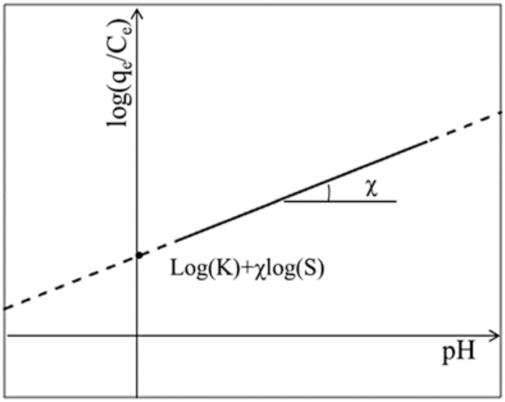


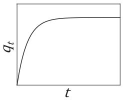
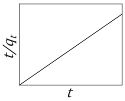
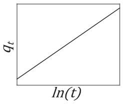
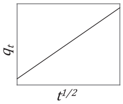
Fig. 2.5 Schematic illustration of the linear trend (Kurbatov plot) obtained by plotting $\log(q_e/C_e)$ on the y axis versus pH on the x axis. The slope of the linear trend is χ, whereas the intersect with the y axis is $\log(K)+\chi\log(S)$, with *S* being the concentration of complexation sites not associated with the metal (Guibaud et al. 2008)

the aim of describing the function of protons in metal adsorption at a macroscopic level. The model consists of mass law equations to describe reactions at individual surface sites and assume protons as the dominant potentially determining ions. The parameters involved in the resulting equations, including the equilibrium constants of surface reactions and the concentrations of functional groups, are discriminating factors in characterizing the efficiency of a sorbate/sorbent system. Such values are usually obtained by adopting Kurbatov plots for titration data, which consist in plotting pH on the x axis versus $\log(q_e/C_e)$, with q_e and C_e being the sorbed and free metal concentration at equilibrium, respectively, on the y axis (Fig. 2.5). A linear relationship is thus obtained. The slope χ corresponds to the number of moles of protons released per mole of metal complexed. The intersect with the y axis provides log(K), where K represents the equilibrium constant. Obviously K and χ are specific for each sorbent/sorbate system (Guibaud et al. 2008). The SCM has mainly been used to study metal adsorption on EPS as confirmed by the huge number of scientific works published on this specific topic (Pagnanelli et al. 2000; Guibaud et al. 2005, 2006, 2008; Comte et al. 2008; Wei et al. 2011).

2.3.1.2 Modeling Batch Adsorption Kinetics

Kinetic studies are aimed at describing the behavior of the sorption system on time (Volesky 2001) and have commonly been applied to study the contribution of the main rate controlling steps invariably involved in the sorption process. Abbas et al. (2014) described the biosorption as a series of several consecutive elementary steps which reproduce: (a) the diffusion of heavy metal ions from the liquid bulk to the liquid film surrounding the sorbent particles; (b) the ion transport from the boundary liquid film to the surface of the sorbent particles; (c) the transfer of heavy metals from the surface to the internal active binding sites; and (d) the interactions between the active binding sites and metals (Fig. 2.3). Generally, the sorption reactions, as well as the external diffusion, are inherently very fast and thus do not constitute the rate-limiting steps of biosorption. In most cases, the intraparticle diffusion is

Table 2.4 Frequently used kinetic models for biosorption

Kinetics model	Equation	Assumptions	Limitations	Commonly reported trends
Lagergren equation (Pseudo first-order) (1898)	$q_t = q_e\left(1 - e^{k_I t}\right)$	Based on sorption capacity; in line with the concept of linear driving force (kinetic order is 1). Approaches for the derivation of the kinetic equation have been reviewed in Liu and Liu (2008)	Preset reaction order unless the reaction mechanisms are well known	
Ho equation (Pseudo second-order) (Ho and McKay 1999)	$\frac{t}{q_t} = \frac{1}{k_{II} q_e^2} + \frac{1}{q_e} t$	Based on sorption capacity, the driving force is the fraction of available sorption sites; kinetic order 2. Approaches for the derivation of the kinetic equation have been reviewed in Liu and Liu (2008)	Preset reaction order unless the reaction mechanisms are well known	
Elovich equation (Chien and Clayton 1980)	$q_t = \beta_e \ln(\alpha\beta_e) + \ln(t)$	Chemisorption processes and slow adsorption rates	Often valid for systems in which the adsorbing surface is heterogeneous; suited only for a qualitative explanation	
Weber-Morris equation (1963)	$q_t = k_{WM} t^{1/2} + C$	Intraparticle diffusion is the rate-limiting step	Intraparticle diffusion may not be the only rate-limiting mechanism	
General rate law equation (Liu and Shen 2008)	$-\frac{d\lambda_t}{dt} = k_x \lambda_t^x$	Non-fixed reaction order; biosorption reaction on the surface of the biosorbent is the rate-controlling step (Liu and Liu 2008)	Not reported	Depending on the reaction order

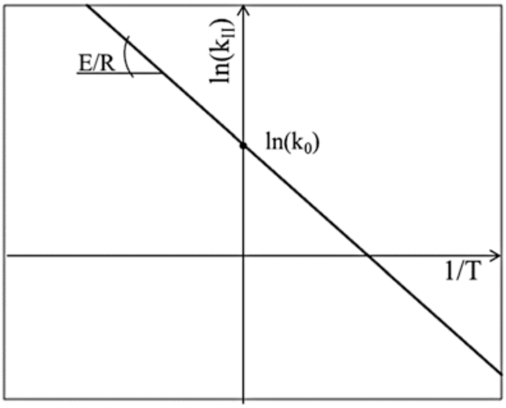


Fig. 2.6 Schematic illustration of the linear trend obtained by plotting $\ln(k_{II})$ on the y axis versus 1/T on the x axis. The intersect with the y axis corresponds to $\ln(k_0)$ and the slope to E/R:

recognized as the rate-limiting step and can be modeled by using the equation introduced by Weber and Morris (1963). As shown in Table 2.4, this equation results in a linear correlation between the variables, which includes the origin when the intra-particle diffusion represents the limiting step (Aksu 2005).

Various models have been proposed to quantify the kinetic behavior of sorption systems (Table 2.4). Some of them are related to the intra or extra particle mass transfer (Gerente et al. 2007), others are based on pseudo-first (i.e. Lagergren) and second-order kinetic equations, which introduce a direct proportionality between the process rate and the number of adsorption sites in first or second power (Michalak et al. 2013). The Lagergren first order and the pseudo second order equations, reported in Table 2.4, are both expressed as a function of the sorption capacity of the solid phase. However, the Lagergren equation has been found to fit better the initial 20–30 min of the sorption process. This is probably due to the trivial evaluation of the real equilibrium sorption capacity, which is generally performed by using an extrapolation. Contrary to the Lagergren model, pseudo-second order kinetics are able to predict the sorption behavior over the entire time range and does not require to preliminary know the amount of solute sorbed at equilibrium when expressed in the linear form.

In addition, the second order rate constant k_{II} can be expressed as a function of temperature by using the following Arrhenius type equation (Aksu 2001):

$$k_{II} = k_0 \exp\left(-\frac{E}{RT}\right)$$

where k_0 is the temperature independent factor, E is the activation energy of sorption, R is the gas constant and T is the solution temperature. By plotting $\ln(k_{II})$ versus 1/T, a linear relationship is obtained whose slope corresponds to -E/R (Fig. 2.6). The activation energy usually assumes negative values as reported in many studies (Aksu 2001; Calero et al. 2009; Horsfall Jr. and Spiff 2005; Mobasherpour et al.

2014), confirming the exothermic nature of the adsorption phenomena and providing information about the rate controlling step of adsorption (Horsfall Jr. and Spiff 2005).

Nevertheless, both first and second order kinetic equations require a presetting of the reaction order, which strictly depends on the reaction mechanism. Liu and Shen (2008) introduced a general rate law equation for biosorption which does not need a presetting a priori of the reaction order unless the sorption mechanisms are known. This equation states that biosorption kinetics follows the universal rate law for a chemical reaction and is written in terms of the adsorption sites available on the biosorbent surface (Liu and Liu 2008).

2.3.2 Modeling of Continuous Systems

The continuous mode of operation has generally been used to test the technical feasibility of biosorption for real applications (Vijayaraghavan and Yun 2008). Mostly continuous stirred tank reactors, fluidized bed, moving bed and packed bed columns have been used (Kumar et al. 2016). Packed bed columns have been recognized as one of the most convenient configurations due to the higher sorbing capacity, the high operational yield and the technical feasibility (Vijayaraghavan and Yun 2008). A packed bed column usually consists of a cylindrical reactor filled with sorbent, passed through by a metal-containing wastewater by gravity or pressure (Fig. 2.4b). The concentration of the solute in the outlet is found to increase over time as the biosorbent becomes saturated. The region of the bed where the adsorption takes place is named mass transfer zone or adsorption zone and moves forward until approaching the end of the bed (Le Cloirec and Andrès 2005).

The breakthrough curve, typically S-shaped, is obtained by plotting the normalized effluent concentration C_{eff}/C_{in} versus time and represents a valuable tool for evaluating the biosorbent efficiency. Indeed, the amount of solute removed at saturation can be easily evaluated by calculating the area above the breakthrough curve, whose slope provides information about the column service time. The main features of the breakthrough curve are the breakthrough and saturation/exhaustion points which theoretically correspond to an abrupt rise (inflection point) in the effluent concentration plot and the complete column saturation, respectively (Fig. 2.7). The time elapsed until attaining the breakthrough point directly affects the service time of the column. In laboratory experiments, packed bed columns are usually operated until the saturation point is attained. Conversely, in industrial applications, the column is usually regenerated when the effluent metal concentration exceeds a breakthrough/service point, which is prefixed depending on the metal toxicity. When the breakthrough point is attained, the effluent concentration can slowly rise to the saturation point (flattened breakthrough curve). However, it is preferable to have a steep slope which corresponds to a shorter mass transfer zone (Vijayaraghavan and Yun 2008). The shape of the breakthrough curve is affected by many parameters, such as flow rate, inlet metal concentration, pH, bed height and bed particle size (Kumar et al. 2016).

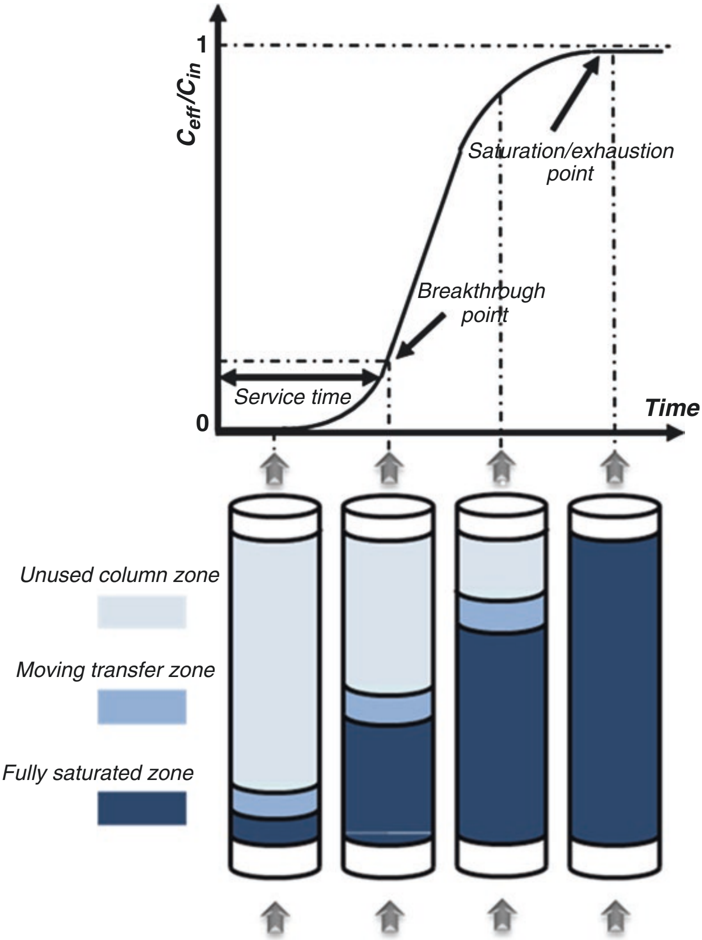
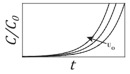
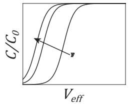
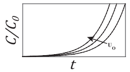
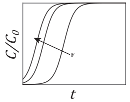
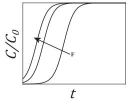
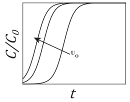


Fig. 2.7 Schematic illustration of the evolution of the mass transfer zone and the corresponding theoretical time-based breakthrough curve for metal sorption in a packed bed column. C_{eff} and C_{in} are the metal effluent and influent concentration, respectively (Adapted from Gupta et al. 2016)

Most of the models for continuous sorption systems have been developed to predict the breakthrough curves. Some examples are reported in Table 2.5. The Adams-Bohart model is usually applied to the initial part of the breakthrough curve and is obtained by combining two kinetic equations, the first describing the solute transfer from the liquid phase, the second governing the sorption accumulation on the biosorbent. A similar equation has been obtained by Wolborska (1999), who also takes the solute axial diffusion into account. The two equations are transformed into the same expression in the case $k = \frac{\beta_a}{N_0}$. The Thomas model has been used in the linear form to quantify the maximum adsorption capacity of the adsorbent bed.

Table 2.5 Mathematical equations for biosorption modeling in continuous systems

Breakthrough curve model	Equation	Assumptions	Limitations	Commonly reported trends
Adams-Bohart (Bohart and Adams 1920)	$\frac{C}{C_0} = \exp\left(k_{AB}C_0 t - k_{AB}N_0\frac{Z}{U_0}\right)$	Adsorption rate proportional to both residual capacity and concentration of sorbing species; low concentration field; the speed of adsorption is limited by the external mass transfer	Describes the initial part of the breakthrough curve only	
Thomas (1944)	$\frac{C_0}{C} = 1 + \exp\left(\frac{k_{TH}}{F}\left(Q_0 M - C_0 V_{eff}\right)\right)$	Langmuir kinetics of adsorption/desorption; negligible axial and radial dispersion; pseudo second-order reaction kinetics; negligible intra particle diffusion and external resistance during the mass transfer processes	Based on second order reaction kinetics; adsorption is usually dependent on interphase mass transfer	
Wolborska model (1989)	$\frac{C}{C_0} = \exp\left(\frac{\beta_a C_0}{N_0}t - \frac{\beta_a Z}{U_0}\right)$	Based on mass transfer equations for diffusion mechanisms with axial diffusion negligible	Best suited in the range of low-concentration breakthrough curve	
Yoon-Nelson (1984)	$\frac{C}{C_0} = \frac{\exp\left(k_{YN}t - \tau k_{YN}\right)}{1 + \exp\left(k_{YN}t - \tau k_{YN}\right)}$	The rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent	Not reported	
Modified dose-response (Yan et al. 2001)	$\frac{C}{C_0} = 1 - \frac{1}{1 + \left(V_{eff}/b_{mdr}\right)^{a_{mdr}}}$	Empirical model	Not reported	
Clark (1987)	$\frac{C}{C_0} = \left(\frac{1}{1 + \left(\frac{C_0^{n-1}}{C_{break}^{n-1}} - 1\right)\exp\left(rt_{break} - rt\right)}\right)^{1/n-1}$	Combination of both mass transfer concept and Freundlich adosrption isotherm	Ignores the phenomenon of dispersion	

The direction of the arrow in the graphs corresponds to increasing influent flow rates

In the Clark model, the breakthrough curve is obtained by adopting the Freundlich equation. The model introduced by Yoon and Nelson (1984) is much simpler as it does not require specific information about the adsorbate/adsorbent system.

2.4 Conclusion

Over the last years, biosorption has received considerable attention from academic researchers, becoming one of the most promising and cost-effective alternative technologies for heavy metal removal and recovery from industrial wastewaters. However, despite the high number of scientific studies on biosorption, several technical and scientific aspects still need to be clarified for the commercialization and the spread of this technology at industrial scale. Based on these considerations, future research may be focused on the characterization and identification of new materials to be used as biosorbents with higher cost-effectiveness and biosorption efficiency, enhancement of selective metal biorecovery through biosorption in multi-metal systems and development of analytical tools based on deterministic mathematical models able to describe multi-sorbate systems.

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Chapter 3
Permeable Reactive Barriers for Heavy Metal Removal

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Abstract Heavy metal contamination of groundwater is a worldwide problem. Landfill leachate and acid mine drainage are possible sources for groundwater contamination by heavy metals. Heavy metals from groundwater can enter the food chain through bio-accumulation and bio-magnification, posing a threat to all forms of life. A permeable reactive barrier is one of the technologies employed for remediation of heavy metal contaminated groundwater. The concept of a permeable reactive barrier involves the emplacement of a permeable barrier containing reactive materials across the flow path of the heavy metal contaminated groundwater to intercept and treat the heavy metals as the plume flows through it under the influence of the natural hydraulic gradient. Site selection and selection of reactive media, as well as construction and operation, are some of the challenges faced in the application of permeable reactive barriers. A variety of inorganic and organic reactive media are employed in a permeable reactive barrier to remove the heavy metals. Heavy metal removal is accomplished through processes such as adsorption, precipitation and biodegradation. In this chapter, various aspects of treating heavy metal groundwater contamination using the permeable reactive barrier technology have been reviewed. The major topics include: (1) causes of heavy metal contamination in groundwater, (2) types of reactive media used in a permeable reactive barrier, (3) criteria for selection of reactive media, (4) mechanisms for removal of heavy metals by reactive media, and (5) comparison of performance of various reactive media.

Keywords Permeable reactive barrier • Heavy metals • Adsorption • Precipitation • Reactive media • Coal ash • Natural clay • Activated charcoal • Zero valent iron • Organic residue

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Contents

3.1 Heavy Metals in Groundwater

Groundwater exists in the pore spaces and fractures in rocks and sediments beneath the earth's surface. It originates as rainfall or snow, moves through the soil, and back to surface streams, lakes or oceans (TGF 2012). Although groundwater represents only a small percentage of the total water resources on earth, its contribution is vital, considering that up to two billion people depend directly upon aquifers for drinking water and 40% of the world's food is produced by irrigated agriculture that relies largely on groundwater (Thiruvenkatachari et al. 2008). TGF (2012) reported that groundwater is used for drinking water by more than 50% of the people in the United States, including almost everyone who lives in rural areas, and the largest use for groundwater is to irrigate crops. Likewise, in Australia groundwater use has increased significantly in the last 10 years owing to surface water scarcity. South Australia uses more than 60% of groundwater for irrigation, while Western Australia uses 72% of groundwater for urban and industrial purposes (Thiruvenkatachari et al. 2008).

Inside the earth's crust, the heavy metals are adsorbed to soil particles. These heavy metals can become mobilised in the groundwater as a result of natural processes or by changes in soil pH or redox. Speciation as well as mobility of metal contaminants can be significantly influenced by a variety of natural processes in the soil environment such as acid/base reactions, precipitation/dissolution, oxidation/reduction, adsorption/desorption and ion exchange processes. The rate and extent of these reactions will be dictated by factors such as pH, redox potential, sorption and ion exchange. Anthropogenic sources such as sewage, landfill leachate, acid mine drainage or industrial waste disposal sites can also contaminate groundwater with heavy metals (Evanko and Dzombak 1997; Hashim et al. 2011). Once mobilised, metal contaminants can be transported through the flow of groundwater. Heavy metal speciation depends upon pH, redox potential, temperature and moisture and it has a significant influence on their toxicity, mobility and reactivity (Allen and Torres 1991; Evanko and Dzombak 1997; Hashim et al. 2011).

At higher concentrations, heavy metals can pose a significant threat to any form of life owing to their associated deleterious effects. Heavy metals tend to persist in natural ecosystems for an extended period of time. Furthermore, heavy metals can also accumulate in successive levels of the biological chain, leading to acute and chronic diseases (Akpor and Muchie 2010; Hashim et al. 2011). For example, copper is the most serious toxic element in mine drainage in Norway, where copper concentrations have reached critical levels for the survival of Atlantic salmon and brown trout in large water courses (Christensen et al. 1996). The fish in the water are exposed directly to heavy metals through their gills. Therefore impaired respiration of fish may result from acute and chronic toxicity. Fish are also exposed to heavy metals through ingestion of food and contaminated sediments (Jennings et al. 2008). Since the human being occupies the top most position in the food chain, the human being always faces the danger of being exposed to a higher concentration of heavy metals through ingestion of contaminated food. Table 3.1 shows the effect of heavy metals on human health (Martin and Griswold 2009; Akpor and Muchie 2010).

3.1.1 *Acid Mine Drainage*

Acid mine drainage is a problem faced by humanity worldwide. Acid mine drainage is produced when pyrite containing mine tailings is exposed to oxygen in the atmosphere and water as per the following equations (Akcil and Koldas 2006):

$$\mathrm{FeS}_{2(s)} + \frac{7}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{SO}_4^{2-} + 2\mathrm{H}^+ \tag{3.1}$$

$$\mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2 + \mathrm{H}^+ \rightarrow \mathrm{Fe}^{3+} + \frac{1}{2}\mathrm{H}_2\mathrm{O} \tag{3.2}$$

$$\mathrm{FeS}_{2(s)} + 14\mathrm{Fe}^{3+} + 8\mathrm{H}_2\mathrm{O} \rightarrow 15\mathrm{Fe}^{2+} + 2\mathrm{SO}_4^{2-} + 16\mathrm{H}^+ \tag{3.3}$$

Acid mine drainage generated from abandoned mines and mine tailings has contaminated water bodies and created large acidified lakes all over the world. Acid

Table 3.1 Heavy metals present in drinking water – effects on human health and the maximum allowable concentrations of heavy metals in groundwater and surface water

Heavy metal	Effect on human health	Maximum allowable value, Thailand (mg/L)[a]	
		Groundwater	Surface water
Arsenic	Lower level long term exposure leads to nausea and vomiting, reduction in red and white blood cell count	0.01	0.01
Cadmium	High level ingestion leads to severe stomach irritation, vomiting and diarrhoea	0.003	0.05
	Lower level long term exposure leads to kidney disease, lung damage and fragile bones		
Chromium	Lower level long term exposure can lead to liver and kidney damage, as well as damage to nerve tissues	0.05	0.05
Lead	Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death	0.01	0.05
	High level exposure in pregnant women may cause miscarriage and in men can damage the organs responsible for sperm production		
Mercury	Exposure to high levels can permanently damage the brain, kidneys and developing fetuses	0.001	0.002
	Short term exposure to high levels of metallic mercury vapours may cause lung damage, nausea, vomiting, diarrhoea, increases in blood pressure or heart rate, skin rashes and eye irritation		

[a] PCD (2016)

mine drainage, which is highly acidic by nature, solubilises heavy metals present in the mine tailings. Owing to its low pH and high heavy metal content, acid mine drainage is highly toxic and poses a significant environmental threat. Virtually no life can survive in such acidified waters. Heavy metals in soluble form can enter the food chain through bio-accumulation and bio-magnification, posing a greater threat to all forms of life (Kijjanapanich et al. 2012). Acid mine drainage from these lagoons percolates through soil, thereby affecting the soil chemistry and contaminating the groundwater which is a valuable source for drinking water and for agriculture (Gibert et al. 2011).

Some examples of the characteristics of acid mine drainage are presented in Table 3.2. Acid mine drainage of the Figueira coal mine (Brazil) is acidic and contains a high concentration of heavy metals, particularly Mn, Zn, Ni, As, Cd and Cr. The groundwater in the vicinity of the tailing storage facility in the Figueira coal mine is contaminated by acid mine drainage, with acidic pH and high concentration of heavy metals, particularly Mn, Zn, Ni and Cd. The surface water in the vicinity

Table 3.2 Variation of metal concentrations in acid mine drainage contaminated groundwater and surface water

Metal (mg/L)	Figueira coal mine, Brazil[a]			Ban Pu coal mine, Thailand[b]			Black swan nickel mine, Australia[c]		Maximum allowable value, Thailand[d]	
	AMD	GW^1	SW	AMD	GW^2	SW	GW^1	GW^2	GW	SW
Fe	631	31.2	4.87	0.108	0.227	1.063	3.21	3.65	–	–
Mn	12.8	34.2	31.8	17.36	0.026	0.233	10.17	0.25	0.5	1
Cu	0.08	0.02	<0.01	0.031	0.014	0.008	0.30	0.08	1	0.1
Zn	22.3	10.1	0.07	0.839	0.646	0.238	0.62	0.09	5	1
Al	95.5	55.2	1.20	–	–	–	33.22	0.30	–	–
Ni	1.13	0.55	<0.08	–	–	–	0.76	0.15	0.02	0.1
As	0.33	–	–	–	–	–	–	–	0.01	0.01
Co	0.15	0.52	<0.05	–	–	–	0.65	0	–	–
Cd	0.11	0.53	–	–	–	–	–	–	0.003	0.05
Cr	0.07	<0.02	<0.02	–	–	–	–	–	0.05	0.05
Pb	0.001	0.003	–	–	–	–	0.02	0.01	0.01	0.05
pH	3.20	3.10	6.80	4.22	7	7.25	5.03	6.71	–	5–9

AMD Acid Mine drainage, *GW* Groundwater, *SW* Surface water, *GW*^{1} Groundwater in the vicinity of the tailing storage facility, *GW*^{2} Groundwater away from the tailings storage facility, – data not provided

[a] Campaner et al. (2014)

[b] Pakdeerattanamit (2011)

[c] Liang-qi et al. (2010)

[d] PCD (2016)

of the Figueira coal mine is also contaminated by acid mine drainage, with high concentrations of Mn (Campaner et al. 2014). Acid mine drainage of the Ban Pu coal mine (Thailand) is acidic and contains a high concentration of Mn (Pakdeerattanamit 2011). The groundwater in the vicinity of the tailing storage facility of the Black Swan nickel mine (Australia) is contaminated by acid mine drainage, with a high concentration of Mn and Ni, while the groundwater away from the tailing storage facility is also contaminated by acid mine drainage with high concentrations of Ni (Liang-qi et al. 2010).

3.1.2 Landfill Leachate

Leachate generated from landfills can be a major source of heavy metals. Landfill leachate is generated when rainwater percolates through the waste layers deposited in the landfill. Physicochemical as well as microbial processes prevailing in the waste pile of a landfill may mobilise and transfer pollutants from the waste material into the percolating water. Landfill leachate may contain organic carbon, inorganic

Table 3.3 Concentrations of individual metals in landfill leachate, contaminated groundwater and surface water

Metal (mg/L)	Rowfabad landfill, Bangladesh[a]			Effurum dump site, Nigeria[b]			Narela Bawana landfill, India[c]		Maximum allowable value, Thailand[d]	
	LCH	GW	SW	LCH	GW	SW	LCH	GW	GW	SW
Fe	7.25	3.26	3.20	25.5	1.45	1.87	23.26	0.542	–	–
Mn	2.12	0.12	0.013	0.257	0.04	–	–	–	0.5	1
Cu	0.65	0.015	0.090	5.24	0.25	0.43	3.52	0.291	1	0.1
Zn	2.5	0.50	0.100	0.875	1.20	–	1.096	0.861	5	1
As	0.09	1.70	1.21	–	–	–	–	–	0.01	0.01
Cd	0.09	0.04	0.027	–	–	–	–	–	0.003	0.05
Cr	1.999	0.092	0.77	0.529	0.07	0.180	0.21	0.116	0.05	0.05
Pb	0.027	0.007	0.003	0.210	–	–	–	–	0.01	0.05
pH	6.3	6.7	7.24	6.9	6.3	6.8	8.4	8.93	–	5–9

LCH Leachate, *GW* groundwater, *SW* surface water, – data not provided

[a] Hossain et al. (2014)

[b] Ohwoghere-Asuma and Aweto (2013)

[c] Gupta and Rani (2014)

[d] PCD (2016)

components and heavy metals as well as xenobiotic organic compounds at lower concentrations (Christensen et al. 2001).

Improper management of landfill leachate has led to many cases of serious groundwater pollution in recent decades (Mor et al. 2006; Jun et al. 2009; Sabahi et al. 2009; Akinbile and Yusoff 2011). Heavy metals in the dumping sites originate from a variety of sources such as pharmaceuticals, photographic chemicals, certain types of detergents, personal care products, fluorescent tubes, waste oil, batteries, electronic waste, electrical equipment and paint. As a result, the clean up of landfill leachate contaminated groundwater is essential (Mohan and Gandhimathi 2009).

Some examples of the characteristics of landfill leachate are presented in Table 3.3. Landfill leachate in the Rowfabad landfill (Bangladesh) contains a high concentration of heavy metals, particularly Mn, As, Cd and Cr. The groundwater and surface water in the vicinity of the Rowfabad landfill are contaminated by landfill leachate, with a high concentration of heavy metals, particularly As and Cr (Hossain et al. 2014). Landfill leachate of the Effurum dump site (Nigeria) contains a high concentration of heavy metals, particularly Cu, Cr and Pb. The groundwater and surface water in the vicinity of the Effurum dump site (Nigeria) are contaminated by landfill leachate, with a high concentration of Cr (Ohwoghere-Asuma and Aweto 2013). Landfill leachate in the Narela Bawana landfill (India) contains a high concentration of heavy metals, particularly Cu and Cr. The groundwater of the Narela Bawana landfill (India) is contaminated by landfill leachate with high concentrations of Cr (Gupta and Rani 2014).

Table 3.4 Technologies for the removal of heavy metals from contaminated groundwater – benefits and drawbacks

Technology	Benefits (+)	Drawbacks (−)
Chemical precipitation	+ Effective remediation of acid mine drainage	− High operating costs − Bulky disposal
Ion exchange	+ Utilised to strip valuable metals from acid mine drainage	− High costs owing to resins
Electrochemical technology	+ No chemical regeneration + No chemical disposal + No resin disposal	− Requires for nearby technical support
Membrane technology	+ Effectively removes all types of contaminants	− Limited flow rates − Too expensive
Adsorption	+ Low cost + Easy operating condition + High metal binding capacity	− Production of waste

3.2 Technologies for the Treatment of Heavy Metal Contaminated Groundwater

3.2.1 *Active Techniques*

Active remediation techniques of heavy metal contaminated groundwater such as chemical precipitation, ion exchange, electrochemical technology, member technology and adsorption have been employed (Mohan and Chander 2001; Vaclav and Eva 2005; Gaikwad et al. 2010; Brousseau et al. 2000). The chemical precipitation of heavy metal contaminated groundwater occurs by pH adjustment to the alkaline range followed by metal hydroxide precipitation (Mohan and Chander 2001). The method is expensive and produces large volumes of inorganic sludge which is often difficult to dispose of owing to its toxic nature (Johnson and Hallberg 2005). Benefits and drawbacks of other active remediation techniques of heavy metal contaminated groundwater are presented in Table 3.4 (Asokbunyarat 2015). Pump and treat remediation methods are often difficult to employ when dealing with groundwater contamination from acid mine drainage and landfill leachate (Kijjanapanich et al. 2012).

3.2.2 *Passive Techniques*

Also passive remediation techniques of heavy metal contaminated water, such as the permeable reactive barrier technology, have been employed (Thiruvenkatachari et al. 2008). Treatment in a permeable reactive barrier can be both biotic and abiotic

(Hashim et al. 2011). As a result, a permeable reactive barrier may employ organic and inorganic media, depending upon the type of treatment imparted. Organic media are often used in permeable reactive barriers as electron donors to initiate the growth of specific microorganisms. Earlier research has shown that suitable natural organic substrates such as rice husks, coconut husk chips, bamboo chips and sludge from wastewater treatment facilities can be used as electron donors to initiate the growth of sulphate reducing bacteria in permeable reactive barriers. Accordingly, sulphide produced by biological sulphate reduction was capable of removing the heavy metals from acid mine drainage through sulphide precipitation (Kijjanapanich et al. 2012).

In abiotic treatment systems, activated charcoal, clay, limestone, red mud, fly ash, zeolite and zero valent iron have been used as reactive materials (Komnitsas et al. 2004a, b, 2006, 2007; Yang et al. 2010; Chaari et al. 2011). These media are capable of removing pollutants such as heavy metals from contaminated groundwater. Researchers have also shown that bottom ash can be used as effective sorption material for removing heavy metals from aquatic solutions (Gorme et al. 2010; Asokbunyarat et al. 2015a). Bottom ash is an attractive low cost adsorbent owing to its coarse particle size, large surface area, its high porosity and chemical composition (high SiO_2, Al_2O_3 and Fe_2O_3 and calcium content) (Mohan and Gandhimathi 2009; Hashim et al. 2011).

3.3 Permeable Reactive Barrier

3.3.1 Permeable Reactive Barrier: The Basic Principle

A permeable reactive barrier is one of the most promising groundwater remediation technologies. A permeable reactive barrier is 'an emplacement of reactive media in the sub-surface designed to intercept a contaminated plume, provide a flow path through the reactive media and transform the contaminants(s) into environmentally acceptable forms' to attain remediation concentration goals down-gradient of the barrier, as shown in Fig. 3.1 (USEPA 1997, 1998).

A permeable reactive barrier consists of an underground emplacement containing permanent, semi-permanent or replaceable reactive media placed across the flow path of a contaminated groundwater plume. This plume moves through the permeable reactive barrier under its gradient, creating a passive treatment system. As the contaminant moves through the reactive material, reactions occurring inside the permeable reactive barrier transform the contaminants into less harmful (non-toxic) or immobile species (USEPA 1998, 2002).

Currently, two basic designs are being used in full-scale implementations of reactive barriers: (1) the continuous trench and (2) the funnel and gate. The continuous trench is simply a trench that has been excavated and simultaneously backfilled with reactive material, allowing the water to pass through the barrier under its natural gradient and its natural flow velocity, as shown in Fig. 3.2a. The groundwater

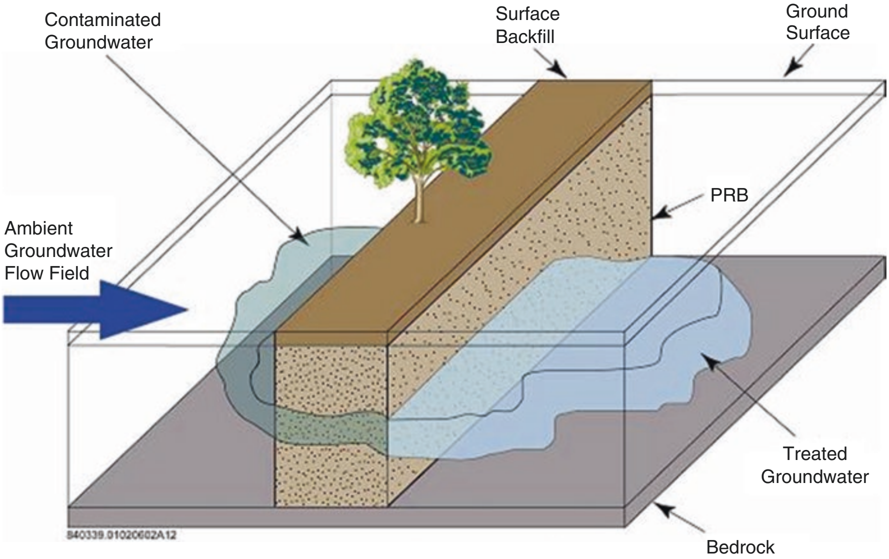


Fig. 3.1 Layout of a permeable reactive barrier. As contaminated groundwater passes through the permeable reactive barrier, the reactive media inside remove the contaminants and the treated groundwater leaves the permeable reactive barrier

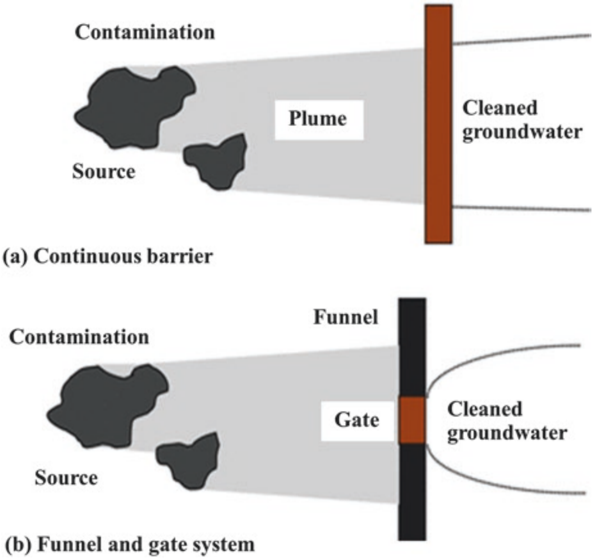


Fig. 3.2 Permeable reactive barrier configurations: (**a**) continuous barrier, and (**b**) funnel and gate system

flow velocity through the permeable reactive barrier will be similar to the velocity in the aquifer. The funnel and gate system consists of a permeable gate (reactive zone) placed between two impermeable funnels, shown in Fig. 3.2b. An impermeable funnel directs the flow of contaminated water to a gate containing the permeable zone of reactive material. The impermeable funnel also helps to increase the velocity of the groundwater flow though the permeable reactive barrier by directing it through a much smaller cross sectional area (USEPA 1997). Factors such as site characteristics, including its hydro-geological details, barrier characteristics like its physical dimensions and placement, and the reactive material characteristics like its quantity and cost dictate the selection between the two permeable reactive barrier configurations. The ‘funnel and gate’ configuration is preferred when the reactive zone employs a lower quantity of reactive material, which is expensive. On the other hand, when cheap reactive material is used, a continuous barrier without construction of the impermeable side walls would be profitable (Roehl et al. 2005; Naidu et al. 2015).

3.3.2 Permeable Reactive Barrier Design

The following factors need to be addressed during the planning and installation of a permeable reactive barrier system (Roehl et al. 2005):

- The boundaries of the property where the permeable reactive barrier is to be installed;
- Mapping of underground utilities such as water, sewage and gas distribution networks, electrical wires and cables;
- Any disruption of site activities that may be caused by the construction of the permeable reactive barrier;
- The need to dewater the excavation pit and the disposal of potentially contaminated water and soil during placement;
- The logistics and on-site material management and its placement, such as reactor filling and dust prevention;
- Occupational hazard and safety issues;
- Undetected underground utilities and abandoned foundations from demolished structures.

Furthermore, the details of the contaminated site, such as the contaminant characterisation, including its type, concentration and total mass, the groundwater composition and hydraulic setting need to be properly investigated when planning a permeable reactive barrier system. Feasibility studies are always helpful, involving the following steps (Roehl et al. 2005):

- What type of remediation approach is preferred, which reactive material is to be used and what the predominant contaminant removal mechanisms are;
- Batch and column investigations which quantitatively measure the contaminant removal capacity, such as mg of contaminant/g of reactive medium;

- Assessment of the residence time in the permeable reactive barrier based on possible reaction kinetics;
- Calculation of the reactive zone thickness.

3.4 Criteria for Selection of Reactive Material

Once the details about the site characteristics are obtained, selection of suitable reactive media such as coal ash, natural clay, activated charcoal and organic residue, as shown in Fig. 3.3, should be made based on the following criteria (Gavaskar et al. 2000; Roehl et al. 2005; ITRC 2011; Naidu et al. 2015):

- *Reactivity:* The reaction rate and equilibrium constant of the contaminant with the reactive material dictate the residence time inside the permeable reactive barrier - hence they should be quantitatively evaluated. A high reaction rate coupled with a low residence time is desirable so that the barrier thickness is kept within acceptable limits.
- *Stability:* Since the reactive material inside the permeable reactive barrier cannot be replaced frequently, it is desirable that the reactive material remains active for a longer period of time. Ideally, the reactive material also should be able to withstand the variations in pH, temperature, pressure and antagonistic factors.
- *Quantity, availability and cost:* Proper estimation of the quantity of the reactive media required must be made. Furthermore, the required quantity of the reactive material must be available at an affordable cost.
- *Hydraulic performance:* The particle size of the reactive material will dictate its hydraulic conductivity (permeability). The hydraulic conductivity of the reactive media must be higher than the surrounding soil so that the groundwater flow penetrates easily through the permeable reactive barrier. As a result, selection of the particle size of the reactive media is critical.
- *Environmental compatibility:* It should be ensured that the reactive media do not form any undesirable by-products with the contaminant and do not dissolve or release any undesirable substance and thereby become a new source of contamination.
- *Safety:* Health and safety issues are of prime importance since handling of the material should not result in any risk to worker health.

Fig. 3.3 Reactive media used in permeable reactive barrier for heavy metal removal from groundwater. Inorganic media, such as coal fly ash and montmorillonite clay, as well as organic media such as activated charcoal and coconut husk chips are often employed

3.5 Removal of Heavy Metals by Reactive Media

3.5.1 Removal Mechanisms

The physical and chemical processes involved in the removal of contaminants in permeable reactive barriers can be classified broadly into three categories: (I) sorption, (II) precipitation and (III) degradation.

(I) *Sorption:* permeable reactive barriers which employ sorption barriers utilise retention mechanisms involving fixation of the target pollutant to the reactive media (Simon et al. 2002). Moreover, the removal process does not destroy or change the oxidation state of the contaminant. The processes include surface adsorption, ion exchange, surface complexation, precipitation and co-precipitation. The extent of adsorption is mainly governed by the size and specific surface area of the sorbent (Roehl et al. 2005). Possible materials employed in permeable reactive barriers include activated charcoal, natural clays, and surface-modified minerals such as organophilic zeolites and diatomites (Simon et al. 2002).

(II) *Precipitation:* When precipitation is the predominant mechanism, contaminants are immobilised within the reactive material zone by the formation of insoluble precipitates (Roehl et al. 2005; Thiruvenkatachari et al. 2008). The reactive materials can modify the pH and redox potential which is favourable for precipitation of metals as metal hydroxides (Hashim et al. 2011). The reactive materials that can be used include lime, limestone, coal ash, powders of chemicals such as $Mg(OH)_2$, $MgCO_3$, $CaCl_2$, $CaSO_4$ and $BaCl_2$ and zero valent metals (Yin and Allen 1999; Hashim et al. 2011). Furthermore, under anaerobic conditions, sulphide may be generated due to biological sulphate reduction which also may lead to metal sulphide precipitation.

(III) *Degradation:* the conversion of pollutants to less harmful compounds also may occur through chemical or biological reactions whenever organic residues are used in permeable reactive barriers. The organic residues serve as electron donors for biological reactions, whereas the heavy metal contaminants serve as electron acceptors. Biological reactions such as sulphate removal may occur in the permeable reactive barriers which facilitate removal of heavy metal contaminants. As an example, sulphate reducing bacteria utilize the organic substrates under the anaerobic conditions to reduce the sulphates to sulphides, and the sulphides can react with heavy metals, resulting in their precipitation as metal sulphides (Nyarko et al. 2014). Organic residues such as alfalfa, leaves, biological sludge, sawdust, agricultural residues, manure and compost can be used in biodegrading permeable reactive barriers (ITRC 2011).

On the other hand, the permeable reactive barrier technology may also offer some disadvantages as:

(I) *Life time of permeable reactive barrier:* When the capacity of the reactive material in the permeable reactive barrier is exhausted, removal of metal ions from groundwater is no longer possible. Under such circumstances, the used media from the permeable reactive barrier must be removed and the permeable reactive barrier must be recharged with fresh reactive media.
(II) *Leaching of adsorbed metal ions:* Sorption of metal ions onto inorganic media is a reversible process. Changes in the operating conditions, such as pH and redox, may result in desorption of sorbed metal ions.
(III) *Formation of metal complexes:* Some heavy metals may form complexes with natural organic matter, which can lead to increased metal mobility.
(IV) *Clogging of permeable reactive barrier:* Whenever precipitation is the dominant metal removal mechanism, the pore volume in the permeable reactive barrier can reduce over the time of the permeable reactive barrier operation. In such a case, clogging can occur inside the reactive media, leading to reduced hydraulic conductivity and distorted groundwater flow.

3.5.1.1 Adsorption

Adsorption Isotherms

Equilibrium sorption isotherm model: Isotherm models, such as the Langmuir, Freundlich and Brunauer-Emmett-Teller models, were tested to fit the experimental data to estimate the equilibrium relationships between sorbent and sorbate in solution at equilibrium of metal sorption. The Langmuir model is based on the assumption that a solid surface has a finite number of identical sites which are energetically uniform (Sawyer et al. 2007; Lalhruaitluanga et al. 2010). The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3.4}$$

where:

C_e: equilibrium concentration (mg/L)
q_e: sorption capacity at equilibrium (mg/g)
q_m: maximum sorption capacity (mg/g)
b: sorption equilibrium constant (L/mg)

The Freundlich model assumes a monolayer sorption with a heterogeneous energetic distribution of active sites accompanied by interaction between adsorbed molecules (Sawyer et al. 2007; Lalhruaitluanga et al. 2010). The Freundlich isotherm can be expressed as:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{3.5}$$

where:

K_f: Freundlich constants related to sorption capacity (mg/g)
n: sorption intensity (g/L)

The Brunauer-Emmett-Teller isotherm is widely applied in the gas-solid equilibrium systems in which the multilayer adsorption phenomena exists (Foo and Hameed 2010). The BET isotherm can be expressed as:

$$q_e = \frac{q_s C_{BET} C_e}{\left(C_s - C_e\right)\left[1 + \left(C_{BET} - 1\right)\left(\frac{C_e}{C_s}\right)\right]} \tag{3.6}$$

where:

C_{BET}: the Brunauer-Emmett-Teller adsorption isotherm (L/mg)
C_s: adsorbate monolayer saturation concentration (mg/L)
q_s: theoretical isotherm saturation capacity (mg/g)

Removal Kinetics

Sorption kinetic model: Sorption of heavy metal ions onto reactive media has been modelled by researchers as pseudo-first- or pseudo-second-order kinetics (Bhattacharyya and Gupta 2006; Amarasinghe and Williamas 2007; Lalhruaitluanga et al. 2010; Sukpreabprom et al. 2014) to fit experimental batch sorption data.

The pseudo-first-order model is based on the assumption that the rate is proportional to the number of unoccupied sites. A linear form for the pseudo-first-order model is given as:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303} t \tag{3.7}$$

where:

q_t: amount of adsorbate adsorbed at time t (min) (mg/g)
q_e: sorption capacity at equilibrium (mg/g)
k_1: rate constant for the pseudo-first-order model (min^{-1})

The first-order rate constant k_1 and q_e can be obtained from the slope and intercept of the straight line of $\log\,(q_e-q_t)$ versus t, respectively.

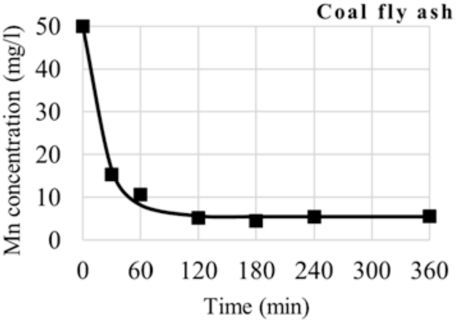


Fig. 3.4 Batch sorption kinetic test: this figure presents the concentration of residual Mn(II) in aqueous solution vs. sorption time during a typical batch sorption kinetic test when coal fly ash is used as sorbent to remove Mn(II)

On the other hand, the pseudo-second-order model is based on the assumption that the rate is proportional to the square of the number of unoccupied sites. A linear form of the pseudo-second-order model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.8}$$

where:

k_2: rate constant for the pseudo-second-order model (g/mg.min)

The second-order rate constant k_2 and q_e can be obtained from the slope and intercept of the straight line of t/q_t versus t respectively.

3.5.2 *Performance Evaluation*

Laboratory tests are often needed to evaluate the suitability of reactive materials, which may include the removal rate of the contaminant and the removal mechanism (including the formation of by-products). Laboratory tests along with site characteristics form the basis for permeable reactive barrier design (Geranio 2007). Two types of laboratory tests are performed: (I) batch studies and (II) column studies.

(I) *Batch studies:* Batch tests are useful as an initial screening tool for the selection of the reactive materials for the permeable reactive barrier. Batch tests are carried out under controlled conditions to assess the rate of pollutant removal. Furthermore, the longevity of different materials also can be evaluated. Typically, batch tests include the removal of dissolved contaminants from aqueous solution by an individual or a mixture of different reactive materials to be tested (Geranio 2007).

Some examples of the trends expected in metal removal during batch studies are presented in Fig. 3.4. In this figure, the results obtained from the kinetic of sorption of Mn(II) from aqueous solution onto coal fly ash at an L/S ratio of 100 mL:0.2 g.

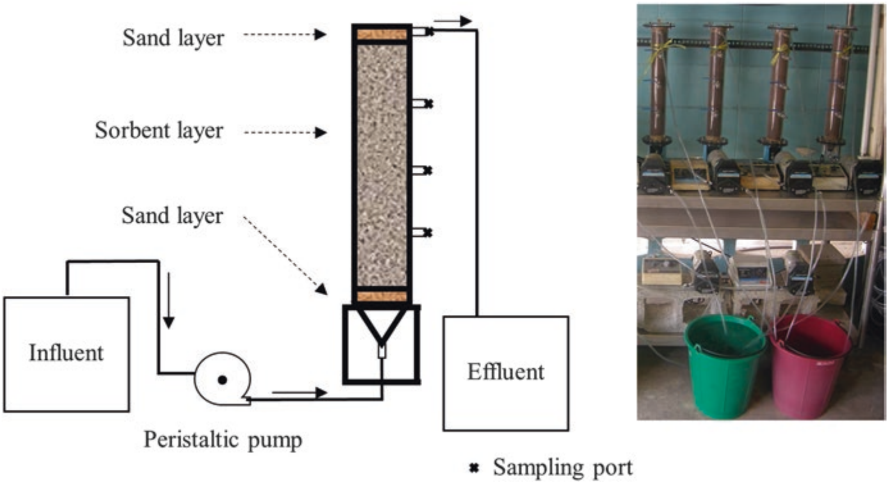


Fig. 3.5 Layout of column sorption reactor. Note that the influent contaminated with heavy metals is fed continuously to the column reactor while the packed media inside the column remove the contaminants. The treated effluent is then discharged

The residual Mn(II) concentration reduced sharply in the first 40–50 min and reached a value of less than 10 mg/L within 120 min. In the initial stages, when the sorption sites on the adsorbent surface were not occupied, sorption of heavy metal ions was rapid. However, as time progressed, the sorption sites were occupied by the heavy metal ions. As a result, the number of unoccupied sites available reduced in time, and hence the sorption rate also dropped significantly (Asokbunyarat et al. 2015a).

(II) *Column studies:* Column tests are a favoured method for treatability testing because of the possibility of extrapolating the results to the dynamic flow conditions which may exist in the field. The layout of a column reactor is shown in Fig. 3.5. Column tests are also used to estimate the half-life of the contaminant removal reaction. The half-lives of the contaminants are then used either to select the reactive media or to design of an appropriate thickness of the reactive wall (Gavaskar et al. 2000).

Some examples of the trends expected in metal removal during column studies are presented in Fig. 3.6. The results obtained from the kinetics of sorption of Mn(II) from acid mine drainage onto coal bottom ash are illustrated in this figure. In the initial stages, the residual Mn(II) concentration was the lowest and remained constant, and then a gradually increased with increase in pore volumes, reaching a steady state close to the initial Mn(II) concentration. As a result, the Mn(II) removal efficiency remained close to maximal in the initial stage owing to the reaction with fresh reactive materials, whereas the Mn(II) removal efficiency decreased in the end stage to fairly low values owing to the decline of the reactive material surfaces

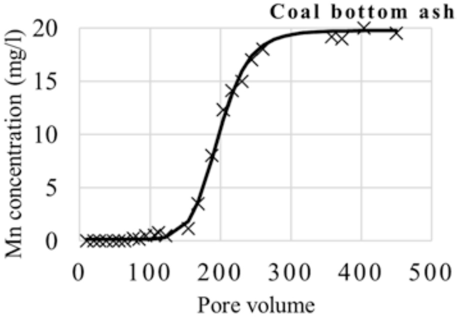


Fig. 3.6 The breakthrough curve in a typical column sorption kinetic test. This figure shows the concentration of Mn(II) from acid mine drainage in the treated effluent vs the effluent collected in terms of pore volume in the column

caused by second mineral precipitates and re-dissolution of previously formed unstable precipitates (Jahangiri-rad et al. 2014).

3.6 Types of Reactive Media Used in Permeable Reactive Barriers

3.6.1 Coal Ash

At present, the world energy demand is over 2.2 million MW and it is increasing at a rate of 1.5% per year, mainly owing to population growth and increasing living standards worldwide (USEIA 2013). Today, coal is one of the world's primary sources for power generation, accounting for about 36% of the global electricity generation (IEA 2014).

The use of coal in power plants generates fly ash, bottom ash and flue gas desulfurisation gypsum as its main by-products. Typically, 1 wt of electricity can be generated from 15 to 18.75 tons of coal, producing 4.3–11 tons of fly ash and bottom ash, depending upon the quality of coal (Asokan et al. 2005). About 600–800 million tons of coal ash are generated worldwide every year, of which fly ash and bottom ash constitute about 65–95% and 5–35%, respectively. Currently, USA, Europe, China and India are the major contributors of coal ash (Jayaranjan et al. 2014).

Coal ash dump sites may contain coal ash in wet or dry form. In the wet disposal system, coal ash is mixed with water as slurry and disposed of in ponds or lagoons, while in the dry disposal systems, coal ash is disposed of in special local landfills (Kim and Prezzi 2008). Coal fly ash and bottom ash can contain several heavy metals, such as arsenic, lead, cadmium, chromium, manganese, copper, zinc and nickel, usually at trace levels. These heavy metals can be leached from coal ash under acidic conditions and can contaminate the soil, surface water and groundwater, and could eventually enter the food chain, leading to genotoxic effects (Brigden et al. 2002; Ahmed et al. 2010).

Several reuse options exist for coal ash. Coal fly ash and bottom ash are extensively reused in concrete, cement, structural fill, road base/sub-base, mining

Table 3.5 Major elemental composition of coal fly ash – note that the coal fly ash contains mainly oxides of elements

Composition	Lignite[a]	Bituminous[b]	Anthracite[b]
SiO_2 (wt%)	14.80–50.00	56.7	43.5–47.3
Al_2O_3 (wt%)	3.40–25.70	38.4	25.1–29.2
Fe_2O_3 (wt%)	0.86–11.80	2.5	3.8–4.7
CaO (wt%)	13.00–54.10	1.1	0.5–0.9
MgO (wt%)	0.50–9.10	0.2	0.7–0.9

[a] Baba and Kaya (2004)
[b] Choi et al. (2002)

applications, hazardous waste stabilisation and as soil amendment material in agriculture (Kurama and Kaya 2008). However, only a small proportion (about 15%) of bottom ash generated in the world is reused (Jayaranjan and Annachhatre 2013). As a result, reuse of bottom ash is a great challenge.

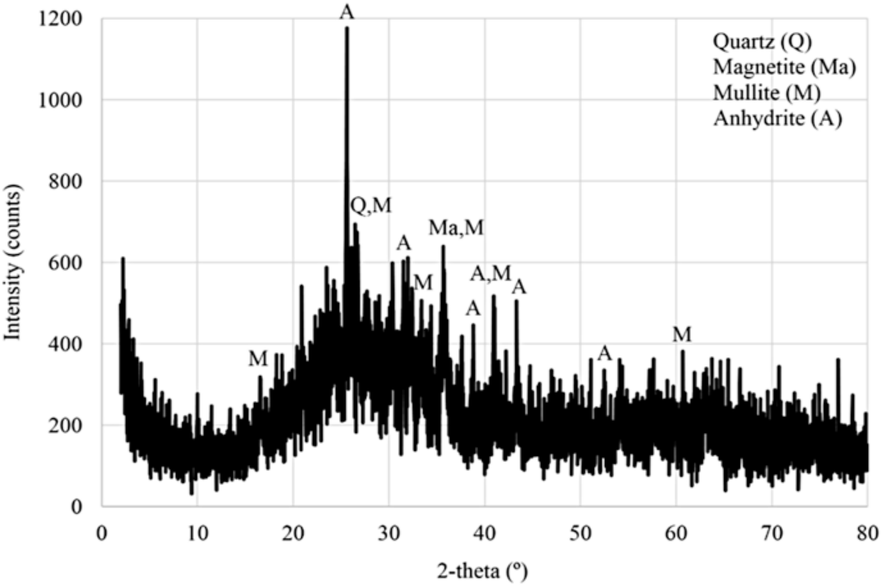
One of the possible reuse options for coal ash is to use it as a sorbent material for the removal of heavy metal ions from aqueous solutions such as wastewater and groundwater. Coal fly ash has been successfully used as an adsorbent for the removal of heavy metals in acid mine drainage (Komnitsas et al. 2004b) and landfill leachate (Mohan and Gandhimathi 2009). Coal bottom ash has also been successfully used as a sorbent for the removal of lead from water (Gorme et al. 2010) and the removal of iron, manganese, copper and zinc from aqueous solutions and acid mine drainage (Asokbunyarat et al. 2015a, b). The fly ash and bottom ash are attractive choices as a low cost sorbent, mainly because of the SiO_2, Al_2O_3 and Fe_2O_3 and high calcium content.

3.6.1.1 Properties of Coal Fly Ash

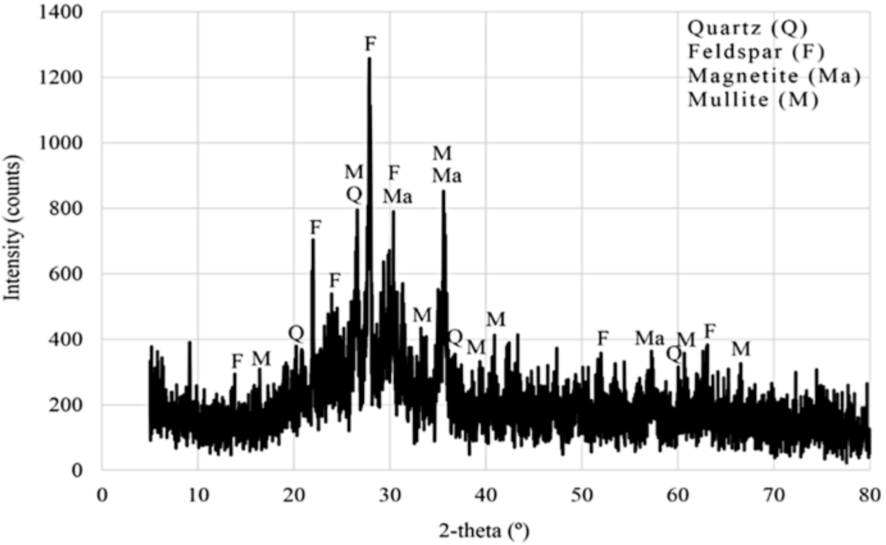
Physical properties of coal fly ash: Coal fly ash particles are grey in colour. Typical values of properties are specific gravity: 2.10–2.81 (Kim and Prezzi 2008), particle size distribution: 0.001–0.075 mm (Kim and Prezzi 2008), moisture content: 7.75 wt%, bulk density: 1.12–1.28 g cm^{-3} and specific surface area: 1.0–9.44 m^2 g^{-1} (Theis and Gardner 1990).

Chemical composition of coal fly ash: The chemical composition of coal fly ash from burning of lignite, bituminous, or anthracite coal is presented in Table 3.5. The data reveal that coal fly ash contains mainly oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO (Ahmaruzzaman 2010; Silva et al. 2010).

The diffractogram in Fig. 3.7a shows X-ray diffraction of a sample of coal fly ash. It was found that coal fly ash consisted mainly of anhydrite ($CaSO_4$) and mullite ($Al_6Si_2O_{13}$). Coal fly ash also consisted of some quartz (SiO_2) and magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$).



(a) Coal fly ash



(b) Coal bottom ash

Fig. 3.7 X-ray diffraction pattern of coal ash: (**a**) coal fly ash – note that the coal fly ash contains mainly quartz, magnetite, mullite and anhydrite, and (**b**) coal bottom ash – note that the coal bottom ash contains mainly quartz, feldspar, magnetite and mullite

Table 3.6 Major elemental composition of coal bottom ash – note that the coal bottom ash contains mainly oxides of various elements

Composition	Lignite[a]	Bituminous[b]	Anthracite[c]
SiO_2 (wt%)	10.80–48.30	48.81–58.9	53.5
Al_2O_3 (wt%)	2.50–24.90	10.12–36.0	27.6
Fe_2O_3 (wt%)	0.50–8.20	2.4–6.10	6.0
CaO (wt%)	8.60–45.10	1.3–11.81	3.4
MgO (wt%)	0.40–4.60	0.2–5.61	2.1

[a] Baba and Kaya (2004)
[b] Pires and Querol (2004)
[c] Russell et al. (2002)

3.6.1.2 Properties of Coal Bottom Ash

Physical properties of coal bottom ash: Coal bottom ash, has a dark grey colour and a particle size of 0.1–10 mm. Other properties include specific gravity of 2.30–3.00, bulk density of 1.15–1.76 g cm^{-3} and specific surface area in the range of 0.17–1.0 m^2 g^{-1} (Theis and Gardner 1990; Ahmaruzzaman 2010).

Chemical composition of coal bottom ash: Coal bottom ash consists mainly of oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO. Table 3.6 presents the typical composition of coal bottom ash from burning of lignite, bituminous and anthracite coal.

The diffractogram in Fig. 3.7b shows X-ray diffraction of a sample of coal bottom ash. It was found that coal bottom ash was mainly amorphous in nature, but also crystalline phases such as feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$), mullite ($Al_6Si_2O_{13}$), magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) and quartz (SiO_2) are present.

The main clean-up mechanisms involved for fly ash and bottom ash with heavy metals are:

(I) Precipitation as metal hydroxide and metal oxyhydroxide

The high calcium content in the fly ash and bottom ash (Tables 3.5 and 3.6) helps in raising the pH of the solution by the generation of hydroxide alkalinity, thereby initiating hydroxide precipitation of heavy metals as a stable phase (Komnitsas et al. 2004b; Hashim et al. 2011). The hydroxide precipitation of heavy metals can been described as follows:

$$Me^{n+} + OH^{-} \rightarrow Me\left(OH\right)_n \quad (3.9)$$

(II) Surface adsorption

The chemical composition and surface charge of fly ash and bottom ash are expected to influence the sorption of heavy metal ions. Fly ash and bottom ash contain mainly oxides of silicon (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3) and calcium (CaO) (Fig. 3.7). SiO_2 and Al_2O_3 have excellent sorption characteristics, mainly because they exhibit a surface charge depending upon the pH of the metal ion containing solution. The central silicon atom has a strong affinity for electrons, which yields a low basicity to the oxygen atoms bound to the silicon atom. As a result, this in turn makes the silica surface act as a weak acid. As a result, silanol (SiOH) groups are formed when the oxygen atoms on the silica surface react with water. Giving the silica surface acquires a positive charge at low pH. On the other hand, at high pH values, a negatively charged surface prevails on the silica surface (Mohan and Gandhimathi 2009). Alumina and iron also show a similar behaviour depending upon the solution pH. Under these conditions, the silica, alumina and iron content of fly ash and bottom ash are expected to be negatively charged, which would allow metal ions (M(II)) and metal hydroxides ($M(OH)_2$) to be complexed at the surface of coal ash, resulting in heavy metal ion removal through adsorption (Chaiyasith et al. 2006; Wang et al. 2006).

$$\mathrm{SiOH} + \mathrm{OH}^- \rightarrow \mathrm{SiO}^- + \mathrm{H_2O} \tag{3.10}$$

$$2\left(\mathrm{SiO}^-\right) + \mathrm{M}^{2+} \rightarrow \left(\mathrm{Si} - \mathrm{O}\right)_2 \mathrm{M} \tag{3.11}$$

$$\mathrm{AlOH} + \mathrm{OH}^- \rightarrow \mathrm{AlO}^- + \mathrm{H_2O} \tag{3.12}$$

$$2\left(\mathrm{AlO}^-\right) + \mathrm{M}^{2+} \rightarrow \left(\mathrm{Al} - \mathrm{O}\right)_2 \mathrm{M} \tag{3.13}$$

$$\mathrm{SO}^- + \mathrm{M}\left(\mathrm{OH}\right)_2 \rightarrow \mathrm{SO} - \mathrm{M}\left(\mathrm{OH}\right)_2^- \tag{3.14}$$

where: SO^- are the free sites on the surface of an adsorbent.

Komnitsas et al. (2004b) studied the efficiency of lignite fly ash barriers for the removal of heavy metals from acid mine drainage. Laboratory investigations were carried out through continuous column experiments with 50% w/w of Greek fly ash and 50% w/w of silica sand as reactive media and synthetic acid mine drainage as feed. pH, Eh, heavy metal (Fe, Zn, Mn, Al, Ni, Cu, Co and Cd), SO_4^{2-} and solid samples were analysed at the end. The results showed that the effluent pH remained strongly alkaline in the range from 11 to 12.9 while the redox potential varied between 200 and 350 mV. Iron, aluminum, copper, zinc, nickel, cobalt, cadmium, copper and manganese concentrations in the effluent remained below detection limit. Geochemical modeling (PHREEQC) indicated that $Al(OH)_3$ could precipitate at pH values higher than 5, while copper could precipitate as cupric and cuprous ferrite at pH values between 5 and 6. Zn co-precipitated mainly with Si to form Zn_2SiO_4 and Cd removal was accomplished by co-precipitation as $CdSiO_3$. The toxicity characteristic leaching procedure (TCLP) tests indicated that the toxicity of the resulting precipitates was below compliance limits. Results from continuous column experiments indicated that a permeable reactive barrier containing lignite fly ash could effectively remove high loads of heavy metals from acidic leachates.

Mohan and Gandhimathi (2009) studied the adsorption of heavy metals from landfill leachate using fly ash from a lignite power plant through batch studies. The results indicated that, as the fly ash dosage increased from 0.5 up to 2 g/L, the heavy metal removal efficiency also increased concomitantly and attained a constant value thereafter. The highest heavy metal removal was recorded at the optimum fly ash dose of 2 g/L. The pH increased rapidly and stabilised to a value of 8.54.

Asokbunyarat et al. (2015a) studied the sorption of heavy metal ions from aqueous solution onto coal bottom ash. X-ray diffraction analysis of coal bottom ash indicated the presence of feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$), mullite ($Al_6Si_2O_{13}$) and magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$). The toxicity characteristic leaching procedure tests revealed that heavy metal ions such as Fe(II), Fe(III), Mn(II), Cu(II), Zn(II), As(III), As(V), Pb(II) and Cd(II) could be leached out from coal bottom ash. Continuous column tests with the bottom ash showed negligible heavy metal ion leach-out at pH 6.0, although some heavy metal ion leaching, mainly of Mn(II), was observed at pH 4.2. Batch sorption studies with individual heavy metal ions (Fe(II), Cu(II), Zn(II) and Mn(II)) revealed that the heavy metal ion sorption onto coal bottom ash followed pseudo-second-order kinetics. Sorption isotherm studies revealed that the Langmuir isotherm could adequately describe the heavy metal ion sorption onto coal bottom ash with maximum adsorption capacity (q_m) ranging from 1 to 25 mg/g for various heavy metal ions. The removal of heavy metal ions by coal bottom ash is attributed to both adsorption and hydroxide precipitation of heavy metals owing to the presence of different oxides such as SiO_2, Al_2O_3, Fe_2O_3 and CaO in coal bottom ash.

Asokbunyarat et al. (2015b) studied the sorption of heavy metals from acid mine drainage onto coal bottom ash. Process parameters such as pH, L/S (liquild-to-solid ratio) and contact time strongly affected the metal adsorption onto coal bottom ash. The heavy metal adsorption onto bottom ash increased with increasing initial heavy metal concentration and contact time. However, it was restricted in sorption behaviour at much higher metal concentrations. Adsorption of heavy metal ions from single and multi component solutions based on the acid mine drainage characteristics of lignite coal mine in Thailand onto coal bottom ash followed the sequence: Fe(II) > Cu(II) > Mn(II) > Zn(II). The adsorption of heavy metal ions from a single-component solution was higher than that from a multi-component solution owing to the effect of competing ions. The pseudo-second-order model satisfactorily described the heavy metal adsorption onto bottom ash. On the other hand, the Langmuir isotherm satisfactorily described the isotherm data indicating that the bottom ash is made up of homogenous and single layered surfaces which are available for heavy metal adsorption.

3.6.2 Natural Clay

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction (lower than 2 μm) of soils, sediments, rocks and water. One of the important properties of clay is their plasticity which is obtained when mixed with water. Clays are capable of removing contaminants from the environment through ion exchange and adsorption. As a result, clay surfaces always attract cations and anions owing to the electrostatic forces existing between the ions present in the solution and the surface charge that the clay acquires when it is mixed with water (Bhattacharyya and Gupta 2008a). There are two basic classes of clays: kaolinite and montmorillonite (Bailey et al. 1999).

Kaolinite includes a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{3+} as the octahedral cation. The formula of kaolinite is $(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$ and the theoretical composition is SiO_2 46.54%, Al_2O_3 39.50% and H_2O 13.96%. Considering the speciation of different metals in this formula, the theoretical net surface charge on kaolinite is zero. However, kaolinite acquires a small net negative charge owing to the fact that its surface is not completely inert (Bhattacharyya and Gupta 2008a).

Montmorillonite is a clay mineral including units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. Its formula is $(Si_{7.8}Al_{0.2})^{IV}(Al_{3.4}Mg_{0.6})^{VI}O_{20}(OH)_4$ and the theoretical composition without the interlayer material is SiO_2 66.7%, Al_2O_3 28.3%, and H_2O 5%. Considering the speciation of different metals in this formula, the theoretical net surface charge on montmorillonite is −0.8 charge/unit cell, which is responsible for the adsorption of cations (Bhattacharyya and Gupta 2008a).

Physical and chemical properties of natural clays: Natural clays have a large specific surface area (up to 800 m^2/g). They have a layered structure and high cation-exchange capacity (CEC). Clays are chemically and mechanically stable. These characteristics of natural clays have made them excellent adsorbents (Bhattacharyya and Gupta 2008b; Chaari et al. 2011). The properties of kaolinite and montmorillonite are shown in Table 3.7. The values of the specific surface area reported in the literature range from 5 to 25 m^2/g for kaolinite and 15.5–82.0 m^2/g for montmorillonite depending on the particle size distribution, particle shape, and distribution of pores in the material. On the other hand, the cation-exchange capacities have been reported to be 0.13 and 2.25 meq/g for kaolinite and montmorillonite, respectively (Bhattacharyya and Gupta 2008b). Of the two species, montmorillonite clays have the smaller crystals, larger surface area and higher cation-exchange capacity. Thus montmorillonite clays exhibit a higher adsorption capacity (Bailey et al. 1999).

The adsorption of metal ions from the aqueous solutions by kaolinite and montorillonite by varying pH, liquid/solid ratio, time and metal ions concentration have been investigated (Bhattacharyya and Gupta 2008b). The results showed that adsorption increased with pH, and montmorillonite had a higher adsorption capacity than kaolinite at all pH values. The adsorption followed second-order kinetics and the second-order rate constant was higher for montmorillonite than for kaolinite,

Table 3.7 Properties of the two basic classes of clays. Note that the montmorillonite clay particles are much smaller in size and offer a higher external as well as internal surface area

Property	Kaolinite	Montmorillonite
Size (μm)	0.1–5.0	0.01–1.0
External surface	Low	High
Internal surface	Low	Very high
Cation exchange capacity (cmol kg^{-1})	3–15	80–100

confirming the higher affinity of the metal ions for montmorillonite. Montmorillonite had a higher Langmuir monolayer adsorption capacity (q_m) of 28.4–28.9 mg g^{-1}, compared to kaolinite ranging from 10.4 to 11.2 mg g^{-1}. Adsorption isotherms of copper, nickel and chromium from Jebel chakir leachate onto smectite-rich clayed rock exhibited an S-shaped curve owing either to precipitation or the presence of competitive effects of other solutes (Chaari et al. 2011). The removal of metal ions in column tests was 69.40%, 57.02%, and 70.21% for copper, nickel and chromium respectively. Asokbunyarat and Annachhatre (2015) studied arsenic removal from arsenic groundwater using mixtures of fly ash, bottom ash, and bentonite clay in different proportions. Column arsenic removal studies revealed that arsenic removal was the highest for the mixture ratio of 60% bottom ash, 20% fly ash and 20% bentonite clay. The removal of arsenic is attributed mainly to its sorption on the negatively charged surfaces of fly ash, bottom ash, and bentonite clay.

3.6.3 Activated Charcoal

Activated charcoal (activated carbon) is extensively used for the removal of impurities from liquid solutions. Surface adsorption is the predominant removal mechanism in activated charcoal treatment, in which molecules of a liquid or gas are trapped by external or internal surface pores. Activated charcoal is a crude form of graphite that has a random or amorphous structure with high porosity, which results in a very high specific surface area ranging from 300 to 2,500 m^2/g (Kobya et al. 2005; Ansari and Shadegh 2007; Wang et al. 2008). The force that fixes the impurities to the adsorbent surface is called the London dispersion force, which is very strong at a short distance. As a result, adsorbate molecules are held tightly in the pores composed of carbon atoms (Calgon 2007).

Activated charcoal can be produced through chemical or thermal processes and the end product can be in granular or powdered form (Calgon 2007). The different physical properties attributed to activated charcoal are primarily due to the raw material and production processes used in its manufacture. Activated charcoal is mainly produced from coal, wood, peat, coconut shells or petroleum coke that all have a high carbon content. Other raw materials such as bamboo are also used as raw material for the manufacture of activated charcoal, mainly owing to its high carbon content and low nitrogen, sulphur and hydrogen content. As a result, bamboo based activated charcoal has a large number of micro-pores and an extremely large surface area compared to wood charcoal (Wang and Yan 2011).

Chemical activation is a single-step method of preparing activated charcoal in the presence of dehydrating chemical agents such as KOH, $ZnCl_2$, $CaCl_2$ and H_3PO_4. Physical activation involves carbonisation followed by activation in the presence of activating agents such as CO_2 or steam. The carbon yield from chemical activation is higher than that from physical activation, primarily owing to the lower temperatures employed during chemical activation (Pirajan and Giraldo 2012).

Lalhruaitluanga et al. (2010) studied lead (II) adsorption from aqueous solutions by raw and activated charcoals of bamboo. The activated charcoal was a more suitable adsorbent than raw charcoal for the removal of lead (II) from an aqueous solution. The adsorption rate followed the pseudo-second-order model. The adsorption isotherm followed the Langmuir model with a maximum adsorption capacity (q_{max}) of 10.66 mg g^{-1} for raw charcoal and 53.76 mg g^{-1} for activated charcoal. Wang et al. (2008) studied the effect of manufacturing conditions on the adsorption capacity for heavy metal ions by Makino bamboo charcoal. The specific surface area of activated charcoal prepared at 900 °C (794 m^2/g) was larger than at 800 °C (594 m^2/g). The activated charcoal produced from steam activation had a larger average pore diameter as well as better adsorption capacity compared to activated charcoal produced from carbon dioxide activation (Wang et al. 2008).

3.6.4 Zero Valent Iron

Researchers have successfully used zero valent iron to treat acidic water contaminated with heavy metals such as chromium, uranium, arsenic, manganese and zinc (Puls et al. 1999; Wilkin and McNeil 2003; Komnitsas et al. 2007; Jun et al. 2009). Metal removal mechanisms by zero valent iron are not very well understood. However, both adsorption and reductive mineral precipitation processes contribute to metal removal (Wilkin and McNeil 2003).

The mechanisms of heavy metal removal by zero valent iron can involve either chemical reaction followed by precipitation or biochemical reaction followed by precipitation:

(I) Removal through chemical reaction and precipitation as metal hydroxide and metal oxyhydroxide

Contaminant reaction with zero valent iron (ZVI) leads to iron corrosion and generation of hydroxide ion (OH^-) which raises the pH of the water (Jun et al. 2009) as per the following reaction:

$$4Fe^0 + 8H_2O \rightarrow 4Fe^{2+} + 8OH^- + 4H_2 \tag{3.15}$$

OH^- thus generated can react with heavy metals to form hydroxide precipitates, facilitating their removal from water as per the following reaction:

$$Me^{n+} + OH^- \rightarrow Me(OH)_n \tag{3.16}$$

Oxyanions may be formed in some cases and heavy metals may exist in the oxidized states in natural water as in the case of hexavalent chromium as CrO_4^{2-}. In some cases, reductive precipitation may occur as described in the following redox reaction (Komnitsas et al. 2007):

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \tag{3.17}$$

(II) Removal through biochemical reaction and precipitation as metal sulphide and metal hydroxide

Under anaerobic conditions, hydrogen gas (H_2) is formed as a product of zero valent iron (ZVI) corrosion. Alternatively, sulphate reducing bacteria can utilize hydrogen gas as an electron donor or an energy source to reduce sulphate with the release of hydrogen sulphide. The hydrogen sulphide then reacts with heavy metals to form an insoluble precipitate as metal sulphide. For example, the precipitation of iron sulphides can be described by the following reactions (Bartzas and Komnitsas 2010):

$$4Fe^0 + 8H_2O \rightarrow 4Fe^{2+} + 8OH^- + 4H_2 \tag{3.18}$$

$$SO_4^{2-} + 4H_2 \rightarrow HS^- + 3H_2O + OH^- \tag{3.19}$$

$$4Fe^{2+} + HS^- + 7OH^- \rightarrow FeS + 3Fe\left(OH\right)_2 + H_2O \tag{3.20}$$

Researchers studied the capacity of zero valent iron to treat landfill leachates containing heavy metals and other hazardous contaminants (Jun et al. 2009). Zero valent iron could selectively remove Zn, Mn, Ca, Mg, Cd, Cr, Sr and Al and removal efficiencies ranged between 46% and 93%. The heavy metals precipitated as hydroxide, carbonate and sulphide compounds as the pH value increased from 6.9 to 8.2. In another study, researchers evaluated the acid-neutralisation and metal removal rates with zero valent iron (Wilkin and McNeil 2003). Experiments at an initial pH of 2.3, 3.5 and 4.5 achieved significant reduction in metal concentrations with an increase in pH value from 2.3–4.5 to 5.5–10.0. The heavy-metal removal rates followed the following sequence: Al>Cu>As>Cd>Ni>Zn, while the corresponding reaction half-lives were from 1.50 (±0.09) h for Al to 8.15 (±0.36) h for Zn. The dominant corrosion product from the reaction was sulphate green rust (likely $Fe_6(OH)_{12}SO_4$).

3.6.5 Organic Residues

In biological systems, permeable reactive barriers employ natural organic substrates as electron donors to facilitate the growth of sulphate reducing bacteria. When an acid mine drainage plume containing sulphate and heavy metals passes through the reactive barrier, the sulphate reducing bacteria in the reactive barrier converts sulphate into sulphide, while consuming the organic substrates as electron donors (Tsukamoto et al. 2004). Heavy metals present in the contaminated feed water are then removed as metal sulphides (Dvorak et al. 1992; Jong and Parry 2003), according to:

$$\mathrm{SO_4^{2-} + Organic\ Matter \rightarrow HS^- + HCO_3^-} \tag{3.21}$$

$$\mathrm{HS^- + M^{2+} \rightarrow MS_{(s)} + H^+} \tag{3.22}$$

Sulphate-reducing bacteria, which are heterotrophic, require specific environmental conditions for their growth and activity, such as anaerobic conditions, pH of 5–8, temperature of 20–35 °C and the presence of a carbon compound to act as carbon source and electron donor.

A variety of organic substrates can be used as electron donors for sulphate-reducing bacteria (Liamleam and Annachhatre 2007). Organic residues such as alfalfa, leaves, biological sludge, sawdust, agricultural residues, manure and compost are commonly used in permeable reactive barriers (Waybrant et al. 1998; Pagnaneli et al. 2009; Gibert et al. 2011). A physical support for bacterial attachment increases their concentration. However, in subsurface soil environments, a lack of readily available organic carbon is the most common limitation for biological sulphate reduction (Gibert et al. 2002). The use of natural organic substrates as electron donors for sulphate reducing bacteria in permeable reactive barriers is more appropriate because of their ease of availability and cost considerations (Costa et al. 2007).

The biodegradable fraction in an organic residue often dictates its selection as an electron donor since the lignin content in the organic residue can affect its biodegradability. Lignin, which is a complex phenolic polymer (Pouteau et al. 2003), serves an important function in plant defence owing to its insolubility and complexity, which makes it resistant to degradation by most microorganisms (Campbell and Sederoff 1996). Chandler et al. (1980) showed that the biodegradable fraction can be an important indicator for the overall degradability of an organic substrate and put forward the following equation:

$$\mathrm{B = -0.028X + 0.830} \tag{3.23}$$

where biodegradable fraction (B) is based on a volatile solid content and X is the lignin content of the volatile solid, expressed as percent dry weight. The biodegradability of the organic substrate decreased with increase in its lignin content (Gibert et al. 2004). Concomitantly, its ability to develop bacterial activity also decreased.

Kijjanapanich et al. (2012) used plant and microbial organic substrates as electron donors for sulphate reducing bacteria for their possible use in permeable reactive barriers. Plant organic residues such as rice husk, coconut husk chips and bamboo chips had a higher lignin content (24.4–46.5%), while the microbial organic residues such as pig farm wastewater treatment sludge and municipal wastewater treatment sludge had lower lignin contents (He et al. 1998; Vu et al. 2003). Kijjanapanich et al. (2012) studied the sulphide precipitation of heavy metals by mixed populations of sulphate reducing bacteria in batch as well as continuous columns. These investigations clearly showed that organic substrates with a lower lignin content degraded faster than organic substrates from plant, which had a higher lignin content. Consequently, a mixture of organic substrates with microbial as well as plant was proposed as electron donor in permeable reactive barriers.

3.7 Comparison of Reactive Materials

A comparison of the relative order of sorption of metal ions onto various sorbents as reported in the literature is presented in Table 3.8. As this data brings out, all researchers indicate that Mn(II) is the most difficult ion to remove by sorption onto various sorbents as evidenced by the fact that its relative order is always the last in comparison with other metal ions. Otherwise, the reported observations are not conclusive with respect to the relative order of metal ion sorption with various adsorbents. It is anticipated that the metal ion removal by various adsorbents depends upon the adsorbent composition, surface charge distribution and the pore size vis-à-vis the metal ion characteristics such as hydration radius, hydration energy and electro negativity. These factors make it difficult to predict the relative order of metal ion sorption for a specific sorbent.

Table 3.9 compares the removal mechanism, metal sorption capacity, kinetic model and isotherm model followed by various sorbents as reported in the literature. As these data reveal, adsorption and precipitation (hydroxide and sulphide precipitation) are the predominant metal removal mechanisms. The data also bring out that the sorption capacity of coconut shell activated charcoal and bituminous-activated charcoal is higher than that of other sorbents. On the other hand, silica-alumina based adsorbents such as natural zeolite, kaolinite, coal fly ash and coal bottom ash have similar sorption capacities. The data also reveal that the sorption capacity of Fe(II) is always the highest, while that of Mn(II) is always the lowest. In most cases, the heavy metal removal follows a pseudo-second-order kinetic fit, while the adsorption follows the Langmuir isotherm model.

Table 3.8 Relative order of sorption of metal ions onto various sorbents – note that Mn(II) is the most difficult to remove through adsorption

Adsorbent	Relative order of sorption	Reference
Coal fly ash	Zn(II) > Cu(II) > Mn(II)	Mohan and Gandhimathi (2009)
Coal bottom ash	Fe(II) > Cu(II) > Zn(II) > Mn(II)	Asokbunyarat et al. (2015a)
Kaolinite	Cu(II) > Mn(II)	Yavuz et al. (2003)
Coconut shell-AC	Fe(II) > Mn(II)	Mohan and Chander (2001)
Bituminous-AC	Fe(II) > Mn(II)	Mohan and Chander (2001)
Natural zeolite	Cu(II) > Zn(II) > Mn(II)	Erdem et al. (2004)
PWTS+RH+CHC	Fe(II) ≥ Cu(II) ≥ Zn(II) > Mn(II)	Kijjanapanich et al. (2012)

AC Activated charcoal, *PWTS* pig farm wastewater treatment sludge, *RH* rice husk, *CHC* coconut husk chips

Table 3.9 Comparison of the metal removal mechanism, sorption capacity, kinetic model and isotherm model of various sorbents – note that in most cases the adsorption kinetics follow the pseudo-second-order model while the adsorption isotherm follows the Langmuir model

Adsorbents	Removal mechanism	L/S ratio (L/kg)	Maximum adsorption capacity, q_m (mg/g)				Kinetic model	Isotherm model	References
			Fe(II)	Cu(II)	Zn(II)	Mn(II)			
Coal fly ash	Hydroxide precipitation, adsorption	10:1	–	–	4.505	–	Pseudo-second-order kinetic	Freundlich isotherm	Agarwal et al. (2012)
Coal bottom ash	Hydroxide precipitation, adsorption	500:1	24.213	13.441	5.423	2.335	Pseudo-second-order kinetic	Langmuir isotherm	Asokbunyarat et al. (2015a)
Kaolinite	Adsorption	100:1	–	10.787	–	0.446	–	Langmuir isotherm	Yavuz et al. (2003)
Montmorillo-nite	Adsorption	500:1	–	28.8	–	–	Pseudo-second-order kinetic	Langmuir isotherm	Bhattacharyya and Gupta (2006)
Coconut shell-AC	Adsorption	167:1	46.4	–	–	16.4	–	Langmuir isotherm	Mohan and Chander (2001)
Bituminous-AC	Adsorption	167:1	14.6	–	–	9.72	–	Langmuir isotherm	Mohan and Chander (2001)
Natural zeolite	Hydroxide and sulfide precipitation	50:1	–	8.96	8.75	4.21	–	Langmuir isotherm	Erdem et al. (2004)

AC Activated charcoal, – data not provided

3.8 Conclusion

The permeable reactive barrier is now a matured technology for the treatment of heavy metal containing groundwater. Contamination of groundwater can take place from seepage of acid mine drainage or from landfill leachate. A permeable reactive barrier, which employs reactive media, is placed across the contaminated groundwater flow and the contaminants are then removed by reactive media in the permeable reactive barrier. For this reason, proper soil and groundwater flow characterisation is of utmost importance. Groundwater flow can be directed through the permeable reactive barrier at the necessary velocity by the use of the funnel and gate system. The necessary residence time of groundwater flow in the permeable reactive barrier is estimated through laboratory scale investigations undertaken to evaluate the kinetics of contaminant removal by reactive media. Media employed in the permeable reactive barrier can be either organic or inorganic by nature. The mechanisms for contaminant removal by media may involve sorption, precipitation or degradation. Organic media may include a variety of agricultural residues as electron donors to initiate biological sulphate reduction activity by sulphate reducing bacteria. Sulphide produced by sulphate reducing bacteria can remove the contaminant heavy metals from the groundwater flow through sulphide precipitation. On the other hand, inorganic media employed in a permeable reactive barrier may consist of natural clays, coal ash, activated charcoal or zero valent iron. Adsorption and hydroxide precipitation can be the dominant mechanisms for the removal of heavy metals by inorganic media. The capacity and the kinetics of the contaminant removal by the inorganic media need to be evaluated through laboratory investigations. The capacity and quantity of the media in the permeable reactive barrier may dictate its life time, beyond which the used media in the permeable reactive barrier must be removed and the permeable reactive barrier must be refilled with new media. Advantages offered by a permeable reactive barrier over conventional pump and treat technologies include low energy requirements as well as reduced cost due to little or no operation and maintenance. On the other hand, the permeable reactive barrier technology may also offer certain disadvantages such as finite life of the reactive barrier as well as possibility of its clogging.

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Chapter 4
Precipitation of Heavy Metals

Alison Lewis

Abstract Precipitation is the process of solid formation from solution by means of a reaction. It is most frequently used in the removal and recovery of metals from solution. In scientific terms, precipitation is affected by a chemical reaction that forms a salt whose solubility in solution is exceeded. The thermodynamic driving force causing precipitation is called supersaturation. Definitions of supersaturation are not consistent in the literature, and a variety of equations are used for the calculation of supersaturation. The major mechanisms comprising precipitation are nucleation, growth and agglomeration. High supersaturation levels favour nucleation, whilst lower levels favour crystal growth. Agglomeration occurs in the presence of large numbers of particles, in a supersaturated environment.

Precipitation is commonly used for metal removal from wastewaters, but is not yet commonly used for metal recovery from wastewaters. Metal hydroxide precipitation is the most commonly used method, although metal sulphide precipitation has many advantages. Other methods of metal removal can be in the form of sulphate (e.g. $CaSO_4.2H_2O$) or fluoride (e.g. CaF) salts.

Crystalliser design for water treatment ranges in complexity from the simplest pipe reactor to the more sophisticated fluidised bed reactor, which is an extremely effective design for metal removal and recovery.

In summary, when using precipitation as an extremely effective metal removal and recovery method, careful attention must be paid to designing precipitation systems that are able to produce precipitates with desirable separation characteristics.

Keywords Precipitation • Supersaturation • Solubility • Nucleation • Growth • Agglomeration • Metal hydroxide • Metal sulphide • Fluidised bed reactor

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Contents

4.1 Introduction

Precipitation is defined as the process that occurs when, by virtue of a chemical reaction, the solubility of a salt in solution is exceeded. In this case, the solution is said to be supersaturated with respect to the precipitating compound, meaning the solute concentration is higher than the solid-liquid equilibrium value. The degree of supersaturation is important because it is the driving force for the precipitation process and is always required to effect precipitation.

In the case of precipitation, the method used to alter the equilibrium conditions and thus to generate supersaturation is the addition of another substance or reagent to the system (Ullmann and Gerhartz 1998).

For example, the mixing of two reagents, such as $CuSO_4$ and Na_2S, results in the following chemical reaction.

$$CuSO_4 + Na_2S \rightarrow CuS(s) + Na_2SO_4 \tag{4.1}$$

The chemical reaction creates the sparingly soluble salt, CuS, which, because its solubility is exceeded, will precipitate out of solution.

4.1.1 Thermodynamics of Precipitation

In more technical terms, if a system is to be in thermodynamic equilibrium, then the requirement is that there must be equal chemical potentials of each component through all phases. Let μ_{Liquid} and μ_{Solid} (J/mol) be the chemical potential of the precipitating salt in the solution and as a solid, respectively. If the system is in equilibrium then:

$$\mu_{Liquid,eq} = \mu_{Solid} \tag{4.2}$$

Suppose the system is driven out of its equilibrium state due to some external action, e.g. addition of another substance, so that the solution becomes supersaturated. The chemical potential of the solute in solution μ_{Liquid} is now higher than the corresponding equilibrium value $\mu_{Liquid,eq}$. The difference between the chemical potential of the solute in the supersaturated and the saturated state is represented by $\Delta\mu$ (J/mol), and is the thermodynamic driving force for precipitation:

$$\Delta\mu = \mu_{Liquid} - \mu_{Liquid,eq} = \mu_{Liquid} - \mu_{Solid} \tag{4.3}$$

This thermodynamic driving force is referred to as the supersaturation.

In the case of precipitation with the solid composed of more than one solute of a chemical formula of the type: $A_{vA}B_{vB}\ldots I_{vi}$, i.e. formed by ν_i units of species i, the equation for the driving force is written:

$$\Delta\mu = RT\ 1\text{n}\frac{\Pi a_i^{v_i}}{\mathrm{K}_{sp}} = \frac{\Pi\left(\gamma_i c_i\right)^{v_i}}{\mathrm{K}_{sp}} = RT\ 1\text{n}\ S_{am} \tag{4.4}$$

$$\mathrm{K}_{sp} = \Pi\left(\gamma_{i,eq} c_{i,eq}\right)^{v_i} \tag{4.5}$$

Where

R = ideal gas constant [J/mol/K]
T = temperature *[K]*
a = activity of the solute [M]
ν_i = number of the ith ion in a molecule of the crystal
γ_i = activity coefficients of the solute in solution [−]
c = molar concentration of the solute in solution
K_{sp} = solubility product of the solid [m^{υ}]
S_{am} = activity-based supersaturation ratio for multiple solutes [−]

Following on from this the supersaturation, S_{am}, is written as:

$$S_{am} = \frac{\Pi\left(\gamma_i c_i\right)^{v_i}}{\mathrm{K}_{sp}} \tag{4.6}$$

There is some discrepancy in the expressions for supersaturation that exist in the literature. For example, Sohnel and Garside (1992) give the following equation:

$$S_a = \frac{a_{\pm}}{a_{\pm,eq}} \tag{4.7}$$

Where

S_a = dimensionless supersaturation based on activities
$a_{\pm}$ = mean activity
$a_{\pm,eq}$ = mean activity at equilibrium (i.e. the solubility product)

Whereas Kashchiev and van Rosmalen (2003) give the following, for ionic molecules which dissociate into solution as ions of type i = 1, 2, …, j:

$$s_a = \left(\frac{a_1^{\upsilon 1} a_2^{\upsilon 2} \ldots a_j^{\upsilon j}}{a_{1,eq}^{\upsilon 1} a_{2,eq}^{\upsilon 2} \ldots a_{j,eq}^{\upsilon j}} \right)^{\frac{1}{(\upsilon_1 + \upsilon_2 + \ldots + \upsilon_j)}} \tag{4.8}$$

Where

ν_i = number of the ith ion in a molecule of the crystal;
a_i = actual activities of these ions in the solution (m^{-3}).
$a_{i,e}$ = equilibrium activities of these ions in the solution (m^{-3}), i.e. the solubility product

For molecules such as $BaSO_4$ and $CaCO_3$, where $\nu_1 = \nu_2 = 1$, i.e. there is one cation and one anion in a molecule of a crystal, this equation simplifies to:

$$s_a = \left(\frac{a_1^1 a_2^2}{K_{sp}} \right)^{\frac{1}{2}} \tag{4.9}$$

Thus, when dealing with the calculation of the supersaturation, it is important to always check on the definition being used, as these are not consistent in the literature.

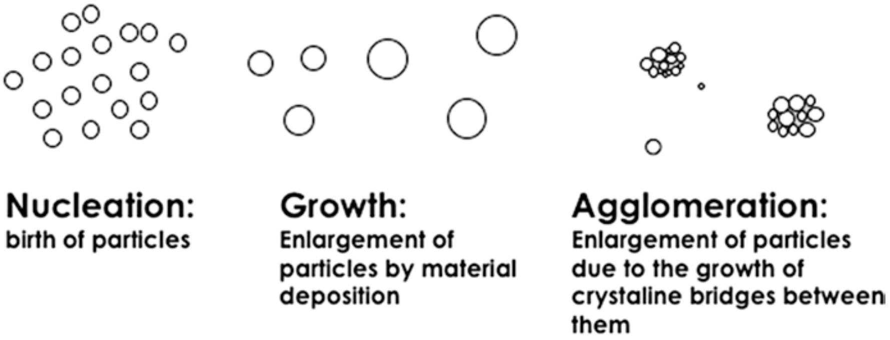

Fig. 4.1 Summary of the three major precipitation mechanisms: nucleation, growth and agglomeration

4.1.2 *Kinetics of Precipitation*

Once it has been established that a precipitation process is thermodynamically possible, in other words, that the solution is supersaturated with respect to the precipitating phase, it is usually of interest to establish the kinetics of the process, i.e. how fast the process is likely to happen. This involves understanding the various mechanisms by which the precipitation process occurs. The mechanisms are summarised in Fig. 4.1.

- **Nucleation**

Nucleation is the initial formation of the solid phase from solution. It occurs once the clusters and aggregates of molecules or ions in a supersaturated solution achieve a critical size, i.e. one at which the entities will grow rather than redissolve (Jones et al. 2004). Primary homogenous nucleation is the birth of a solid phase spontaneously from solution, whereas primary heterogeneous nucleation is induced by the presence of foreign particles. Secondary nucleation is induced by the presence of existing crystals and can take many forms, including contact nucleation such as crystal-crystal contact or crystal-crystalliser contact, shear nucleation such as that due to fluid flow, fracture nucleation due to particle impact, attrition nucleation due to particle impact from fluid flow and needle nucleation due to particle disruption (Jones et al. 2004).

The rate of nucleation is a function of supersaturation, with very high supersaturation levels favouring primary nucleation, and slightly lower levels favouring secondary nucleation.

- **Growth**

Growth is the process whereby crystals become enlarged due to the deposition of crystalline material on an existing crystal surface.

The growth rate is also a function of the supersaturation, with growth occurring at lower levels of supersaturation than that required for nucleation. The type of

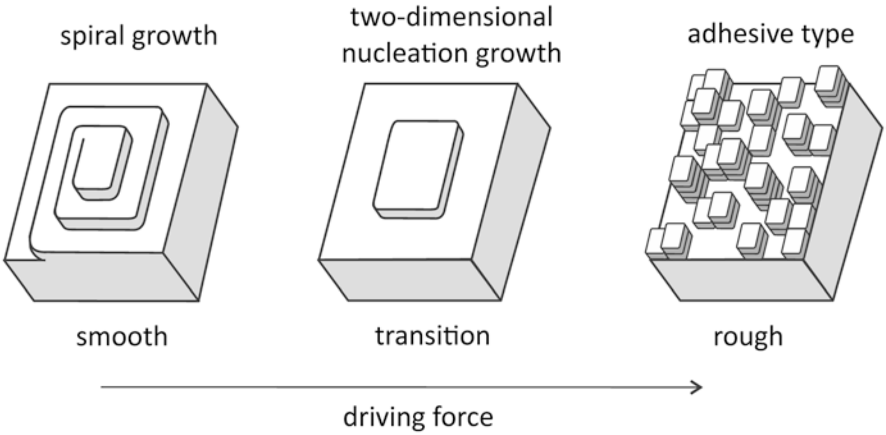

Fig. 4.2 Relationship between supersaturation and type of growth (Lewis et al. 2015)

growth that will occur is also influenced by the supersaturation levels, with rough growth favoured at high supersaturation levels, birth and spread growth favoured at intermediate supersaturation levels, and spiral or smooth growth favoured at low supersaturation levels. See Fig. 4.2.

It is the relative rates at which nucleation and growth occur that determine the final particle size distribution. As would be expected, when the rate of nucleation is high relative to the growth rate, the crystals formed are small and highly numerous (Kroschwitz and Seidel 2006). This is frequently the case in precipitation from solution in water treatment processes.

- **Agglomeration**

Agglomeration is the process in which two or more particles are brought in contact and stay together for a sufficiently long period such that a crystalline bridge between the particles can grow. Thus a stable particle or agglomerate is formed.

As for nucleation and growth, the rate of agglomeration is a function of the supersaturation but also, since it is a collision-driven process, a function of the square of the numbers of particles present. Therefore, it follows that, when there is a high degree of nucleation in a process, which leads to the formation of high numbers of particles, the collision rate, and thus the agglomeration rate, is likely to be high.

Sometimes particle agglomeration is the only available method of size enlargement in a precipitation process. Because of the large numbers of particles involved, it usually plays an important, but not always desirable, role in the formation of larger particles in precipitation and crystallisation processes (Lewis et al. 2015). As would be expected, agglomerates usually have a lower degree of purity than crystals that become larger due to crystal growth, as mother liquor tends to become trapped in the interstitial spaces between the agglomerated crystals.

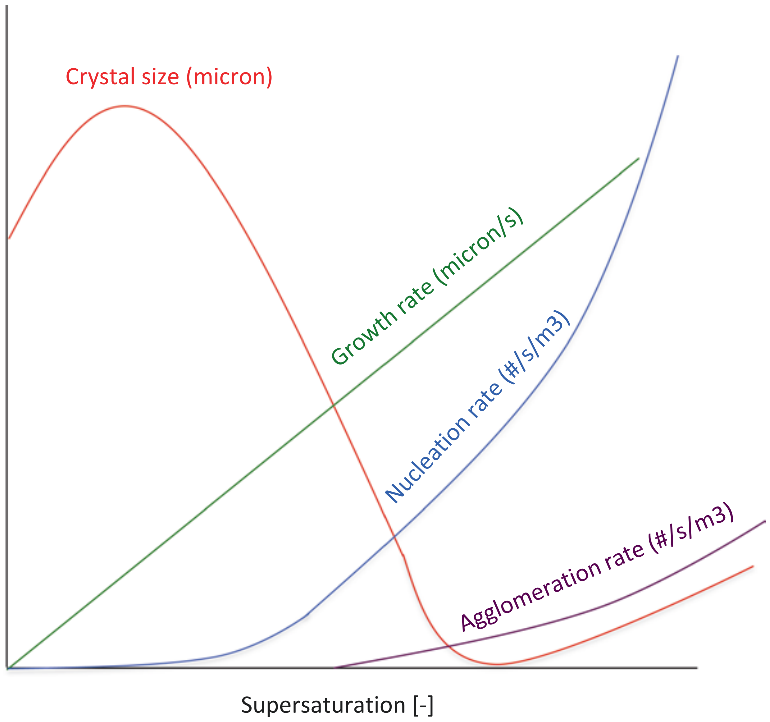

Fig. 4.3 Relationship between supersaturation, nucleation, growth and agglomeration as well as crystal size. With an increase in supersaturation, the growth rate increases linearly. After a critical supersaturation, the nucleation rate increases exponentially. Agglomeration becomes significant at higher supersaturation levels (Lewis et al. 2015)

Figure 4.3 summarises the relationships between the supersaturation, the crystal size and the three main precipitation mechanisms outlined above.

4.2 Use of Precipitation in Removal and Recovery of Metals from Wastewater

Precipitation is commonly used for metal removal from various types of wastewaters, including hydrometallurgical effluents and acid mine drainage. Once the metals have been precipitated, they can be filtered, centrifuged, or separated by another means from the remaining aqueous phase. In addition, if a voluminous precipitate is formed, it can effectively "sweep" ions and particles from the wastewater (USEPA 2000).

Although chemical precipitation is used in around 90 % of treatment plants treating industrial wastewaters (Schiewer and Volesky 2000; Grijalva 2009), recovery of metals by precipitation is not yet common practice. Currently, the primary objective is the removal of the metals for the purpose of water treatment, and not for the metal values themselves.

Table 4.1 Solubility constants of metals for four different metal salts

	Solubility products (Log K_{sp})			
Metal	OH^-	CO_3^{2-}	PO_4^{3-}	S^{2-}
Ag^+	−7.7	−11.1	−17.6	−49
Cd^{2+}	−14.3	−13.7	−32.6	−28.9
Co^{2+}	−15.9	−12.8	–	–
Cu^+	−19.4	−9.6	−35.1	−36
Fe^{2+}	−15.9	−10.6	−36	−16.8
Fe^{3+}	−37.1	–	–	–
Hg^{2+}	−25.4	−22.5	–	−52
Ni^{2+}	−17.2	−6.8	−31.3	−18.5
Pb^{2+}	–	−13.1	−44.5	−28.1
Zn^{2+}	−15.6	−10.3	−36.7	−22

The United States Environmental Protection Agency (USEPA) initiated some of the early patents on metal removal by chemical precipitation in order to treat wastewater (Wemhoff 1984; Greenberg 1990). There are a number of possible chemical precipitation methods for removing heavy metals[1] from wastewater, including hydroxide (OH^-), sulphide (S^{2-}), carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) precipitation. The solubilities of these most commonly employed metal salts is given in Table 4.1 (Grijalva 2009).

Other precipitation methods for wastewater treatment employ calcium hydroxide for the removal of fluoride from industrial wastewater as calcium fluoride (Aldaco et al. 2005).

4.3 Metal Hydroxide Precipitation

4.3.1 *Advantages*

Metal hydroxide precipitation is the most widely used of the chemical precipitation techniques for water treatment, mostly because it is cheap, easy to implement and can be relatively easily controlled by controlling pH. Traditionally, water treatment processes, especially water neutralisation processes, have been based on chemical neutralisation using a base such as quicklime (CaO), hydrated lime ($Ca(OH)_2$, limestone ($CaCO_3$) or the hydroxides of Mg, Na and NH_4^+. When a solution containing dissolved metal ions is contacted with a base, the result is precipitation of the metals in solution as metal hydroxides.

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[1] There is no widely agreed criteria-based definition of a heavy metal. See Duffus, J. H. (2002). "Heavy metals" a meaningless term? (IUPAC Technical Report)." Pure and Applied Chemistry **74**(5): 793–807. http://dx.doi.org/10.1351/pac200274050793

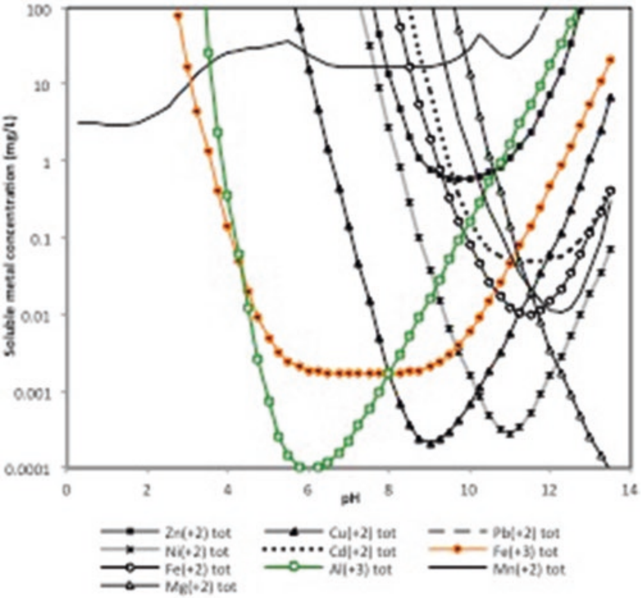

Fig. 4.4 Metal hydroxide solubilities as a function of pH (Lewis 2010)

4.3.2 *Disadvantages*

Although this method is the most widely used, it has several disadvantages, namely high cost, lack of effectiveness in reducing sulphate in solution and the formation of large volumes of sludge, which require disposal (Erdem and Tumen 2004).

In addition, the final metal concentration level that can be achieved is not very low and concentrations remain at levels from 0.5 to 2 mg/L (Grijalva 2009). See Fig. 4.4, which shows that the minimum dissolved concentration that can be achieved by hydroxide precipitation is ±0.0005 ppm at pH levels between 6 and 12. An additional difficulty is that hydroxides tend to form gelatinous precipitates that are difficult to thicken or filter (Peters 1985).

4.4 Metal Sulphide Precipitation

4.4.1 *Previous Studies*

Although several studies have been conducted on precipitation of metal sulphides from solution (Bryson and Bijsterveld 1991; Mishra and Das 1992; Rickard 1995; Harmandas and Koutsoukos 1996; Veeken et al. 2003; van Hille et al. 2004, 2005;

Bijmans et al. 2009; Sampaio et al. 2010), the physico-chemical processes of nucleation and crystal growth involved in the precipitation of metals as sulphides still remain uncertain.

The review article by Lewis (2010) pointed out how the study of metal sulphide precipitation has been extremely fragmented, with the research being carried out in the disparate areas of: (1) fundamental studies, which have usually focused on mechanisms and have been carried out at very low (micromolar) concentrations, (2) applied studies, which have usually focused on metal removal and aqueous phase reaction kinetics, (3) solid phase studies, which have focused on the crystallisation kinetics of the formed solids; (4) precipitation studies, which have focused on precipitation of metal sulphide nanocrystals. The last area of focus has been (5) metal sulphide precipitation in effluent treatment such as acid mine drainage and industrial hydrometallurgical processes.

4.4.2 Advantages

Metal sulphide precipitation is another method of removing metal ions for wastewater treatment. This method has the advantage of the potentially high removal efficiency and selective metal precipitation over a broad pH range.

One of the main advantages of sulphide precipitation can be seen in Fig. 4.5, which shows the metal sulphide solubilities as a function of pH. Figures 4.5 shows that the solubilities of a range of metal sulphides is extremely low. This means that there is potential for effective metal removal to extremely low concentrations.

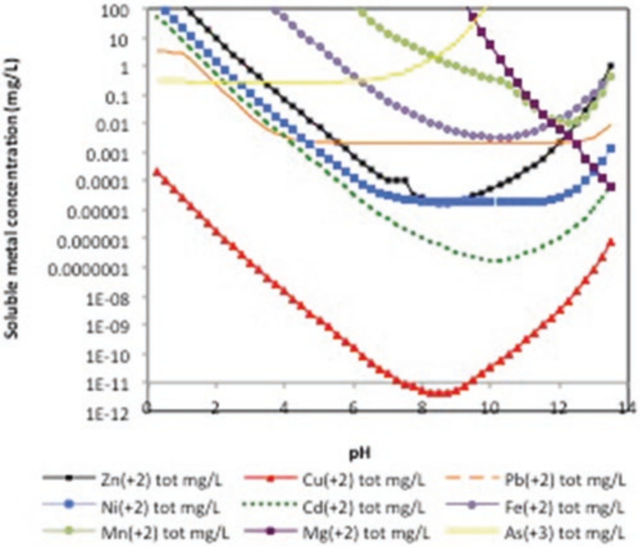

Fig. 4.5 Metal sulphide solubilities as a function of pH (Lewis 2010)

For example, the minimum residual Cd concentration when Cd is removed as a metal sulphide is less than 0.0001 mg/L, which occurs at any pH greater than 6 (see Fig. 4.5, compared to the minimum residual Cd concentration of 0.048 mg/L when Cd is removed as a hydroxide at pH 11.5 (See Fig. 4.4).

In chemical process applications, this treatment technology has been relatively limited due to the cost of the chemicals, but also due to safety concerns around the generation of hydrogen sulphide gas, particularly when treating acidic effluents (Nduna and Lewis 2014).

However, metal sulphide precipitation has more recently been successfully used as a means to remove metals from solution in the treatment of acid mine drainage, also called acid rock drainage. Here, sulphate-reducing bacteria are used, during which process the acidic sulphate is reduced to sulphide by the bacteria. Tabak et al. (2003) developed a resource recovery-based remediation process to clean up a polluted mine site in the USA. Veeken and Rulkens (2003) investigated selective precipitation of heavy metals using a sulphide-selective electrode for control. Kaksonen and Puhakka (2007) carried out a review of various passive and active SRB-based alternatives as well as some process design aspects, such as reactor types, process configurations, and choices of substrates for sulphate reduction. Huisman et al. (2006) described a biological process that produced sulphide H_2S from elemental sulphur, waste sulphuric acid or sulphate present in effluents. This H_2S was then used in an engineered, high rate bioreactor to treat metal containing effluents.

Aside from the safety concerns mentioned above, the use of H_2S as a gaseous form of sulphide has many advantages, including the fact that the produced metal sulphides have good settleability and filterability (Huisman et al. 2006). The mechanism by which the H_2S improves the particle properties is due to the fact that the gaseous sulphide source decreases the rate of generation of supersaturation by exploiting the mass-transfer resistance to dissolution of $H_2S(g)$ and thus exerts a measure of control over the precipitation process (Karbanee et al. 2008).

4.4.3 Disadvantages and Challenges

The essential problem with being able to use metal sulphide effectively for metal removal and recovery remains the particle characteristics of the formed metal sulphide precipitates. Because of the extremely low solubilities of the metal sulphide salts, this means that the process will be driven by very high supersaturations. As a consequence of this extremely high driving force, the resulting precipitation reaction is difficult to control and a large number of submicron particles are formed during the process. Thus, solid-liquid separation and subsequent recovery become a significant technical challenge and, despite the low solubility and theoretically high efficiency of metal sulphide precipitation processes, the practical efficiency is often significantly lower.

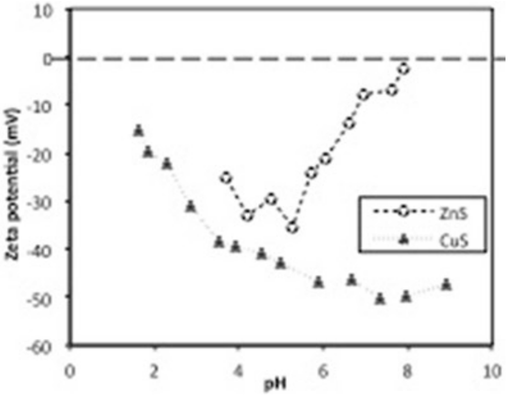

Fig. 4.6 Relationship between the pH of precipitation and the zeta potential of the precipitated particles for CuS and ZnS (Lewis and Nduna 2014)

In addition, colloidal metal sulphide precipitates exhibit surface properties that often prevent agglomeration and therefore settling of the precipitates. This has been demonstrated in a number of works that examined the effect of the pH at which the metal sulphide particles were precipitated and their resulting zeta potential (Mokone et al. 2010; Nduna et al. 2013). The findings show that there is a strong relationship between the measured zeta potential of the final particles and the precipitation pH. As can be seen in Fig. 4.6, for CuS, there is a marked decrease in zeta potential, i.e. the zeta potential becomes more negative, as the precipitation pH increases from 2 to 9. In contrast, for ZnS, the zeta potential increases, i.e. becomes less negative, as the precipitation pH is increased from 6 to 8. This is due to the effects of two counteracting phenomena. As the pH increases, the effect of the increasing concentration of S^{2-} ions is felt, and the zeta potential decreases. At the same time, the metal cations exert a counteracting positive effect.

Other works have focused on how the metal to sulphide molar ratio affects the final precipitated particles (Mokone et al. 2010, 2012a, b). It was found that, in the CuS system, a large number of small copper sulphide particles, with highly negatively charged surfaces and poor settling characteristics, were formed in the presence of a stoichiometric excess of sulphide at pH 6. In contrast, for ZnS, the metal to sulphide molar ratio did not have a significant effect on the number and size of the particles formed. This emphasises that the concentration of reactive sulphide species in solution is crucial in determining the nature and surface characteristics of the particles produced.

A number of methods can be used to mitigate the effect of the very high supersaturation conditions experienced in metal sulphide precipitation, including recycling a portion of the precipitated settled solids to the reaction vessel (Adams et al. 2008), adding the reagent, usually H_2S, to a mixture of feed solution and recycled solids (Merritt et al. 1985) or redesigning the reactor itself to minimise locally high supersaturation levels (Lewis et al. 2015).

4.4.4 Post Precipitation Conditions

It is also known that downstream processing conditions have an effect on the surface properties of the colloidal particles produced during metal sulphide precipitation. This downstream processing can include the addition of divalent and trivalent cations such as (Ca^{2+}) and (Al^{3+}) that can favourably modify the precipitate properties. Mokone et al. (2012a, b) showed that, where supersaturation cannot be managed, downstream processing that changes the surface properties of colloidal metal sulphide precipitates can lead to effective solid-liquid separation.

4.5 Sulphate Salts

It is also possible to remove and recover sulphur as sulphate salts, without the reduction step. An example of this is the removal of sulphate via precipitation of gypsum ($CaSO_4.2H_2O$) from acid mine drainage and lime (Dill et al. 1998). In this case, calcium hydroxide is provided as the source of calcium and, in the case of acid mine drainage, the added calcium ions react with sulphate ions, and produce a gypsum precipitate, among other mineral compounds. As in the case of metal sulphide precipitation, it has been found that gypsum forms very small particles during precipitation, which are difficult to separate from the treated liquid through gravitational settling or filtration. According to Bowell (2004), the low solubility of $CaSO_4.2H_2O$ results in a low residual SO_4^{2-} level of about 0.24 g/100 ml at 20 °C, after $CaSO_4.2H_2O$ removal. However, metals are not removed via this method, except via adsorption onto the precipitated gypsum.

4.6 Crystalliser Design for Wastewater Treatment

In order to successfully remove metals from wastewater using precipitation, the design of a crystalliser or reactor that can deliver the necessary particle characteristics is crucial. The default industrial practice is the stirred tank reactor, with reagents being added at a single point and mixed into the reactor bulk using a central impeller. This method leads to very poor particle characteristics, whether sulphide or hydroxide precipitates.

4.6.1 Pipe Reactor

An extremely simple metal sulphide precipitation reactor that is frequently used in industry is the “pipe reactor”. This simple pipe junction design, schematically illustrated in Fig. 4.7, exploits the very rapid kinetics of the metal sulphide precipitation

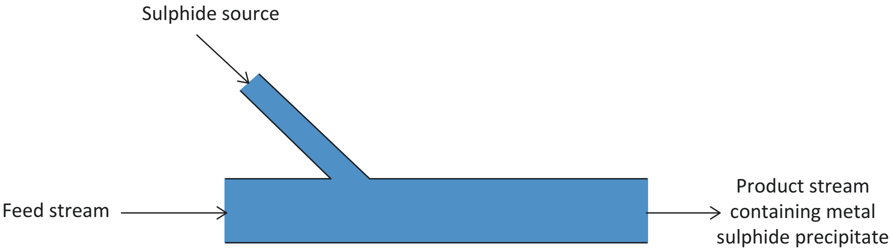

Fig. 4.7 Schematic of the pipe reactor commonly used in industry

reaction, which occurs in the pipe itself. The advantages of this reactor are the simplicity and ease of operation. The disadvantages are that the local supersaturation induced by introducing the sulphide in this manner is extremely high, and thus the particle properties are usually poor.

4.6.2 Fluidised Bed Reactor

One of the most successful methods that has been employed for wastewater treatment via precipitation is the use of the Fluidised Bed Reactor.

4.6.2.1 Crystalliser Description

Fluidised Bed Reactors have been identified as an effective reactor configuration for processes in which the product is a sparingly soluble species that is difficult to separate. Fluidised Bed Reactors have been extensively used in industry with applications in the softening of potable water (Aldaco et al. 2007) and in the removal of heavy metals, phosphates and fluorides from wastewater (Seckler 1994). Aqueous waste streams generated from acid mine drainage, electroplating and base metal refining operations, with dissolved metal concentrations varying from 10 to 100,000 ppm have also been successfully treated using precipitation in fluidised bed reactors (Wilms et al. 1992; Zhou et al. 1999; Guillard and Lewis 2001, 2002; Kaksonen et al. 2003; van Hille et al. 2005; Costodes and Lewis 2006).

Fluidised bed reactors provide ideal conditions for controlled precipitation and as a result present many advantages over conventional chemical precipitation processes. Some of the advantages of fluidised bed reactors are:

- Fluidisation allows for good mixing on both the macro and meso-scale, so that local supersaturation levels can be controlled.
- Supersaturation can be controlled through multiple reagent inlet ports.
- The product can be separated from the treated water using gravitational separation, as the large crystals migrate to the bottom of the bed where they are

harvested (Al-Othman and Demopoulos 2009). Fines generated during precipitation can be recycled and allowed to agglomerate, thus forming large particles, which can be recovered, thus increasing the solid-liquid separation efficiency (Heffels and Kind 1999; Guillard and Lewis 2001). Fluidised bed reactors are typically modelled as plug flow reactors (Levenspiel 1999, 2002)

- Physical phenomena are accurately described by the axial dispersion model (Toyokura et al. 1973; Wojcik 1999).
- Crystal-impeller collisions, like those in a stirred tank reactor, which result in attrition, and therefore fines generation, are eliminated.

In a fluidised bed reactor, the vessel is charged with a batch of pre-characterised seeds, which are subsequently fluidised by the aqueous metal stream entering the reactor from the bottom. The reagent is fed through inlet ports situated on the side of the reactor. Figure 4.8 illustrates the working principle of the reactor.

As precipitate is deposited on the seeding material, the particle size distribution along the height of the column changes. Larger, denser particles migrate to the bottom of the reactor where they are removed as a product, while the lighter particles remain suspended higher up in the bed. In continuous processes, new seeding material is introduced at the top of the reactor, while large particles are removed at

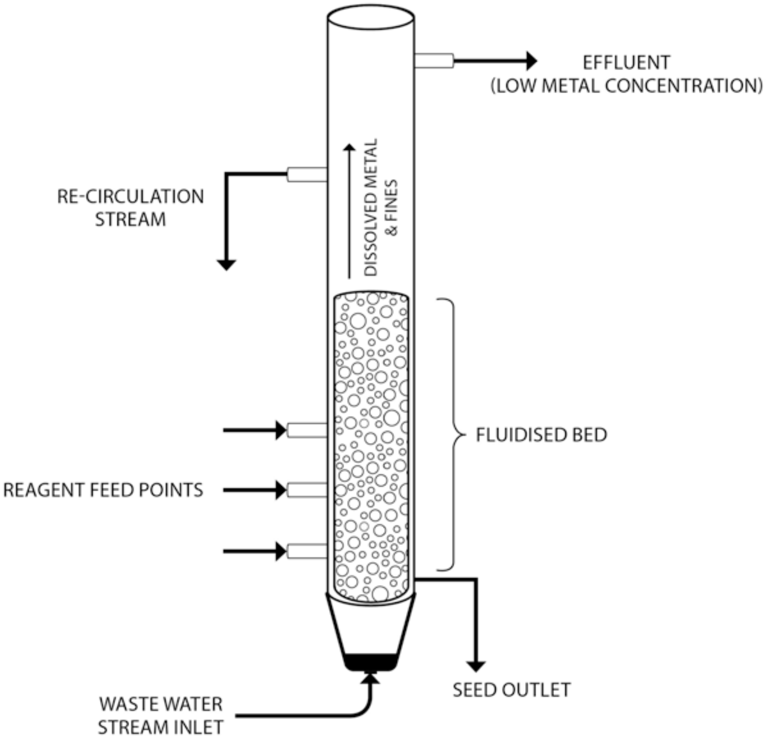

Fig. 4.8 Schematic of a fluidised bed crystalliser (Adapted from Seckler 1994)

the bottom to maintain a constant bed height (Guillard and Lewis 2001; van Hille et al. 2005). The remaining mother liquor exits the top of the reactor. In some cases, the effluent stream is recirculated to increase conversion of unreacted metal. Key parameters of operation are the reactant feed rates, recirculation rate, the initial height of the bed at zero flow and size and type of seeds.

4.6.2.2 Seeding

The fluidised bed reactor operates on the principle of seeded precipitation, i.e. the supersaturated solution is seeded with small particles of the crystallising material in order to promote particle growth onto the seeds and to prevent homogenous nucleation in the bulk solution. The choice of seed material intended for use in a fluidised bed reactor is such that bubbling or channelling inside the bed as well as high pressure drops across the bed are avoided (Rhodes 2008). Guillard and Lewis (2001) successfully crystallised nickel carbonate on silica seeds; van Hille et al. (2005) crystallised copper sulphide on silica seeds, and Seckler (1994) crystallised calcium phosphate onto silica seeds. A study by Tai et al. (1999) found that the use of silica requires an induction time for crystal growth. This is due to the activation energy of crystal growth on seeds of a different crystal being higher than for seeds of the same material.

The specific surface area of the seeding material has an influence on the efficiency of the entire process since precipitation mechanisms such as nucleation, growth and agglomeration are all surface dependant (Wang and Anderson 1992). These mechanisms are therefore sensitive to the nature of the surface, the specific surface area, as well as the number of active sites available (Randolph and Larson 1988).

The specific surface area provided by the seeding material is initially very large, but declines as seeds increase in size and are subsequently removed from the reactor. The specific active surface area of seeds needs to remain sufficiently large to promote crystal growth. Hence, coated seeds should remain relatively small, that is diameters less than 1 mm (Seckler 1994). It is also important to ensure that seed sizes remain small since larger crystals tend to generate more secondary nuclei in agitated systems than smaller crystals (Mullin 2001).

4.6.2.3 Supersaturation in a Fluidised Bed Reactor

It is very difficult to obtain a uniform supersaturation in any reactor and high local supersaturation zones lead to spontaneous primary nucleation The supersaturation profile within a fluidised bed reactor forms a gradient with a high degree of supersaturation closer to reagent inlet ports towards the lower region of the reactor, and decreases along the height of the reactor as a result of the progressing precipitation reaction.

In an attempt to control supersaturation, feeding the base reagent through multiple inlet ports along the side of the reactor has been found to be effective (Seckler 1994; Guillard and Lewis 2001; van Hille et al. 2005). Other techniques include stepwise addition of the precipitating agent and solvent dilution (Al-Othman and Demopoulos 2009). Stepwise addition of the alkaline solution allows the slow release of reaction components. This was shown to grow large crystals and is successfully applied to acid neutralisation precipitation processes (Tai 1999; Karidakis et al. 2005; Gómez 2013). Solvent dilution on the other hand, allows for a lower concentration of the alkaline solution and better control over reaction components (Mullin 2001).

Seckler (1994) showed inconsistent supersaturation levels within a fluidised bed crystalliser, with the general trend observed of decreasing levels of supersaturation along the height of the bed, while the highest levels are around the reactor inlet points (Guillard and Lewis 2001).

4.6.2.4 Product Quality and Efficiency

The desired product quality of the precipitated compounds is that they are easily separable from the residual solution for reuse. The presence of fines makes separation and recovery difficult. In fluidised bed reactors, elutriation of fines out of the bed by the effluent is the primary factor contributing to inefficiencies (Seckler 1994; Guillard and Lewis 2001; van Hille et al. 2005). The formation of fines is usually avoided by using seeded precipitation, however in the presence of high supersaturation zones at the reactant inlet ports or due to channelling, particularly in the fluidised bed, fines may still form through primary nucleation. Furthermore, high-energy dissipation zones (predominantly at the bottom of the reactor and inlet ports) trigger fines formation through attrition when crystals collide. However, maintaining a small average seed size minimises fines formation through this mechanism.

In practice, metal removal via precipitation in fluidised bed reactors yields good results. Seckler (1994) achieved metal recoveries of between 80 % and 95 % in phosphate precipitation, while Guillard et al. (2002) achieved removal efficiencies exceeding 90 % in nickel carbonate precipitation using fluidised bed reactors. Metal concentrations from 10 up to 100,000 ppm can be treated (Van Ammers et al. 1986).

4.7 Conclusion

Precipitation has the potential to be an effective method of removing metals from solution to very low concentrations. It has the drawback of producing particles that can be difficult to separate. Appropriate reactor design, such as the fluidised bed reactor, is one of the possible methods to mitigate this. In addition, most of the studies focus on removal, not recovery, of metals from solution. This is an area that needs to be addressed in the future (Table 4.1).

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Chapter 5
Constructed Wetlands for Landfill Leachate Treatment

Carlos Arturo Madera-Parra and Daniel Ascúntar Ríos

Abstract Sanitary landfills are the most widely used method of solid waste disposal around the world. Landfill leachate (LL) is recognized as one of the most critical issues for landfill operators. Landfill leachate may contain large amounts of organic matter (biodegradable, and refractory to biodegradation), as well as ammonia-nitrogen, heavy metals (HM) and chlorinated organic and inorganic salts. Various landfill leachate treatment technologies have been broadly used, including biological processes (aerobic, anaerobic and anoxic) and physicochemical processes (oxidation, precipitation, coagulation/flocculation, ozonation, activated carbon adsorption, electrochemical oxidation, Fenton process, membrane filtration). Constructed wetlands are classified among the biological methods that use phytoremediation for polluted liquid treatment. They are defined as engineered systems that use natural processes (vegetation, soils and microorganisms) to remove, transform and degrade pollutants from wastewater, creating an efficient synergic effect. The effectiveness of constructed wetlands for landfill leachate treatment has been extensively demonstrated and its full-scale implementation is rising among regions given its adaptability and capacity to efficiently treat landfill leachate.

Keywords Constructed wetlands • Landfill leachate • Macrophytes • Phytoremediation

Contents

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5.1 Introduction

Residential, industrial and commercial human activities generate a heterogeneous combined material known as solid waste. It can be classified according to its production source, given that it can be domestic, industrial, commercial, or from other activities. Its characteristics and hazardous potential may also be used to identify the type of material and its recommendable management. Organic or inorganic, toxic or non-toxic, solid waste has to be clearly categorized to ensure a proper treatment and disposal.

An appropriate solid waste management will indubitably reduce negative effects on the environment and, consequently, on human health. There are a number of steps that would ensure suitable management for this type of material, including monitoring, collection, transport, processing, recycling and final disposal. All of them are included in a global discipline named Integrated Solid Waste Management (Hoornweg and Bhada-Tata 2012).

A worldwide accepted technology for solid waste management, known as landfilling, is the most common method of organized solid waste disposal around the globe, primarily for its obsolete advantages of hiding a problem, covering it and walking away. The lack of awareness of waste concealing consequences generated a spread of landfills all over the world, ingenuously implementing what later may have turned out to be open dumps without any technical criteria to prevent their severe environmental impacts. Even so, controlled or uncontrolled landfills will unavoidably generate a heavily polluted liquid, called leachate, that requires proper treatment to prevent environmental and human health afflictions (EPA 2002).

A large number of environmental impacts are related to landfill leachate, a liquid with a high potential to negatively disrupt the ecosystem characteristics, with a consequent effect on human health. Landfill leachate components are known for their toxicity, as well as their carcinogenic and mutagenic potential on fauna and flora. Hence, as landfills are widely used around the world, landfill leachate management becomes a critical issue and treatment is required (Madera and Valencia 2009).

Various landfill leachate treatment technologies have been broadly used, including biological (aerobic, anaerobic and anoxic) and physicochemical (oxidation, precipitation, coagulation/flocculation, ozonation, activated carbon adsorption, electrochemical oxidation, Fenton process, membrane filtration) processes. These technologies have advantages and disadvantages regarding technical, economic, social and environmental features, all of which should be assessed when selecting the proper management option for landfill leachate treatment.

Constructed wetlands are classified among the biological methods that use phytoremediation for polluted liquid treatment. They are defined as engineered systems that use natural processes (vegetation, soils and microorganisms) to remove, transform and degrade pollutants from wastewater, creating an efficient synergic effect (Akinbile et al. 2012). The effectiveness of constructed wetlands for landfill leachate treatment has been extensively demonstrated and its full-scale implementation is rising among regions given its adaptability and capacity to cope with landfill leachates. This chapter is focused on the importance of the proper management of landfill leachate, presenting alternatives for its treatment and particularizing the potential of constructed wetlands for full scale implementation.

5.2 Characteristics of Landfill Leachate

5.2.1 Formation and Generation of Landfill Leachate

Landfill leachate is a highly polluted and complex residual liquid that results from rainwater infiltration through buried solid waste, assisted by biochemical processes inside the landfill and water content from waste itself (Renou et al. 2008). It is recognized as a high-strength wastewater, characterized by a high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD), high concentration of inorganic salts and potential toxicity (Žgajnar et al. 2009).

The complexity of landfill leachates engenders special requirements for its collection, storage, treatment and disposal. Soil and water pollution, with their consequent impact on human health, are the major risks at stake when this residue is not properly managed, which entails a global environmental problem, given that urban areas generate about 1.3 billion tons of solid waste per year, with an expectation to rise up to 2.2 billion tonnes by 2025 (Hoornweg and Bhada-Tata 2012). The risks become greater since landfills are the most common technology used for solid waste disposal worldwide and the quality and quantity of landfill leachate varies according to each region. Therefore, a continuous growth in solid waste production is directly proportional to the increase in landfill leachate generation.

5.2.2 Landfill Leachate Age

The concealed waste age after landfilling has a significant effect on leachate quality. Leachate from young landfills has a high organic matter content and its reduction can be observed over a 10-year period of monitoring. According to the landfill age, landfill leachate can be classified in time ranges: from 3 to 5 years, a landfill leachate can be considered young, from 5 years and over, landfill leachate is considered medium or old age (Rong 2009).

Leachate produced in younger landfills is characterized by high concentrations of volatile acids, as a result of fermentation (acid phase). In ripe landfills, the organic fraction consists of humic and fulvic acids. Young landfills may produce leachate with a chemical oxygen demand (COD) above 10,000 mg/l, while a 10 year-old landfill generates a leachate with a COD is below 3000 mg/l (Kulikowska and Klimiuk 2008).

Young leachate has a high biodegradability due to the high BOD/COD ratio, contrary to old ones, which have a low BOD/COD ratio and thus a low biodegradability. Biological treatments are more effective for young leachate than for old or partially stabilized leachate, indicating that the most effective way to treat them is with physicochemical processes (Madera and Valencia 2009). Kostova (2006) summarized leachate characteristics according to their age (Table 5.1).

Table 5.1 Leachate characteristics according to its age

Leachate constituent	Concentration (mg/L)			
	Transition phase	Acid-formation phase	Methane fermentation phase	Final maturation phase
	0–10 years	5–10 years	10–20 years	Over 20 years
BOD_5	100–11,000	1000–57,000	100–3500	4–120
COD	500–22,000	1500–71,000	150–10,000	30–900
BOD/COD	0.2–0.5	0.67–0.80	0.35–0.67	0.13
TOC	100–3000	500–28,000	50–2200	70–260
NH_4^+-N	0–190	30–3000	6–430	6–430
NO_3^--N	0.1–500	0.1–20	0.1–1.5	0.5–0.6
TDS	2500–14,000	4000–55,000	1100–6400	1460–4640

Source: Kostova (2006)

5.2.3 Landfill Leachate Characterization

Solid waste composition, age, landfill management, climate and hydrological regimes, chemical and biological activities, moisture, temperature and pH influence the landfill leachate composition. The same type of waste buried in different regions may produce leachate with broad differences in its characteristics, given that all the factors mentioned above play a role on its components (Mohd et al. 2012). Organic and inorganic matter (biodegradable, but also refractory to biodegradation), humic-type compounds, nitrogenous species, heavy metals and salts are the main constituents of landfill leachate (Renou et al. 2008).

A large number of compounds found in landfill leachate are hazardous to the environment and human health. A study conducted by Öman and Junestedt (2008) found 140 organic, metal-organic and inorganic compounds in landfill leachate, 55 of which were reported as hazardous, implying that there are many still unknown. Risk assessments and leachate treatment methods are continuously upgraded and improved in order to respond to this situation.

Landfill leachate contains dissolved and suspended organic and inorganic pollutants, as well as toxic chemicals, entailing a high potential of contaminating groundwater, surface water and soil, with subsequent negative effects on living organisms and human health (Ahel et al. 2004; Pazoki et al. 2012), such as heavy metals, complex organic compounds, hydrocarbons, phenols and nitrates. This makes it necessary to identify and assess both the quantity and quality of the leachate in order to establish the best-suited technology for pollutant removal or transformation, given that each pollutant may follow different conversion routes according to the selected treatment.

5.2.3.1 Organic Components of Landfill Leachate

Since the determination of specific organic substances is often complicated and time consuming, COD, BOD and TOC are the most commonly used parameters for its evaluation. As waste degrades, the concentration of these indicators decreases. Compounds such as phenols, phthalates, terpenes, phenols and monocyclic and polycyclic aromatic hydrocarbons are also some of the organic substances that have been identified in leachate, mostly attributed to the presence of plastics that are commonly dropped in landfills, soaps, cosmetics or oil-based products (Ifeanyichukwu 2008). As stated by the Environmental Agency of the United Kingdom (2009), dissolved organic matter in landfill leachate from municipal solid waste contains a mixture of heterogenic characteristics, mostly composed of low molecular weight polysaccharides, cellulose, hemicelluloses, proteins, volatile fatty acids, lipids and waxes, as well as, humic and fulvic acids.

Dissolved organic matter in landfill leachate changes as the landfill ages (Table 5.2), with an increase in humic relative to fulvic acids and increasing aromaticity and molecular weight in old leachates. Landfill leachate also contains colloidal

Table 5.2 Organic components dynamics on the subsurface

Process		Description
Physical	Volatilisation	Transfer of contaminants from an aqueous phase to the vapour phase
	Dispersion	Spreading of contaminants due to heterogeneities in groundwater systems
	Diffusion	Spreading of contaminants in response to concentration gradient within a fluid
	Sorption	Association of a contaminant in a gaseous or aqueous phase with a solid material
Biological	Aerobic	Microorganisms use oxygen as an electron acceptor to degrade contaminants
	Anaerobic	Alternative electron acceptors (i.e., NO_3^-, SO_4^{2-}, Fe^{3+} and CO_2) are used by microorganisms to degrade contaminants
Chemical	Hydrolysis, dehydrohalogenation, and other chemical reactions	Chemical transformation that degrade contaminants without microbial facilitation

Source: Beaven et al. (2009)

material which is predominantly organic, but also includes an inorganic fraction comprising aluminium, iron and silica (Beaven et al. 2009). Organic components can follow different routes of transformation and transportation during landfilling.

Usually, the BOD/TOC ratio is high in the initial stages of landfills, after which the oxidation of organic carbon reduces the value of the BOD/TOC over time. COD reduction is produced at a slower rate, since the refractory fraction may remain for a higher period in Landfill leachate (Rong 2009), as seen in Table 5.1.

5.2.3.2 Inorganic Components of Landfill Leachate

Nitrogenous compounds in landfill leachate are mainly ammonia and nitrates (Fig. 5.1). Biodegradation of proteins and amino acids inside landfills leads to a production of high concentrations of ammonia (or its ionic species ammonium under acidic conditions), specially for stabilized landfills (Suárez and Cardona 2013) and its presence may vary according to the leachate age, as shown in Table 5.1. Ammonia from landfills is released during the decomposition of proteins contained in animal and vegetable waste, but also from manufactured materials that contain nitrogen compounds (Pivato and Gaspari 2006), such as rubber, plastic and fertilizers. Both sources can contain phosphorous (P) as well, an element that may follow a different route of transformation than nitrogen, at slower rates (Rong 2009).

Phosphorus is found in the form of phosphates, which may cause eutrophication, growth of algae, and dissolved oxygen depletion when it reaches a water stream. Some phosphates in leachate may come from sewage sludge, detergents and human waste (Ifeanyichukwu 2008). Since phosphorus may influence denitrification processes, any proposed treatment to remove or transform nutrients from landfill leach-

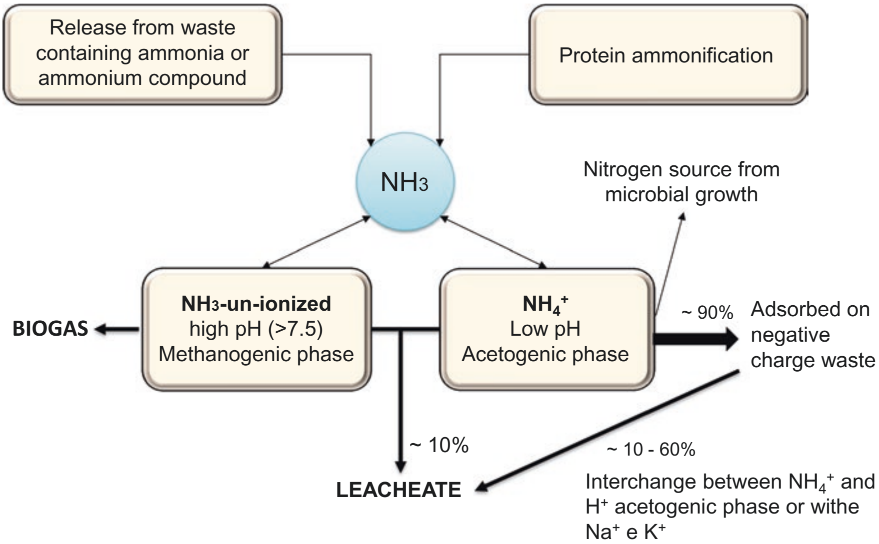

Fig. 5.1 Fate of ammonia in landfills (Source: Pivato and Gaspari 2006)

ate must take into consideration N and P dynamics, especially if it involves a biological phase (Cortez et al. 2011).

A high content of heavy metals may be found in municipal landfill leachate, usually when domestic wastewater is mixed together with industrial waste or sludge, or due to the lack of separation of hazardous materials from domestic waste, combining all sorts of residues. Moreover, there are household products that can become sources of heavy metals in the dumping site such as batteries, electronic waste, paint residues, domestic pesticides, pharmaceuticals and personal care products (PCP) and light bulbs (Mohan and Gandhimathi 2009).

Metal dynamics inside the landfill can be variable, given its sorptive capacity and variability at neutral to high pH levels, keeping them inside the landfill for longer periods. Besides pH, the solubility of metals is strongly influenced by the redox potential, the presence of complexing agents such as chlorides, sulphates, carbonates and organic acids. Moreover, their mobility relies on the properties of the solid waste phases in or on which metals can be bound (Zupančič et al. 2010). Studies have shown that after 30 years, less than 0.02% of toxic metals are leached from landfilled solid waste (Kjeldsen et al. 2002).

Heavy metals present in landfill leachate are mainly Hg, Zn, Pb, Ni, Cu and Cd. The presence of some of these metals in water, soil and air may result in toxicity, accumulation, health effects, mutation of species, disruption and many other negative impacts. Thus, metals should be removed or their concentration reduced before leachate is discharged into a receiving ecosystem (Rong 2009; Ifeanyichukwu 2008). Given that inorganic compounds such as phosphorous and heavy metals are quite variable amongst landfill leachates from different regions, concentration ranges data are scarce in the literature.

5.2.3.3 Other Components of Landfill Leachate

In addition to the components previously mentioned, modern society has a tendency to continuously introduce new types of pollutants into landfill leachate, creating a dangerous cocktail that currently has an unknown environmental impact on the ecosystem, since high concentrations of single substances may not be toxic, but chronic effects from a mixture of compounds present at very low concentrations can cause negative effects (Hallgren 2009).

Hazardous compounds have been detected in landfill leachates, including aromatic compounds, halogenated compounds, phenols, pesticides, heavy metals and ammonium compounds. Many of these compounds have been quantified at very low concentrations (μg/l), with the uncertainty that some of those compounds are present below the quantification limits of standard analytical methods. However, this does not eliminate environmental threats, since many of them can cause negative effects at low concentrations and synergistic effects can be expected (Öman and Junestedt 2008).

A wide range of pharmaceuticals and personal care products (PCP) has been detected in domestic sewage, with a consequent arrival into the aquatic environment. Even though a small content of these substances is discharged from a single household, the multiplication of discharges, at trace levels, from urban areas can generate harmful effects to the receiving ecosystem (Eggen et al. 2010).

Several landfills around the world discharge their leachate directly into surface water, soil, or sewers that transport it to wastewater treatment plants, in some cases without previous treatment (Eggen et al. 2010). This results in an environmental spreading of the above-mentioned compounds (Pharmaceuticals and PCP, pesticides, petroleum derivate solubilised products and heavy metals), which are mainly synthetic-based, persistent, complex and have low to zero affinity for biodegradation.

5.3 Landfill Leachate Treatment Options

5.3.1 Review of Landfill Leachate Treatment Technologies

Rather than discharging landfill leachate directly into the environment, its management can follow different routes: it can be recirculated into the same landfill or treated by different methods, commonly using biological processes to transform or degrade organic matter and nutrients by aerobic, anaerobic and anoxic pathways. Physicochemical processes are efficiently used as well, including oxidation, precipitation, coagulation/flocculation, ozonation, activated carbon adsorption, electrochemical oxidation, Fenton process, and membrane filtration (Bortolotto et al. 2009; Castrillón et al. 2010; Orescanin et al. 2011).

The most common treatment systems for landfill leachate include conventional activated sludge, aerated lagoons, sequencing batch reactors (SBR) and upflow anaerobic sludge blanket (UASB) reactors, especially for young leachate with high BOD concentrations, given that the COD removal from old landfill leachate becomes difficult given the presence of bio-refractory compounds, which implies that these conventional systems require additional treatment stages for efficient pollutant removal (Ahmed and Lan 2012), resulting in higher costs. Biological treatment methods are cost-effective and simple to operate, and commonly used to treat landfill leachate with high concentrations of biodegradable organic matter. Many worldwide experiences confirm that biological treatment methods present quite satisfactory treatment performances for young landfill leachate (Ince et al. 2010).

Biological methods may be restricted to treating stabilized landfill leachate originated from an old landfill site, giving the recalcitrant characteristics of its components. Therefore, some physicochemical treatment technologies can be applied for the elimination of inert substances from landfill leachate, especially after biological treatment as a refining step (Ince et al. 2010). The presence of high-molecular weight and inhibitory effects on biological activity may cause low removal efficiency treatment systems or can even require a coupling of technologies (Žgajnar et al. 2009).

For mature landfill leachate, biological methods may not be effective, unlike physicochemical and advanced oxidation processes, which can reach high efficiencies but become expensive. Technology coupling can generate economical savings, process optimization and fulfil discharge limits, by achieving degradation of complex compounds (Cortez et al. 2011). Table 5.3 shows the effectiveness of different technologies for landfill leachate treatment.

5.3.2 Biological Systems for Treatment and Management of Landfill Leachate

Biological treatment gives good efficiencies at low cost for implementation, operation and maintenance, and is an attractive alternative for landfill leachate management (Bortolotto et al. 2009). Biological methods involve the degradation of pollutants by aerobic or anaerobic microorganisms, with a consequent generation of carbon dioxide, biogas and sludge (Renou et al. 2008).

5.3.2.1 Experiences Using Biological Systems for Landfill Leachate Treatment

Biological processes have been shown to be very effective in removing organic and nitrogenous matter from young landfill leachate when the BOD/COD ratio is over 0.5. Older landfill leachate with refractory compounds may limit biological degradation (Renou et al. 2008). Lagoons, activated sludge, sequencing batch reactors (SBR) and rotating biological contactors (RBC) are biological methods applied for

Table 5.3 Effectiveness of leachate treatments versus leachate age

	Leachate age				
Type of treatment	Young	Medium	Old	Target of removal	Remarks
Channelling					
Combined treatment with domestic sewage	Good	Fair	Poor	Suspended solids	Excess biomass and nutrients
Biological					
Aerobic processes	Good	Fair	Poor	Suspended solids	Hampered by refractory compound and excess biomass
Anaerobic processes	Good	Fair	Poor	Suspended solids	Hampered by refractory compound, long-time and biogas
Physical/chemical					
Coagulation/flocculation	Poor	Fair	Fair	Heavy metals and suspended solids	Hampered by sludge production and subsequent disposal
Chemical precipitation	Poor	Fair	Poor	Heavy metals and NH_3-N	Requires further disposal due to sludge generation
Adsorption	Poor	Fair	Good	Organic compounds	Carbon fouling can be a problem and GAC adsorption is costly
Oxidation	Poor	Fair	Fair	Organic compounds	Residual O_3
Stripping	Poor	Fair	Fair	NH_3-N	Requires other equipment for air pollution control
Ion exchange	Good	Good	Good	Dissolved compounds, cations/anions	Used as a polishing step after biological treatments and treatment cost is high
Membrane filtration					
Microfiltration	Poor	–	–	Suspended solids	Used after metal precipitation

(continued)

Table 5.3 (continued)

	Leachate age				
Type of treatment	Young	Medium	Old	Target of removal	Remarks
Ultrafiltration	Poor	–	–	High molecular weight compounds	Costly and limited applicability due to membrane fouling
Nanofiltration	Good	Good	Good	Sulphate salts and hardness ions	Costly and requires lower pressure than reverse osmosis
Reverse osmosis	Good	Good	Good	Organic and inorganic compounds	Costly and extensive pre-treatment is required before reverse osmosis

Source: Abbas et al. (2009)

landfill leachate treatment, all of which have displayed advantages and disadvantages. More recently, membrane bioreactor (MBR) technology, an advanced biological treatment, has emerged as a promising alternative, even for old landfill leachate, with features that include better effluent quality, process stability, smaller footprint, increased biomass or mixed liquor suspended solids (MLSS) retention and low sludge production (Ahmed and Lan 2012).

5.3.2.2 Phytoremediation

When using biological methods, knowledge of the physiological and molecular mechanisms is fundamental for satisfactory efficiencies. Plants are widely used for the removal of pollutants from polluted matrixes (water and soil), with an important experimental and practical approach in recent decades. This technology is called phytoremediation, a remarkable engineered option to optimize and improve landfill leachate treatment as well (Mojiri 2012). It takes advantage of the understanding of how plants function by applying information that has been known for years in agriculture, silviculture and horticulture to deal with environmental problems (EPA 2000).

Phytoremediation includes the combination of several disciplines such as engineering, agronomy, soil science, chemistry, hydrology, and biology, but is not limited for implementation by them. Years of research have made it possible to advance from laboratory experiments and pilot-scale experiences to successful full-scale field applications (Granley and Truong 2012). It can be applied in both water and soil, removing organic and inorganic pollutants by several mechanisms (Fig. 5.2).

Phytoremediation is a low cost technology, but requires strategy and expertise for proper application. It has many advantages, such as performance with minimal

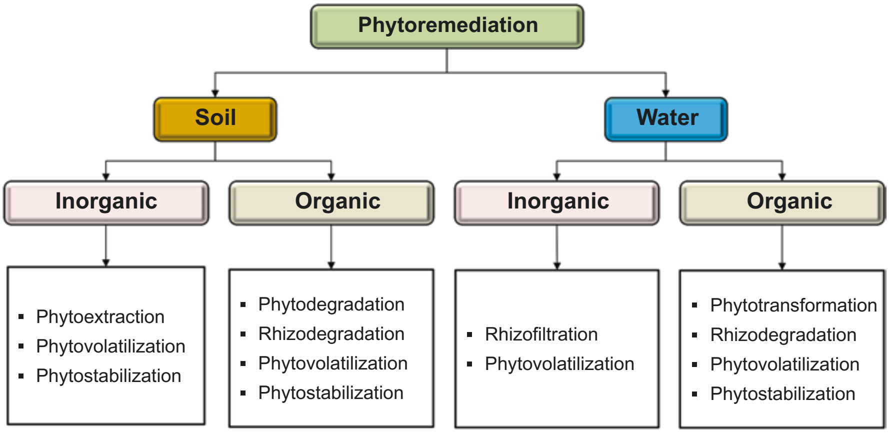

Fig. 5.2 Pollutant removal mechanisms for organic and inorganic pollutants (Source: Adapted from K-State 2012)

environmental disturbance, suitable for a broad range of pollutants, has fewer by-products than conventional methods and degrades organic pollutants to CO_2 and H_2O (Mojiri 2012). It is a potential option for landfill leachate treatment, with scientific support that goes back to the 1970s, when experimental approaches started. Kim and Owens (2010) stated that applying phytoremediation to landfill leachate treatment may provide water and nutrient sources for enhanced plant performance, a reduction of leachate volume and removal of biodegradable and non biodegradable contaminants.

Landfill leachate is usually treated in wastewater treatment plants, which involves transport and relatively costly treatment. However, in many cases, landfill leachate can be treated locally in the landfill area in a more efficient and cost-effective way. Alternatives comprise phytoremediation systems, such as constructed wetlands or irrigation of energy crops, such as willow growing on Short Rotation Coppice, on either restored landfill caps or on arable land adjacent to the landfill site (Rosenkranz 2013).

When using phytoremediation for landfill leachate treatment, adverse effects may manifest for plant growth giving the accumulation of toxic compounds, such as Na^+ and Cl^- in soils. Hence, before implementing the technology, the resilient capacity of both plant and soil to such harsh conditions should be tested in order to determine if landfill leachate can be treated with such technology or whether other alternatives have to be included, like dilution of the landfill leachate or technology coupling (Kim and Owens 2010).

5.4 Constructed Wetlands for Landfill Leachate Treatment

Natural wetlands have historically been used for wastewater treatment and polishing, but their performance was not accounted for during the treatment process (Akinbile et al. 2012), mostly because of uncontainable variables such as arbitrary hydrodynamics, fauna and flora competition and other features that cannot be controlled under natural conditions. This is where engineering appears in order to use natural processes to solve anthropogenic problems, by adjusting a natural wetland ecosystem into a configuration known as constructed wetlands.

Constructed wetlands are classified among the biological methods that use phytoremediation for wastewater treatment. They are defined as engineered systems that use natural processes (vegetation, soils and microorganisms) to remove, transform and degrade pollutants from wastewater, creating an efficient synergetic effect. The effectiveness of constructed wetlands for landfill leachate treatment has been extensively demonstrated and their full-scale implementation is rising in different regions given their adaptability and capacity to treat landfill leachate. This chapter focuses on the importance of proper management of landfill leachate, presenting alternatives for its treatment and particularizing the potential of constructed wetlands for implementation.

Constructed wetlands, as a phytoremediation technique, have become an attractive and feasible technology for liquid waste management, given its many advantages such as low energy consumption, low cost implementation and operation, high efficiency for pollutant removal and aesthetical characteristics which give it a valuable social acceptance (Akinbile et al. 2012). On-site treatment using constructed wetlands is one of the low cost methods of landfill leachate treatment that has been widely practiced in several countries for years. Constructed wetlands planted with reed or willow are effective in treating landfill leachate and are especially successful at removing high levels of nitrogen (Białowiec et al. 2012a; Wojciechowska et al. 2010).

5.4.1 Constructed Wetland Configurations

According to the dominating plant, constructed wetlands may be classified (Table 5.4) into systems with free-floating, floating leaved, rooted emergent or submerged macrophytes (Vymazal 2010). They can also be characterized by flow conditions which, according to WSP (2008), distinguish three types of constructed wetlands:

(a) *Surface flow or free water surface constructed wetland*: large, shallow lagoons that may contain *submerged, emergent or floating plant species*. The microorganisms responsible for biological treatment of the wastewater form biofilms on the stems and leaves of the plants. These systems are used for secondary or tertiary treatment, in order to remove or transform nitrogen and phosphorous.

Table 5.4 Characteristics of plants for constructed wetlands

Types of plants	General characteristics and common examples	Function or importance of treatment process	Function or importance for habitat	Design and operational considerations
Free-floating aquatic	Roots or root-like structures suspended from floating leaves. Will move about with water currents. Will not stand erect out of the water. Common duckweed (*Lemna*), and big duckweed (*Spirodela*)	Primary purposes are nutrient uptake and shading to retard algal growth. Dense floating mats limit oxygen diffusion from the atmosphere. Duckweed will be present as an invasive species	Dense floating mats limit oxygen diffusion form the atmosphere and block sunlight from submerged plants. Plants provide shelter and food for animals	Duck weed is a natural invasive species in North America, special considerations to its biomass production may be required and uncontrolled spread should be prevented
Rooted floating aquatic	Usually with floating leaves, but may have submerged leaves. Rooted to bottom. Will not stand erect out the water. Water lily (*Nymphea*), and Pennywort (*Hydrocotyle*)	Primary purposes are proving structure for microbial attachment and releasing oxygen to the water column during daylight hours. Dense floating mats limit oxygen diffusion from the atmosphere	Dense floating mats limit oxygen diffusion form the atmosphere and block sunlight from submerged plants. Plants provide shelter and food for animals	Water depth must be designed to promote the type of plants (i.e. floating, submerged, and emergent) desired while hindering other types of plants
Submerged aquatic	Herbaceous (i.e. non-woody). Rooted to the bottom. Stand erect out the water. Tolerate flooded or saturated conditions. Cattail (*Typha*), Bulrush (*Scirpus)*, and Common Red (*Phragmites*)	Primary purposes are providing structure for microbial attachment and releasing oxygen to the water column during daylight hours		Retention time in open water zone should be less than necessary to promote algal growth, which can destroy these plants through sunlight blockage

(continued)

Table 5.4 (continued)

Types of plants	General characteristics and common examples	Function or importance of treatment process	Function or importance for habitat	Design and operational considerations
Emergent aquatic	Herbaceous (i.e. non-woody). Rooted to the bottom. Stand erect out the water. Tolerate flooded or saturated conditions. Cattail (*Typha*), Bulrush (*Scirpus*), and Common reed (*Phragmities*)	Primary purpose is providing structure to induce enhanced flocculation and sedimentation. Secondary purposes are shading to retard algal growth, windbreak to promote quiescent conditions for settling, and insulation during winter months	Plants provide shelter and food for animals. Plants provide aesthetic beauty for humans	Water depths must be in a range that is optimum for the specific species chosen (planted)
Shrubs	Woody, less than 6 m tall. Tolerate flooded or saturated soil conditions. Dogwood (*Cornus*), and Holly (*llex*)	Treatment function is not defined: it is not know if treatment data from unsaturated or occasionally saturated phytoremediation sites in upland areas is applicable to continuously saturated wetland sites	Plants provide shelter and food for animals (especially birds). Plants provide aesthetic beauty for humans	Possible perforation of liners by roots
Trees	Woody, greater than 6 m tall. Tolerate flooded or saturated soil conditions. Maple (*Acer*), and Willow (*Salix*)	(Same as for shrubs)	(Same as for the shrubs)	(Same as for the shrubs)

Source: (EPA 2000)

(b) *Subsurface horizontal flow constructed wetland*: also known as Vegetated Submerged Bed Systems. It consists of shallow basins filled with coarse sand or gravel as filter media. Plants are grown on the surface of the filter bed and polluted liquid flows horizontally through the bed below the surface.

(c) *Vertical flow constructed wetland*: shallow sand filter beds with a distribution system on the surface that allows polluted liquid to percolate vertically through the unsaturated media as plants support the vertical drainage process, with an intermittent hydraulic loading alternated with resting intervals between discharges, providing an effective aeration mechanism because pores of the filter bed refill with oxygen during these intervals.

Table 5.5 Removal mechanisms for determined pollutants in constructed wetlands

Removal mechanism	Removed contaminant
Bioconversion	OM, solids, N, P
Predation	Pathogens
Adsorption	OM, solids, N, P.
Sedimentation	OM, solids, N, P, pathogens
Filtration	OM, solids, N, P, pathogens
Plant uptake	N, P
Volatilization	N
Ultraviolet radiation	Pathogens
Release of antibiotics by plants	Pathogens
Ammonification, nitrification/ denitrification (limited)	N

Source: Adapted from NDWRCDP (2004) and Seabloom and Hanson (2004)
OM – Organic Matter, *N* – Nitrogen, *P* – Phosphorous

Pollutant removal, transformation and degradation mechanisms in constructed wetlands are abundant and diverse, considering that its objective is to reproduce and enhance processes that natural ecosystems use to transfer materials in a well-balanced cycle (Table 5.5). These processes, which in nature are exposed to several uncontrollable variables, are employed in constructed wetlands with the intention to minimize external effects, potentiate biological activity and accelerate the transformation of organic matter (OM), nutrients (N, P) and other substances.

Decreased energy consumption, degradation or transformation of different types of pollutants, and enhancement of habitat for fauna and flora are some of the many advantages and benefits of treating landfill leachate in constructed wetlands. Studies of the long-term use of constructed wetlands for landfill leachate treatment have demonstrated significant economic advantages, mainly through lowered construction, transportation and operation costs (Kamarudzaman et al. 2011).

5.4.2 *Experiences of Landfill Leachate Treatment by Constructed Wetlands*

As described before, landfill leachate is a highly polluted wastewater; and conventional technologies have been employed to treat it before discharging it into the environment. However, since constructed wetlands benefits are evident for different types of wastewaters (domestic, industrial, urban and agricultural runoff), its implementation for landfill leachate treatment has become a growing interest for many scientists (Vymazal 2010).

Constructed wetlands have become an attractive technology for landfill leachate treatment, displaying low energy consumption and high removal efficiencies. But the knowledge of the active pollutant transformation processes is limited, which has become another incentive of the rising awareness in fully comprehending the internal processes in constructed wetlands, in order to enhance their performance and adaptation to the particular landfill leachate characteristics. The natural processes occurring in constructed wetlands by phytoremediation can aid in landfill leachate treatment (Fig. 5.3).

Figure 5.3 shows that pollutants can follow different routes for their removal, degradation and transformation: for example, organics may volatilize or biodegrade, ammonia nitrogen may undergo nitrification and denitrification processes. Metals can be accumulated into the biomass, precipitate in the soil or undergo ion exchange processes in the bottom sediments. High landfill leachate salinity may disturb plant's metabolism, although according to literature reports, the plant most commonly used in constructed wetlands, *Phragmites australis*, can withstand relatively high chloride concentrations (Wojciechowska et al. 2010). Constructed wetlands have been successfully applied for leachate treatment in the USA and in European countries (Norway, UK, Slovenia and Sweden). Different types and configurations of constructed wetlands are applied for landfill leachate treatment (with surface and sub-surface flow of sewage, several treatment stages with different flow conditions), as different types of plants have also been used (Table 5.6).

Akinbile et al. (2012) evaluated the performance efficiency of pilot-scale constructed wetlands with gravel and sand as support media and planted with *Cyperus haspan* for landfill leachate treatment in Malaysia. The wetland cell showed good performance for removal of TSS, COD, BOD_5, ammonia (NH_3-N) and total phosphorous with average removal efficiencies between 40% and 98%. In the case of

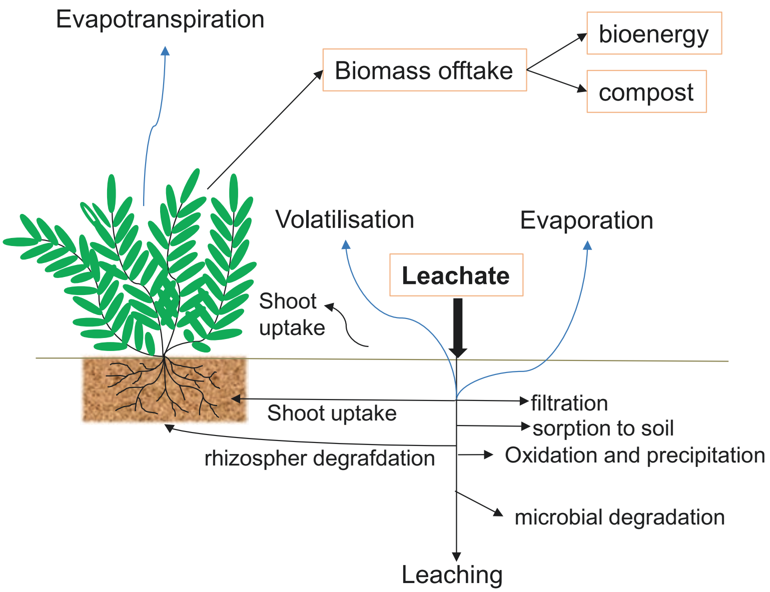

Fig. 5.3 Treatment processes and mechanisms during landfill leachate phytoremediation (Source: Adapted from Jones et al. 2006)

Table 5.6 Characteristics of investigated constructed wetlands (CW) for landfill leachate treatment

CW location	Year of landfill construction/year of CW construction	Waste received per year (t/year)	Leachate inflow to CW (m^3/day)	CW configuration	Plants	Landfill leachate pre-treatment	Remarks regarding CW operation
Szadòlki, Poland	1973/2001[a]	2310	6–240	Two parallel horizontal flow-constructed wetlands beds, area 50 × 50 m each, depth 0.6 m	*Red Ohragmitesaustralis*	None	Low hydraulic conductivity (2.55×10^{-5}), clogging
Gatka, Poland	1993/1997	220,000	5	Willow plantation / filter 43 × 31 m, depth 0.8 m)	*Willow Salix*, *orchard grass Dactylis glomerata L.*	Retention tank 1000 m^3 vol.	Low hydraulic conductivity (5.87 $\times 10^{-5)}$, clogging
Örebro, Sweden	1979/2003	15,000	Max 22	10 hydrophyte ponds with a surface flow of leachate, total volume 53,000 m^3/d, water depth 0.5-1 m	Duckweed *Lemna, reed Phragmites australis, bulruh Scirpuespalla, cattail Typha latifolia, sedge Carex*	Cyclically aerated tank 20,000 m^3 vol. with ammonia stripping	Constructed wetlands operated only in vegetation season (April–October); during winter the leachate is recirculated to the landfill

Source: Wojciechowska et al. (2010)

[a] Modernization of beds took place the period 2006–2008

metals, the constructed wetlands efficiencies were as follows: 34.9–59.0% for Fe, 29.0–75.0% for Mg, 51.2–70.5% of Mn and 75.9–89.4% for Zn. This performance of the wetland cell showed that landfill leachate can be treated effectively using subsurface constructed wetlands. It also suggested that specialized media such as zeolite can improve the porosity and penetration of plant roots and prevent clogging.

Likewise, other studies showed that plant species have an important role in constructed wetlands technology. Białowiec et al. (2012b) demonstrated that constructed wetlands at microcosm scale, planted with reed and willow, treating landfill leachate have an effect on the redox potential levels and nitrogenous species in the water column. They found that plants had a significant influence on the redox potential relative to the plant-less system, registering anoxic conditions in the reed wetland cell. In the other wetland cell, the redox potential fluctuated significantly in the rhizosphere, mainly during light hours, with higher declines in the morning. Total nitrogen, nitrate and chemical oxygen demand were considerably lower in the planted wetland cell than in the unplanted unit. This clearly shows that the redox potential, an indicator of whether the type of activity is anoxic, aerobic or anaerobic within the constructed wetland will vary according to the type of plant used and how the nitrogenous species will behave during microbial degradation. Besides, this also suggests that the planted constructed wetlands may be more efficient in transforming nitrogen present in landfill leachate than a common filter that is represented by an unplanted unit, showing that plants can have a great influence on the conditions and processes in constructed wetlands.

Bulc (2006) evaluated during 7 years the performance of a hybrid configuration of a constructed wetlands cell, composed by three interconnected cells, two vertical flow and one horizontal flow, and planted with *Phragmites australis* and *Typha latifolia* treating old landfill leachate of the Slovenian's capital city. The removal of COD, BOD_5, ammonia and sulphides was above 50% and negative values were obtained for sulphate and nitrate. Iron removal was above 80%. Effluent quality was lower than the standard limit of the country. Temperature did not affect the performance of the wetland cells. However, it varied with precipitation. These results indicate that constructed wetlands cells used as a tertiary system or as an independent system could be a low-cost technology for old landfill leachate.

A landfill leachate treatment system that consisted of extraction, aeration, settling, intermittent vertical sand filtration and a surface flow wetland treatment with recycle and discharge has operated seasonally at the Saginaw Township landfill (closed in 1980s, Michigan, USA) for 10 years. The 0.85 ha cattail wetland (detention time of 180 days) displayed an ammonia mass reduction of 99.5% for 9 years, with a 95% mass removal in the start-up year. Metals were not present in all effluent samples, with modest reductions in those always present (zinc 16%, arsenic 29%, barium 78%, and chromium 67%). Volatile organic compounds were removed to below detection, excepting BTEX, which occurred in only 2% of the outflow samples. Base neutral organics, PCBs and pesticides were also removed to below detection, except phthalates with an outlet detection frequency of 29%. No pesticides or PCBs were detected in the system outflow (Kadlec and Zmarthie 2010). These results demonstrate that constructed wetlands have a high potential for removing, transforming or degrading several types of pollutants from landfill leachates.

Kamarudzaman et al. (2011) studied the performance of horizontal and vertical wetland cells planted with *Limnocharis flava* at bench-scale for the removal of metals (Fe and Mn) present in landfill leachate. They found that both wetland cells performed well in the removal of metals, reaching values between 91.5–99.2% and 94.7–99.8% for Fe and Mn, respectively, confirming the high potential of constructed wetlands to remove recalcitrant pollutants from landfill leachate and the advantage of *Limnocharis flava*, which combined sorption, filtration and biological activity to remove Fe and Mn, given that both planted and unplanted units reached high efficiencies.

Yalcuk and Ugurlu (2009) evaluated three pilot-scale constructed wetlands, two with vertical flow (VF1 and VF2) and one with horizontal flow for landfill leachate treatment. All three wetland cells were planted with *Typha latifolia*. They also assessed the effect of different media materials (gravel and zeolite surface). The average removal efficiency was above 40% for ammonium, 30% for COD, 47% for PO_4^{-3}-P and 18% for Fe, respectively. Besides, better NH_4^+-N removal performance was observed in the vertical flow constructed wetland cells with a zeolite layer compared to the vertical flow constructed wetland with gravel and horizontal flow. In contrast, the horizontal wetland cell was more effective in COD removal. These marked differences indicate that not only the plant type is a strong variable that influences the overall performance of a constructed wetland for landfill leachate treatment, but also the flow conditions and bedding material provide a specific environment inside a constructed wetland that may enhance adsorption or even supply a specific habitat for different types of microbial communities.

All these recent lab-scale and pilot-scale experiences indicate that constructed wetlands may become an excellent option for landfill leachate treatment by adapting natural wetland processes through engineered units that emulate physical, chemical and biological mechanisms in order to remove, transform or degrade pollutant components present in landfill leachates. Nevertheless, the functioning of these mechanisms is yet to be fully described, with the intention of maximizing its performance and minimizing the main disadvantages of this technology, such as adaptation, area requirements, biomass disposal and clogging.

Even though successful experiences have been divulged, there are a large number of scientific studies that show that phytoremediation of landfill leachate with constructed wetlands has failed. This failure can be due to excessive landfill leachate application and poor management because of a fundamental lack of understanding of the plant-soil interactions. Bialowiec et al. (2010) mentioned that constructed wetlands required a large land demand in order to respond the continuous changes in quality and quantity of landfill leachate.

Aronsson et al. (2010) mentioned that for a successful phytoremediation application, it is good to use a method for quantifying the degree of stress on a plant species caused by landfill leachate exposure. They found that landfill leachate with sodium concentrations of 200 mg/L and 600 mg/L of chloride has a negative effect on plants (willows). However, is not well understood what causes plant damage in a field situation or how threshold values of total salinity, sodium or chloride concentrations limit degradation rates.

5.4.3 Heavy Metal Removal

Constructed wetlands have been used successfully for the removal of heavy metals present in landfill leachate and wastewaters. Heavy metals are widely known to be non-essential elements for plants and can cause adverse effects on the plant's photosynthetic system, chlorophyll synthesis, and antioxidant enzyme production, resulting in various forms of damage to the plants (Milone et al. 2003). Metals like lead, cadmium, mercury, and chromium can simultaneously prevail in the environment as a result of various human activities.

Constructed wetlands have a good retention of heavy metals (Maine et al. 2009). Several studies from authors worldwide have shown the capacity of macrophytes for accumulation and sequestration of metals in above (shoot) and below (root) ground plant parts in non-metabolic-active tissues in less harmful forms (Küpper et al. 2007).

The choice of the plant species is an important issue in constructed wetlands because they should survive the potential toxic effects of the influent and its variability. It has been found that some of the macrophytes such as aquatic plant species, including free-floating species such as *Eichhornia sp., Lemna sp., Azolla sp.* and *Salvinia sp.,* submerged species such as *Potamogeton sp.* and *Myriophyllum sp.* as well as emergent species like *Limnocharis flava*, *Typha sp., Scirpus sp., Spartina sp., Phragmites sp.,* and *Cyperus sp.* have shown potential for removing metals from different wastewaters. Additionally, those plants are capable of translocating heavy metals into the shoots, and sequestering them in non-metabolic-active tissues in less harmful forms (Lesage et al. 2007; Dhir et al. 2009; Liu et al. 2010; Vymazal 2010; Soda et al. 2012; Anning et al. 2013; Voijant-Tangahu et al. 2013).

More than 400 taxa were reported hyperaccumulating heavy metals (Suresh and Ravishankar 2004) and other contaminants, ranging from annual herbs to perennial shrubs and trees. Owing to their multiple ramified root systems with abundant room for microbial activity, the *Poaceae* family is considered to be particularly suitable for phytoremediation (Aprill and Sims 1990). Likewise, fourteen and two species are hyper-accumulators of Pb and Cd, respectively (Ye-Tao et al. 2009). This feature has led to research on species that are not hyper-accumulators, but which possess rapid growth. In this sense, native or indigenous species can play a very important role in removing heavy metals from the water matrix.

There are four mechanisms involved in heavy metal ion removal in wetlands: adsorption to fine-textured sediments and organic matter, precipitation as insoluble salts, absorption and induced changes in biogeochemical cycles by plants and bacteria, and deposition of suspended solids due to low flow rates (Lesage et al. 2007).

The choice of plants is an important parameter in constructed wetlands, as they must survive the potential toxic effects of heavy metals present in the wastewater and its variability. The most widely used constructed wetland design in Europe is the horizontal subsurface flow system vegetated with the common reed (*Phragmites australis*), although other plant species, such as cattails (*Typha* sp.), bulrushes (*Scirpus* sp.) and reed canary grass (*Phalaris arundinacea*) have also used for both domestic and industrial wastewater treatment (Calheiros et al. 2007).

In tropical countries, locally available species of *Phragmites*, *Cyperus*, bulrush and *Typha* have been the most common choices to date. Most recently, Konnerup et al. (2009) successfully used *Heliconia psittacorum* and *Canna generalis* in order to increase the aesthetic value of wetlands and to increase the local people's awareness of wastewater treatment in Thailand. Furthermore, in Colombia, Madera-Parra et al. (2015) assessed three native species (*Gynerium sagittatum*, *Colocasia esculenta* and *Heliconia psittacorum*) for landfill leachate treatment at bench scale under tropical conditions. They obtained high removal efficiencies (>80 %) for heavy metals like Cd(II), Pb(II), and Cr(VI), and the quality of the CW effluent for the case of Cd, Pb, and Cr was below the Colombian standards for wastewater treatment plant effluents discharging into a fresh water course intended for human consumption downstream.

5.4.4 Subsurface Flow Constructed Wetlands for Landfill Leachate Treatment

Horizontal flow constructed wetlands have been successfully used for the treatment of different types of wastewater during the last 40 years. Most systems have been installed for municipal sewage treatment. However, the wastewaters from agriculture, industry and landfill leachate are receiving more attention nowadays (Vymazal and Kröpfelová 2009). For this reason, the main features of horizontal flow constructed wetlands will be briefly described below.

5.4.4.1 Media Selection for Horizontal Flow Constructed Wetland

According to the EPA (2000), the support material of a horizontal flow constructed wetland system performs several functions: it (1) is a rooting material for plant species, (2) helps to evenly distribute the flow at the inlet/outlet, (3) provides surface area for microbial growth, and (4) filters and traps particles. For successful plant establishment, the uppermost layer of the media material should be conducive to root growth. A variety of media sizes and materials have been tried, but there is no clear evidence that points to a single size or type of medium, except that the medium should be large enough that it will not settle into the void spaces of the underlying layer. It is recommended that the planting media do not exceed 20 mm in diameter,

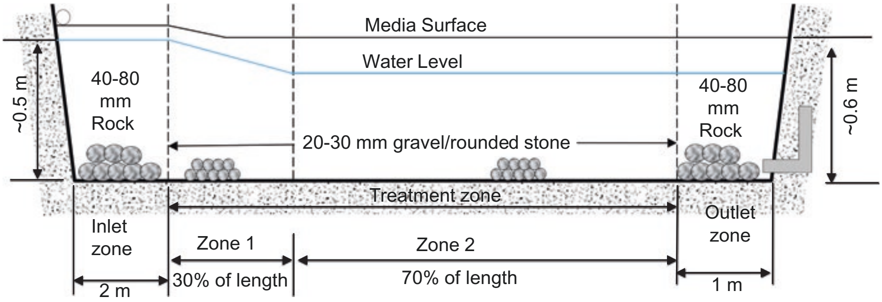

Fig. 5.4 Proposed zones in a horizontal flow constructed wetland (Source: Adapted from EPA 2000)

and the minimum depth should be 100 mm. The media in the inlet and outlet zones (Fig. 5.4) should be between 40 and 80 mm in diameter to minimize clogging and should extend from the top to the bottom of the system.

The entrance zone should be about 2 m long and the outlet zone should be about 1 m long. These zones with larger media materials will contribute to even distribution or collection of the flow without clogging. The use of gabions (wire rock baskets used for bank stabilization) to contain the larger media simplifies construction. Gabions may also make it easier to remove and clean the inlet zone media if it becomes clogged.

Any portion of the medium that is wetted is a surface on which microbes can grow and solids settle and/or accumulate. The experience with soil and sand media shows that it is very susceptible to clogging and surfacing of flows, even under minimal TSS concentrations in the influent, so soil and/or sand media should be avoided. Gravel and rock media have been used successfully, with media of smaller diameter being more susceptible to clogging, and larger media more difficult to handle during construction or maintenance. Crushed limestone can be used, but is not recommended for horizontal flow constructed wetland systems because of the potential for media breakup and dissolution under the strongly reducing environment of a horizontal flow constructed wetland, which can lead to clogging.

Medium materials with a high iron or aluminium content will have more sites for phosphorus binding and should enhance phosphorus removal, but only during the first few months of operation of the constructed wetlands, given the saturation of the capacity of the media material. Other types of materials like shredded tires, plastic trickling filter media, expanded clay aggregates and shale with potentially high phosphorus absorptive capacity have been used, but there is inadequate data to make a recommendation about their use (EPA 2002). As a result, support media or bedding material becomes an important component of a horizontal flow constructed wetland, given that it provides special conditions for mechanisms performing differently according to the composition and shape of this medium. Table 5.7 displays the characteristics of the most commonly used media.

Table 5.7 Characteristics of support media of constructed wetlands

Type of media	Effective size, D10 (mm)	Porosity (n)	Hydraulic Conductivity (K_s, m/s)
Coarse sand	2	0.32	1.2×10^{-2}
Gravelly sand	8	0.35	5.8×10^{-2}
Fine gravel	16	0.38	8.7×10^{-2}
Medium gravel	32	0.40	11.6×10^{-2}
Coarse rock	128	0.45	115.7×10^{-2}

Source: Sundaravadivel and Vigneswaran (2009)

The selection of the support media for horizontal flow constructed wetlands deserves special attention, considering that it has a remarkable influence on one of the main drawbacks of this technology: clogging. Therefore, before implementing a horizontal flow constructed wetland for landfill leachate treatment, detailed analyses should be made by relating variables such as landfill leachate characteristics and plant root growth which, coupled with media particularities, could augment or diminish clogging effects.

5.4.4.2 Plant Selection for Horizontal Flow Constructed Wetlands

Plant species play a crucial role in pollutant removal from landfill leachate through absorption, cation exchange, filtration and chemical changes through the roots; as well as by providing specific microenvironments inside the constructed wetlands that enhance its performance. There are a large number of studies that show that plant species can accumulate heavy metals in their above and underground tissues, i.e. *Typha latifolia* and *Cyperus malaccensis*. Therefore, selection of the plant species is a very important step for implementing constructed wetlands phytoremediation, which is often done by considering previous applications and research.

Plant species selection is influenced by the site characteristics, which will affect the plant growth, acclimation and development. It is recommended that a list of potential plant species is prepared in order to select the most appropriate plant species (Mojiri 2012). Table 5.8 shows several types of plants that can be considered hyper-accumulators species, given their capability and affinity for removing large quantities of metals during phytoremediation. Plants species vary considerably in their capacity to accumulate heavy metals. Duckweed (*Lemna minor*), salix, cattail (*Typha latifolia*) and common reed (*Phragmites australis*) are among those plant species that can accumulate large amounts of heavy metals (Liu et al. 2010).

Plants species play significant roles in pollutant removal, degradation and transformation during landfill leachate treatment in constructed wetlands (Table 5.9). Several mechanisms that flora normally use in natural ecosystems are enhanced in a constructed wetland, like evapotranspiration, metabolism, translocation, sorption and nutrient uptake (Table 5.10 and Fig. 5.5). Moreover, the roots of the plants pro-

Table 5.8 Metal hyper-accumulator species with respective metal accumulated

Plant species	Metals
Thlaspic aerulescens	Zn, Cd
Ipomea alpina	Cu
Sebertiaa cuminata	Ni
Haumania strumrobertii	Co
Astragulas racemosus	Se
Arabidopsis thaliana	Zn, Cu, Pb, Mn, P
Thlaspi goesingens	Ni
Brassica oleracea	Cd
Arabidopsis halleri	Zn, Cd
Sonchusasper	Pb, Zn
Corydalis pterygopetala	Zn, Cd
Alyssum bertolonii	Ni
Astragalus bisulcatus	Se
Strackhou sitryonii	Ni
Hemidesmus indicus	Pb
Salsola kali	Cd
Sedum alfredii	Pb, Zn
Pteris vittata	As
Helianthus anus	Cd, Cr,Ni

Source: Mojiri 2012

Table 5.9 Major roles of macrophytes in constructed wetlands

Constructed wetlands plant part	Role
Aerial plant tissues	Enhancing wildlife and aesthetic values
	Influence on microclimate (insulation during harsh climate conditions)
	Aesthetic appearance
	Storage of nutrient and other pollutants (e.g. heavy metals)
Plant tissues on support media	Producing litter organic carbon for denitrification and other microbial processes
	Provide sites for attached microorganisms.
Roots and rhizomes	Promoting the settling and retention of suspended solids
	Dispersing flow to minimize short-circuiting
	Providing surfaces for the development of microbial biofilms
	Transporting into their root-zone by excretion of photosynthetic oxygen to enhance bioconversion
	Assimilating pollutants
	Releasing of nutrients in slowly available organic forms
	Releasing of antibiotics.

Source: Tanner et al. (2006) and Sundaravadivel and Vigneswaran (2009)

Table 5.10 Phytoremediation mechanisms in constructed wetlands

Phytoremediation mechanism	Definition
Phytoextraction/phytoaccumulation	Pollutant uptake, transport, and translocated to above ground tissues. This mechanism is typically used to remove metals and other compounds from the soil
Phytodregradation (phytotransformation)	Plant species take up, store, and biochemically degrade or converted in harmful contaminants to harmless by-products. Plant species produce enzymes or other products that contribute to this mechanism. Primarily used for organic contaminants
Rhizofiltration/rhizodegradation	Plant roots grown in aerated water precipitate and concentrate toxic pollutants. The contaminants are either adsorbed onto the root surface or absorbed by the plant's root. The contaminants are broken down by enhanced microbial activity in the rhizosphere
Phytovolatilization	Plant species extract volatile metals and organic compounds from soil and water and volatilize them in their foliage.
Phytosequestration/phytostabilization	This process sequesters or reduces the bioavailability of the contaminants through precipitation or immobilization of contaminants in the soil, on the root surface, or within the root tissues
Phytostabilization	Plants stabilize the pollutants in soils or sediments, rendering them harmless, and control soil pH, redox generating speciation, precipitation and sorption

Source: K-State (2012)

vide sites for bacteria to grow and deliver oxygen to them (Akratos and Tsihrintzis 2007).

Plants species can assimilate several pollutants and nutrients (nitrate, ammonium and phosphorus), metals, metalloids, petrochemical compounds (fuels, solvents), pesticides and soluble radionuclide.

Aquatic plant species, including free-floating species such as *Eichhornia sp., Lemna sp., Azolla sp.* and *Salvinia sp.,* submerged species such as *Potamogeton sp.* and *Myriophyllum sp.,* and emergent species like *Limnocharis flava*, *Typha sp., Scirpus sp., Spartina sp., Phragmites sp.* and *Cyperus sp.,* have shown potential for removing metals and other pollutants from different types of wastewaters (Zupančič et al. 2009; Akinbile et al. 2012). Calheiros et al. (2007) found that constructed wetlands planted with *Typha latifolia* for the treatment of industrial wastewater gave good results.

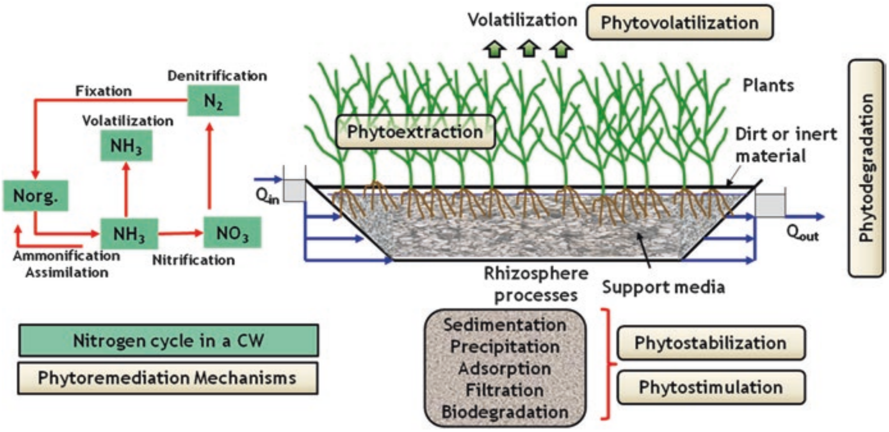

Fig. 5.5 Phytoremediation mechanisms and nitrogen flow in a constructed wetland (Source: Sketched by the authors 2014)

5.4.4.3 Design Considerations for Horizontal Flow Constructed Wetland

Horizontal flow constructed wetlands are designed based on the hydraulic retention time (HRT) and the average design water flow. For removal of BOD, nitrate and TSS from domestic wastewater a short hydraulic retention time is usually necessary, while ammonia and metal removal usually require longer retention times (Crites et al. 2006). The dimensioning of horizontal flow constructed wetlands is usually based on either volume or area (Ewemoje and Sangodoyin 2011). The design of horizontal flow constructed wetlands has changed from early empirical rules to advanced computer models, which try to explain the complexity of hydrodynamics in a porous medium, combined with many physical and biochemical processes involved in pollution removal (Ascuntar et al. 2009; Langergraber et al. 2009; Marsili and Checchi 2005). Horizontal flow constructed wetlands have been designed using either a simple “rule of thumb” set at 5 m^2 PE^{-1} or a plug-flow first order model (Kadlec and Wallace 2008). Recently, more complex hydro-dynamic, compartmental models have been developed (Langergraber et al. 2009).

Usually a first-order reaction kinetic model is used for determination of the area-specific removal capacity of contaminants in constructed wetlands. The removal rate constants (k) are often estimated based on inlet-outlet performance data from operational constructed wetlands technology, but the performance can be affected by several factors, such as wetland configuration, hydraulic and organic load. Another approach to estimate the removal rate constants that are less affected by some of these factors is to explore the concentration profiles of the pollutants from the inlet to the outlet in the wetland cell and to use these profiles to estimate removal rate constants (Diem et al. 2010).

Many texts and design guidelines for horizontal flow constructed wetland have been published such as Kadlec and Knight (1996), USEPA (2000), WPCF (1990), Reed et al. (1995), Cooper (1990), Campbell and Ogden (1990), Ellis et al. (2003), and DNR (2007). There are a few guidelines recorded for tropical climates, like MWC (2005, 2010), and UN-HABITAT (2008). Despite this, there are still voids regarding the application, design and performance of this technology in tropical conditions, especially in the initial design, with oxygen availability and nitrogen removal the most common setbacks in these regions (Chek et al. 2011).

The performance of constructed wetland cells under tropical conditions has not been extensively documented yet. Despite this, it has been assumed that constructed wetland processes are more efficient in equatorial regions than those in temperate conditions. This could be due to the positive effect of year-round plant growth and higher microbiological activity induced by warmer weather on constructed wetland processes (Katsenovich et al. 2009). Diem et al. (2010) found that the area based removal rate constant under tropical climatic conditions appears to be significantly higher than previously reported for constructed wetland cells in temperate areas, the higher water temperatures being the most plausible explanation. They also found that estimation of removal-rate constants based on pollutant concentration profiles from the inlet to the outlet is more robust in relation to variations in hydraulic loading rate and wastewater composition.

The design of constructed wetlands for landfill leachate treatment is partially relying upon known, quantifiable wetland treatment processes and performance but, regrettably, the complexity of landfill leachate requires that new concepts must be invoked. In other words, landfill-leachate treatment is not only removal of organic matter (BOD, TSS) and nutrients. Some of the important additional factors when treating landfill leachate can be summarized as follows (Kadlec and Wallace 2008): (a) higher Fe removal, (b) higher ammonia concentrations must be removed, (c) growth and physiological apparatus of plant species should not be affected, (d) rainfall and evapotranspiration have a significant role in constructed wetland cells with low inflow conditions, (e) reduction of other pollutants present in landfill leachate like volatile hydrocarbons (BTEX), (f) reduction of trace toxicants (PAHs, PCBs) and (g) accumulation and removal of trace metals.

The elimination of excessive amounts of iron, which may be present in leachates due to ferrous scrap materials, is best achieved separately from a wetland system. Either type of subsurface flow wetland is prone to clogging due to solids accumulation of precipitated iron. Iron usually oxidizes upon extraction from the anoxic environment of the landfill, creating a reddish mud that quickly clogs porous media. Therefore, it is better to oxidize the leachate in a basin that can also provide sedimentation of this material, especially when the quantities are excessive. For moderate amounts of iron, an inlet spreader deep zone can serve as the iron accumulator. In other cases, using the vertical flow constructed wetland nitrification system is recommended, followed by a free water surface constructed wetland, which also provides removal of volatile hydrocarbons via stripping, storage and biodegradation of heavier hydrocarbons, and storage of trace metals.

The final effluent from this treatment train can be recycled to dilute the high ammonia concentrations in the incoming leachate. This may be necessary to reduce the toxicity of the landfill leachate, because ammonia can be toxic to plant species

(Kadlec and Zmarthie 2010). This indicates that a combination of different configurations of constructed wetlands can effectively overcome the adverse factors.

Considering its characteristics, the toxic effects of landfill leachate on plant species should be avoided in the initial growth period and phytotoxicological testing may be helpful to select the appropriate leachate dosing rates. In this sense, Bialowiec and Randerson (2010) used phytotoxicological tests to study the response of willows when exposed to landfill leachate at different timings. Willow plants were able to survive in landfill-leachate solutions with electrical conductivity (EC) values up to 5.0 mS/cm when exposed to landfill leachate from the beginning, whereas plants were killed when the EC exceeded 3.0 mS/cm at later exposure. This indicates an ability of willow plants to acclimate and tolerate higher strengths of landfill leachate if they are cultivated in this condition from the infant stage.

5.4.5 *Feasibility of Constructed Wetlands for Landfill Leachate Treatment*

With respect to landfills, very often terms such as stability, completion, end-point and threat to the environment are used in discussions about sustainability. Scharff and Holding (2006) showed that there are many factors to take into account in order to establish if a landfill poses any threats or risks to human health and to the environment. Landfills can be considered “stable” when the buried solid waste mass does not pose a threat to human health and the environment. This situation has to be assessed by landfill leachate quantity and quality, gas production and composition.

A landfill with physical, chemical and biological stabilization is in the completion stage. In this situation, the liquid and gas emissions from the landfill do not pose any pollution risk in the landfill’s environmental setting. At completion, active aftercare pollution control (e.g. leachate management and gas management) and monitoring systems are no longer required. Finally, waste at final storage quality provides a situation where active environmental protection measures at the landfill are no longer necessary and the leachate is acceptable in the surrounding environment.

Landfill leachate treatment and disposition become an essential concern when implementing integrated solid waste management, given that it transports all sorts of pollutants that were landfilled during the site’s activity and represents a high risk of harming human health. For this scenario, choosing the most suitable treatment technology will be critical in an optimal integrated solid waste management framework and constructed wetlands offer a great variety of advantages that could fit perfectly into this concept by also offering a major leap in sustainable development, as a high-polluted liquid waste can be potentially reused and useful biomass can be produced.

Several technologies (chemical, physical and biological) have been discussed in this chapter that can efficiently treat landfill leachate, showing their advantages and disadvantages. Nonetheless, constructed wetlands were proposed as an alternative that could fit perfectly in a sustainable approach for multiple reasons, such as their proven effectiveness for pollutant removal, not only for organic matter and nutrients, but also for metals and recalcitrant compounds, confirmed by several researches in different types of climates. The low costs, adaptation capability and aesthetic appeal are also features that entitles constructed wetlands as a suitable component for a successful solid waste management.

5.4.6 Integrating Constructed Wetlands in Landfill Leachate Management Solutions

Landfill leachate is one of the most critical issues for landfill operators and may contain large amounts of organic matter (both biodegradable and recalcitrant), as well as ammonia-nitrogen, heavy metals and chlorinated organic and inorganic salts. Phytoremediation applications have been recommended as cheaper and more effective alternatives for the removal and recovery of pollutants from aqueous solutions and soil. Phytoremediation is a specific technology that uses fast-growing plants that have a huge demand for nutrients and moisture, making the technology a natural fit for on-site use of landfill leachate as a resource to the plant-based system. This advancement greatly reduces the financial burden and environmental problems associated with landfill leachate disposal, which is one of the most persistent and expensive problems within the solid waste sector. Phytoremediation can be applied in both open and closed landfills (Granley and Truong 2012).

Recycling and recovery are useful strategies implemented in several parts of the world to reduce the contamination and amount of waste handled. Besides, resources could be utilized to generate revenue to fund waste management (UNEP 2005). This principle, which forms the premise for an integrated solid waste management system, could be associated with the implementation of a constructed wetland technology for landfill leachate treatment, given that the constructed wetlands generate biomass for different uses and a high quality effluent for potential reuse.

Constructed wetlands not only represent a feasible alternative for landfill leachate management, but they can also be adapted to several climate conditions and a wide range of plant species, given that researchers have demonstrated the capability of many vegetal classes to remove, degrade and transform landfill leachate pollutants. Moreover, regions with a wide biodiversity could enhance the performance of constructed wetlands to obtain better treatment performance.

Table 5.11 Landfill conditions in several selected cities in Colombia

City	Landfill	# Municipalities	Landfill name	Population	Area (ha).	Solid waste disposed t day^{-1}	Closure year	Landfill leachate management
Bogotá	R	6	Doña Juana	6,778,691	472	5891.8	2012	Primary treatment
Medellín	R	22	La Pradera	2,219,861	354	2787	ND	Stabilization pond
Cali[a]	R	6	La Colomba	363	14,018	1800	2038	UASB
Barranquilla	R	4	Los Pocitos	1,112,889	135	1600	2041	NT
Cartagena	L	1	Loma de los Cocos	895,400	64	750	2015	ND
Neiva	R	12	Los Ángeles	315,332	155	323.9	2053	Landfill leachate storage
Pereira	R	17	La Glorita	428,246	–	650	2010	NT
Bucaramana	R	13	El Carrasco	509–918	92	734.3	2011	NT
Ibagué	L	1	La Miel	495,246	46	355.9	2020	NT

Source: Adapted from Noguera and Olivero (2010)

ND No data, *R* Regional, *L* Local, *NT* No treatment

[a] Information about Cali does not include the Navarro dump

5.5 Experiences of Landfill Leachate Management in Colombia

Currently the solid waste generation in Colombia is 26,537 t day^{-1} and almost 94% of this amount is disposed in landfills (SSPD 2012). Table 5.11 presents the information regarding the conditions of landfills in nine cities of Colombia that concentrate around 40% of the population of the country (18 million inhabitants).

5.6 The Presidente Sanitary Landfill

In the south-western part of Colombia, the Presidente regional landfill is employed as waste disposal management alternative for 18 municipalities of the Valle del Cauca Department. It was opened in 1998, with a projected shelf life of 30 years, and is managed by Bugaseo S.A. E.S.P. Table 5.12 presents the main features of the Presidente landfill.

Approximately 610 tons of solid waste arrives daily at the Presidente landfill, where this material is completely disposed of in the current operative cell. According to the operator, they receive both domestic and industrial waste, properly characterized before disposing it in the regular cell or in the security cell, if it's considered hazardous. The landfill has been adequate with its respective gas extraction wells and leachate collection system, properly covered with impervious material using geomembranes. A run-off collection system also surrounds every disposal cell in order to prevent erosion and drain storm water, which prevents an increase in leachate generation. Figure 5.6 presents the components of the Presidente landfill.

Presidente landfill leachate is transported from the landfill collection system to 11 oxidation ponds that store and pre-treat leachate before it is pumped to the membrane treatment system. Landfill leachate is treated in a facility, which includes membrane filtration with a Vibratory Shear Enhanced Process. Figure 5.7 shows an outline with all the components of the leachate treatment system and Fig. 5.8 presents these components in photographs.

Table 5.12 Presidente landfill's main features

Landfill name	Presidente
Location	San Pedro City, Valle del Cauca region, Colombia.
Actual capacity/used capacity	1000/610 t day^{-1}
Type of landfill	Above ground area landfill
Leachate production	1.0 L s^{-1}
Leachate treatment	Yes, physical treatment
Treated leachate discharge	No discharge. Effluent Reused for irrigation

Source: Bugaseo S.A. E.S.P. (2014)

Fig. 5.6 Presidente landfill components (San Pedro, Colombia) (Source: Photographs by the authors 2014)

According to the landfill management, the membrane system can remove about 99% of the landfill leachate organic load, fulfilling the required standard established by the Colombian national environmental regulation, which entails an efficiency higher than 80% for organics and solids load (kg day^{-1}). Unfortunately, no performance data are available for publishing.

The Presidente landfill is projected to be closed by the year 2025 and, after its closure, the area will be properly restored, but it will not be available for further use, which means that this landfill area will be constantly monitored over the coming years until the landfill displays activity and all environmental risks are controlled.

This treatment system includes three independent operation lines, each one with a capacity to treat 3 L s^{-1}, which entails an overall capacity of 9 L s^{-1}. The shelf life

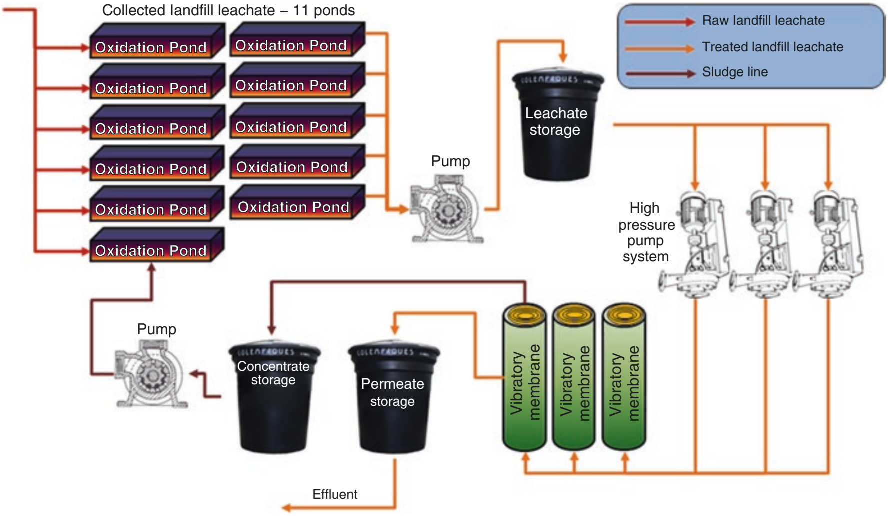

Fig. 5.7 Diagram of the Presidente landfill leachate treatment plant (Source*:* Sketched by authors 2014)

of the membranes is 10 years. This state-of-the-art technology reduces the contaminant load from a highly polluted type of wastewater and allows the Colombian environmental regulations to be fulfilled and mitigate the landfill's negative impact.

5.7 The Navarro Open Dump: Sanitary Landfill

An interesting experience of poor solid waste management and the use of engineering to remediate damaged ecosystems and recover environmental passives is registered in Santiago de Cali city (Colombia). Historically, Santiago de Cali disposed its urban solid waste in an open dump called Navarro (Fig. 5.9): with a population of nearly 2.5 million inhabitants, the city's urban waste reached almost 1800 tons per day. For over 30 years, this was the city's solid waste disposal site. Since 1999, intervention began to change the face of this open dump and engineering was used to try and turn it into a sanitary landfill in order to mitigate its negative impacts on the environment (Fig. 5.9).

The negative impact of Navarro reached the social sphere directly as a big community settled inside the landfill for several years before the intervention took place. This community survived by scavenging through waste, recovering potential recyclable materials and even feeding from the food leftovers that reached the landfill. Inevitably, living under such conditions created a public health problem with awful effects on the people settled there. As a consequence of the site intervention, this community was relocated.

Fig. 5.8 Photographs of the Presidente landfill leachate treatment plant (Source: Photographs by the authors 2014)

Fig. 5.9 Navarro landfill – before and after intervention (Santiago de Cali, Colombia) (Source: Pueblo 2012, Photographs by the authors 2014)

Fig. 5.10 Ponded old leachate from the Navarro landfill (Source: Photographs by the authors 2013)

Currently, the former open dump Navarro can be considered an almost closed sanitary landfill, given that waste disposal has been prohibited since 2009. From that moment onwards, a strategy started to be developed in order to manage the generated leachate, which was still a pending issue. Outsourcing was used to propose a potential solution to treat over 450,000 m^3 of old leachate, stored in eight lagoons (Fig. 5.10). This solution would also have to deal with the current leachate of $0.5\ l\ s^{-1}$ that is still being generated by the landfill.

In 2014, the construction of the leachate treatment plant was finished and it was started in June of the same year. Coagulation, flocculation and reverse osmosis were selected as the optimal treatment technologies for this type of leachate (Fig. 5.11). A dissolved air flotation system was installed as pre-treatment by coagulation and flocculation using ferric chloride. This stage is outlined to protect the further treatment stage, which consists of a two-step reverse osmosis system. The first step entails vertical reverse osmosis units and the second one has horizontal units

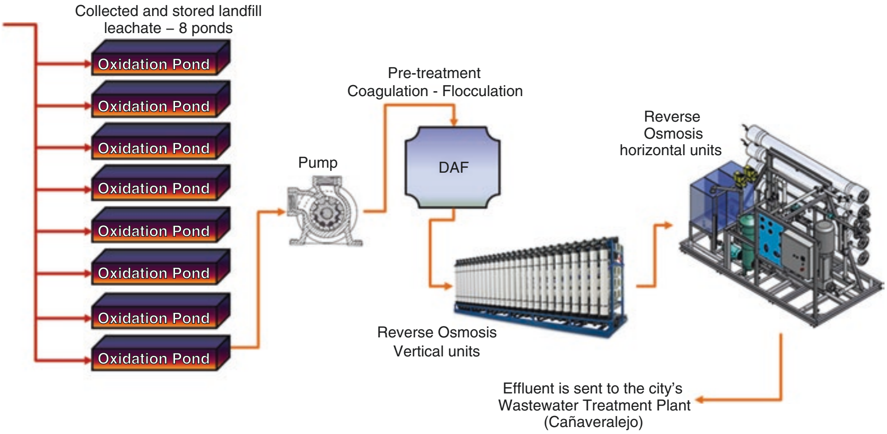

Fig. 5.11 Diagram of the Navarro landfill leachate treatment plant (Source: Sketched by the authors 2014)

Fig. 5.12 Photographs of the Navarro landfill leachate treatment plant (Source: Photographs by the authors 2014)

(Fig. 5.12). An efficiency of 99% of pollutant removal is expected from this treatment system.

Sludge from the dissolver air flotation system and the concentrate from reverse osmosis will be collected and transported to two former lagoons, which were emptied, reconstructed and covered with special geomembranes, in order to use them as storage units for this reject material. The Navarro leachate treatment plant performs physical and chemical processes to reduce the contaminant load from a highly polluted type of wastewater by efficiently combining two technologies, which will allow them, in theory, to fulfil the Colombian environmental regulation and mitigate the landfill's negative impact. Given that the Navarro landfill has been closed for the last 5 years, an eco-city is being planned in its surroundings, as a restoration alternative to mitigate the aesthetic impact of this facility and benefit from the potential soil use in this area.

5.8 Conclusions

Nowadays, optimal treatment of landfill leachate in order to reduce the leachate's environmental impact and human health risk is a challenge, since the variation in the amount and composition over time and location is a major threat that professionals must address. Biological systems like constructed wetlands, planted with the optimal plant species selected, may accomplish water quality requirements according to the current local or regional standards and attain reduction levels similar to those obtained with highly mechanized systems, with potentially lower costs. Hence, the development of constructed wetlands at full-scale is an attractive technology for landfill leachate treatment in countries with low resources and high necessities to protect the environment and public health.

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Chapter 6
Bioelectrochemical Systems for Heavy Metal Removal and Recovery

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Abstract Although metal bearing wastes are toxic, they possess economic value and hence need attention towards remediation/recovery. Various physical and chemical methods are being practiced for treating metal laden wastewaters, but are limited owing to the problems associated with maintenance and operational costs. Biological methods that use microbes as catalyst are cost effective and easy to operate, but only a little progress has been made in terms of recovery than the treatment. Recently, there is a shift in focus from bioremediation of metal wastes towards the recovery of valuable metals which are scanty. In this context, bioelectrochemical systems (BES) have emerged as a potential technological platform for recovery of metal ions from metallurgical waste (end-of-life products), process streams and wastewaters. In bioelectrochemical systems, microbial oxidation of organic substrate at the anode is coupled to abiotic or biotic reduction of metal ions at the cathode. With this perspective, this chapter gives an insight on the redox mechanisms of bacteria towards metal recovery along with the influence of

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in situ and *ex situ* potentials in bioelectrochemical systems. The exo-electron transport mechanism in bacteria for metal reduction and speciation is also discussed. Besides, the chapter also provides an overview on the metal speciation in bioelectrochemical systems along with electrochemical, physical and chemical methods for metal removal and recovery from wastewaters. Emerging metal recovery concepts based on bioelectrochemical systems are also presented in detail.

Keywords Microbial fuel cell (MFC) • Electrochemical methods • Bioelectrochemical treatment (BET) • Microbial electrolysis cell (MEC) • *In situ* immobilization • Microbial reduction • Exo-electron transport (EET) • Metal speciation • Electron flux • Metal respiration • Solid electron acceptor • Dissimilatory metal reduction bacteria (DMRB) • Redox mediators • Biopotential

Contents

Abbreviations

Ag	Silver
AMD	Acid mine drainage
As	Arsenic
Be	Beryllium
BES	Bioelectrochemical system
Cd	Cadimum
$CdCl_2$	Cadimum chloride
Co	Cobalt
Cr	Chromium

Cu	Copper
CymA	Quinol oxidase
DDTC	Diethyl-dithiocarbamate
DET	Direct electron transfer
DMRB	Dissimilatory metal reducing bacteria
E	Cell potential
e^-	Electrons
EET	Exo-electron transport system
E^o	Cell potential at standard-state condition
F	Faraday's constant
Fe	Iron
H^+	Protons
$HCrO_4$	Hydrogen chromate
Hg	Mercury
M	Metal
Mn	Manganese
MSW	Municipal solid waste
N	Number of moles of electrons
NF	Nanofiltration
NHE	Normal hydrogen electrode
Ni	Nickel
O_2	Oxygen
OMCs	Outer-membrane cytochromes
OmpB	Outer-membrane protein B
OmpC	Outer-membrane protein C
Pb	Lead
Qc	Reaction quotient
R	Ideal gas constant
RO	Reverse osmosis
Sb	Antimony
Se	Selenium
SHE	Standard hydrogen electrode
T	Temperature
Ti	Titanium
U	Uranium
US EPA	United States Environmental Protection Agency
Zn	Zinc
ZVI	Zero-valent ion

6.1 Introduction

Many metal ions are essential trace elements in the metabolism of living organisms, but they can cause acute and chronic lethal effects at elevated concentrations. Specifically, heavy metals discharged from industries and other sources are bound to have grave effects on humans and other living organisms and thus create serious health and environmental problems (Olojo and Awoniran 2012; Guo et al. 2010; Mathuriya and Yakhmi 2014; Galanis et al. 2009; Wu et al. 2012). The general properties of heavy metals include non-biodegradability, ability to accumulate in living beings via food chains, transformation into highly toxic compounds from low toxic compounds, e.g. mercury causes harmful effects even at very low concentrations (Volesky 1990; Bishop and Robinson 2002; Wang et al. 2011). Rapid industrialization and waste streams generated by industries such as the mining, metallurgical operations, electroplating, leather tanning and surface finishing industry are the primary sources of heavy metal pollution (Galanis et al. 2009; Wu et al. 2012). The widespread lethal effects are caused by lead, cadmium, mercury, arsenic and chromium as they are commonly used in mundane activities. Owing to their potential toxic and carcinogenic effects, as many as 13 metals, i.e. Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn, are included in the US EPA priority pollutants list (US EPA). Therefore, stringent limits have been adopted for the discharge of various metal ions in wastewaters to avoid environmental contamination. However, heavy metals at lower concentrations ranging from μg to mg/L that create severe adverse effects are discharged in the aquatic bodies (Wang and Ren 2014).

Various physicochemical methods, viz. ion exchange, chemical precipitation, electrolysis, electrodialysis, membrane filtration and photocatalysis as well as electro-chemical methods have been developed for the removal of metals from metal contaminated waters (Fu and Wang 2011; Pedersen et al. 2003; Kurniawan et al. 2006a; Barakat 2011). Different wastewater sources containing diverse ranges of metal concentrations and treatment techniques are presented in Table 6.1. Aside from pollution, metals are precious raw materials to a country's economy and need to be secured for sustainable production of key components of various products such as low carbon energy technologies, automobiles, electronic and biomedical devices (Nancharaiah et al. 2016). Heavy metal recovery also has commercial applications as the metals are valuable in various areas of modern technology including industrial, medical and household applications.

More generally, physical, chemical and electrochemical methods have been conventionally adopted for the removal and recovery of metal contaminated waters. Among these, electrochemical methods that employ electrodes to carry out redox reactions are widely used with an applied potential. Each metal has a specific potential and a specific electrode is required to determine the type of metal recovered/removed. Though electrochemical methods are effective for recovering the metals efficiently, many of these methods require high operational and maintenance costs. Hence, to resolve these problems, an alternative technology is envisaged, especially through biological processes (Dermentzis et al. 2011). Studies have documented that microorganisms act as an effective biocatalyst which interacts with a broad range of metals, thereby influencing the mobility of metal ions in natural and engineered environments (Kato et al. 2013; Van der Maas et al. 2005; Francis and Nancharaiah 2015; Nancharaiah and Lens 2015a). Henceforth, research is being focused on developing innovative methods to recover metals in order to make the treatment cost effective through metal biotechnologies (Wang and Ren 2014; Nancharaiah and Lens 2015b).

Table 6.1 Various metal bearing wastewater

	Metal ion (mg/l)											
Wastewater	Al	As	Cd	Cr	Co	Cu	Fe	Pb	Ni	Ag	Zn	References
Sewage treatment plant		0–0.0019	0–0.0033	0.04–0.56		0.079–0.58	0.48–3.9	0–0.039	0.0067–0.77	0–0.0014	0.26–.75	Karvelas et al. (2003) and Varga et al. (2013)
Tannery			0.056	391	1.55		4.4	0.872	0.179		0.023	Paruch and Roseth (2008)
Mining	0.161		0.004		0.0126	0.244	0.033		0.142		0.023	Chakraborty and Chakrabarti (2006)
Electroplating industry				0.71	0.97		618	0.46	0.64		584	Chen et al. (2013)
Industrially contaminated groundwater							65		0.11		0.51	Adey et al. (1996)
Battery factory	0.2–7.3		0.02–0.12	<0.0044–0.08		<0.0033–0.38	0.02–20	4.0–13	0.07–0.38		28.29	Yabe and Oliverira (2003)
Hazardous waste landfill					0.24		0.1		1.8	0.037	1.15	Pavelka et al. (1993)
Acid mine drainage		13.8	1.9		0.2				2.2		120	Jimenez-Rodrıguez et al. (2009)
An acidic industrial effluent				<5	<5	<5		30	<5			Cinanni et al. (1996)
Copper smelting		1.5	85	2.3	0.04	164.48	88	4.6			455.6	Basha et al. (2011)

(continued)

Table 6.1 (continued)

	Metal ion (mg/l)											
Wastewater	Al	As	Cd	Cr	Co	Cu	Fe	Pb	Ni	Ag	Zn	References
Road wash water	0.467–26.1			0.004–0.107		0.011–0.17	2.59–26.8	<0.018–0.053	<0.006–0.05		0.105–1.56	Paruch and Roseth (2008)
Tannery			0.056	391	1.55			0.872	0.179		0.684	Tariq et al. (2005)
Treatment method	CO	–	CP, FL, UF, NF, RO, AD, EC	FO, UF, IE, AD, EC	EC	CP, FL, FO, UF, NF, RO, IE, AD, EC	–	–	CP, FL, FO, NF, RO, AD, EC		CP, FL, FO, UF, NF, RO, IE, AD, EC	

CP Chemical precipitation, *FL* Flocculation, *FO* Flotation, *UF* Ultra filtration, *NF* Nano-filtration, *RO* Reverse osmosis, *IE* Ion exchange, *CO* Coagulation, *AD* Adsorption, *EC* Electrochemical technique

In this perspective, bioelectrochemical systems (BES) are developed for the production of sustainable energy and value added products by using bacteria as biocatalyst (Venkata Mohan et al. 2008a; 2014a, b; 2016; Logan 2010; Li et al. 2013). Bioelectrochemical systems have been intensely investigated in recent years for the treatment of different wastewaters with varied composition and characteristics (Venkata Mohan et al. 2009, 2010; Mohanakrishna et al. 2010; Velvizhi and Venkata Mohan 2011; Li et al. 2014; Pant et al. 2012; Wang and Ren 2014). Bioelectrochemical systems can be either single or dual chambered based on the separation of the anodic and cathodic cells towards the redox mechanism (Huang et al. 2013; Srikanth and Venkata Mohan 2012a, b; Venkata Mohan et al. 2008b, 2009, 2014a; Choi and Cui 2012; Venkata Mohan and Srikanth 2011). Bioelectrochemical systems are a new approach in removing and recovering metals from different wastewater types, since heavy-metal ions have the property of accepting electrons which directly influence the performance of bioelectrochemical systems in the cathodic processes (Rodrigo et al. 2010; Iskander et al. 2016; Li et al. 2016). The reduced metal ions could also be deposited on the cathodes to be recovered or, as mediators to be oxidized by terminal electron acceptors (Rodrigo et al. 2010; Lefebvre et al. 2012a).

Heavy metals like Cu^{2+}, Hg^{2+}, and Cr^{6+} exist in high oxidation states in oxic wastewaters and have a high redox potential for their redox couples (Cu^{2+}/Cu^{0}, Hg^{2+}/Hg^{0} and Cr^{6+}/Cr^{3+}), which are the properties required for a metal ion to be an efficient electron acceptor at the cathode (Wang et al. 2008). The reduction of metal ions can be catalyzed by the microbes along with the electron flow from the anode. The metal not only has effects on the biocatalyst, but also on the electrolyte conductivity and internal resistance (Lefebvre et al. 2012b; Rousseau et al. 2013). The advantages of using bioelectrochemical systems are multifold such as its environmental benefits and synthesis of value added products.

A bioelectrochemical system is the combination of conventional biological and electrochemical treatment processes considering the benefits of both processes. In this context, this chapter presents an overview of bioelectrochemical systems for removal and recovery of metal ions by both *in situ* and *ex situ* processes. The study also elaborates the metal speciation in bioelectrochemical systems considering the external factors and explaining the exo-electron transport mechanisms for metal respiration by bacteria.

6.2 Conventional and Electrochemical Processes in Metal Recovery

6.2.1 Conventional Techniques for Heavy Metal Recovery

The two major reasons that attract the removal and recovery of metals are the toxicity effect and their high economical value. Various treatment techniques have emerged in the recent years to treat heavy-metal-laden wastewaters

(Fig. 6.1). However, remediation of all these metals/metalloids cannot be achieved by secondary wastewater treatment methods like precipitation or adsorption etc. Hence, advanced/tertiary wastewater treatment methods, viz. membrane filtration and chemical precipitation can be used to remove heavy metals (Kurniawan et al. 2006b).

Membrane filtration is a widely used technique for the removal of heavy metals and is also capable of removing both organic and inorganic contaminants (Yang et al. 2001; Juang and Shiau 2000). However, the application of this process is limited owing to its high cost and problems associated with fouling (Sablani et al. 2001; Vigneswaran et al. 2005). Nanofiltration (NF) is a segregation/separation mechanism, which involves steric and electrical effects (Ahn et al. 1999; Van der Bruggen and Vandecasteele 2003; Qdais and Moussa 2004). This technique is very significant, as the small and charged solutes can be passed through the membrane and various metals, viz. Ni, Cd, Cu and Cr, can be recovered from wastewater (Qdais and Moussa 2004). Reverse osmosis (RO) also accounts for heavy metal removal of solutes, based on the pressure difference across the ion gradient membrane (Bohdziewicz et al. 1999; Ozaki et al. 2002; Benito and Ruíz 2002). Yet, these techniques also exhibit few limitations such as membrane fouling owing to the presence of small pores.

Besides membrane filtration, ion exchange is a widespread technique for heavy metal recovery. During this process, charged ions can be interchanged through the charged ion exchange resin/membrane between the solid and liquid phases, where

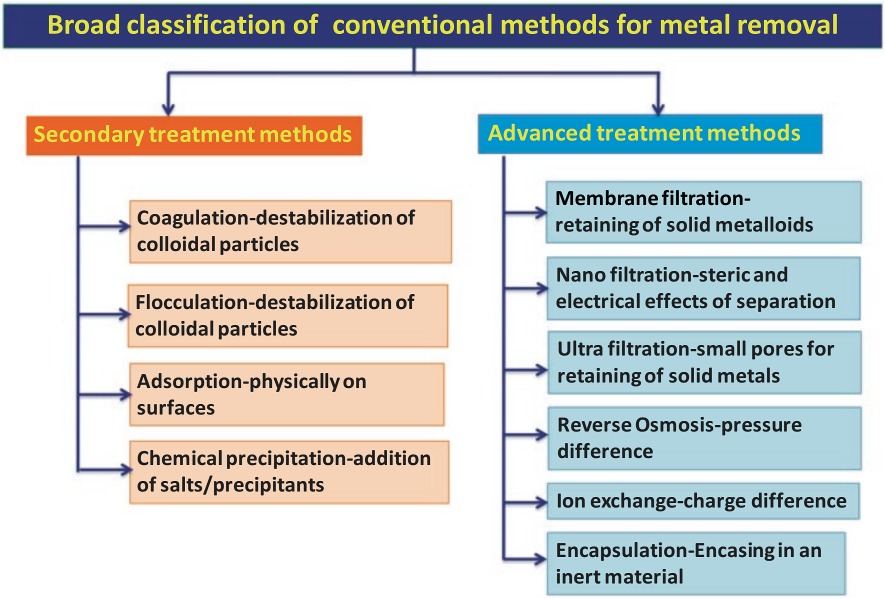

Fig. 6.1 Flow chart depicting the broad classification of physico-chemical methods for metal or metalloid removal and recovery

the valuable metal ions/compounds can be recovered from the electrolyte (Papadopoulos et al. 2004; Rengaraj et al. 2001; Vigneswaran et al. 2005; Daṃbrowski et al. 2004). Similarly, coagulation-flocculation, another technique works on the principle of destabilizing the colloidal particles upon the addition of a coagulant that results in sedimentation of metal ions as sludge (Semerjian and Ayoub 2003). Alum salts are added as a coagulant during the process which can be altered by using both poly-ferric sulphate and polyacrylamide as the flocculants to overcome the repulsive forces and sodium diethyl-dithiocarbamate (DDTC) as a trapping agent (Andrus 2000). Dithiocarbamate helps in the formation of a metal precipitate that helps in the recovery of the metal. Though the process is advantageous, it has certain limitations involving high operational costs and generation of sludge in high volumes.

Apart from the aforementioned techniques for heavy-metal removal/recovery, chemical precipitation is one of the most widely used techniques in the industries upon pH adjustment to 11 (Benefield and Morgan 1999). The dissolved metal ions will be converted as insoluble solids by a precipitant such as lime (Tünay and Kabdaşli 1994). More commonly, metals will be precipitated in the form of hydroxide from the solution (Tünay and Kabdaşli 1994). Lime precipitation can be employed for heavy-metal removal/recovery, viz. Cd (II), Mn (II) and Zn (II) cations (Charerntanyarak 1999). Though there are many conventional processes to treat these metal bearing wastewaters, they possess inherent limitations, viz. operational costs and non-ecofriendly nature during application.

6.2.2 Electrochemical Techniques for Heavy Metal Recovery

Electrochemical treatment techniques could make the metal recovery relatively easy and more selective than the conventional methods. Electrochemical techniques have the unique capabilities of carrying out redox reactions which aid in metal removal/recovery (Chen 2004). An electrochemical cell used in a metal removal process comprises of an anode and cathode to carry out the respective oxidation and reduction reactions (Simonsson 1997). The driving force to carry out these reactions is the potential difference between the redox reactions that drive the reducing equivalents specifically for the reduction reactions towards metal recovery. A well-controlled electrode potential regulates the overall recovery of heavy metals from wastewaters used within an electrochemical cell, by forming the precipitate/deposition on electrode surface upon charge neutralization, which can be separated further. In addition, pH of the electrolyte, current generation, conductivity and oxygen/hydrogen evolution affect the overall process efficiency during the metal recovery.

6.2.2.1 Anodic Oxidation

An electrochemical cell consisting of an anode chamber is meant for the oxidation reactions that will aid in the delivery of protons and electrons as energy source towards the electrochemical reactions that would help in the reduction at the cathode. In general, the electrolyte which is water/wastewater/buffer, will undergo electrolysis/oxidation due to the difference in potential (Simonsson 1997). The applied potential plays a significant role in the redox reactions carried out at both the anode and cathode. The externally applied potential helps in maintaining the required potential for the reduction of a particular metal compound by meeting its thermodynamic potential (Rajeshwar et al. 1994). The electrode material at the anode is also an important parameter to be considered during the electrochemical reactions for developing high electrode potentials. High electrode potentials enable enhanced oxidation reactions towards metal recovery (Bockris 1971). The process parameters, viz. pH, also significantly alter the process, as the change in pH is directly proportional to the change in electrode potential. The electrons and protons discharged as a result of electrolyte breakdown will reach the anode (electrode) and pass through the circuit towards the cathode for the reduction reactions. The anodic oxidation reactions can occur either by direct means or by mediated mode (Kotz et al. 1991). The electrons generated in the anode chamber will be carried to the cathode via a circuit that will further aid in metal removal/recovery. In certain cases, heavy metals can be placed into the anode chamber to undergo transformations in oxidation state upon the application of the potential. Generally, metal oxidation at anode chamber encounters problems associated with high oxygen gas evolution, over potentials and electrode stability. Dimensionally stable anode could be an alternate to overcome over potentials as well as high gas evolution processes. Only partial oxidation of metals can take place at anode, since the electrochemical reactions involve a series of oxidation reactions followed by reduction reactions. However, addition of metal catalysts as mediators enhances the metal recovery in the anode chamber by subjecting the partially oxidized metal to a series of redox reactions. At the anode, the following electrochemical reaction takes place upon the application of potential (Eq. 6.1):

$$\mathrm{H_2O} \rightarrow 1/2\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \tag{6.1}$$

6.2.2.2 Cathodic Reduction

Cathodic reactions are meant for the reduction of any metal compound/metal to a non-toxic, more reduced form (transition in metal oxidation state). Choice of metals to be employed at cathode need to be specific as the complete transition in oxidation state might lead to toxicity in some metals. The redox equivalents liberated in the anode chamber will reach the cathode and will be utilised towards the reduction reactions (Muller 1991). The major limiting reaction at the cathode is the formation of H_2 that leads to a decrease in current efficiency and subsequent metal recovery. Reduction of metal ions becomes spontaneous at the cathode provided the redox potential of the cathodic half-cell reaction is either comparable or higher than the anode potential. Huge quantities of metal ions present in the wastewaters discharged from electroplating and metal polishing industries can be recovered at the cathode using electrochemical techniques. Cathodic removal/recovery of heavy metals from various waste streams is an attractive and viable process, since the metal can be recovered in its pure metal/metalloid form or as a concentrated solution that can be recycled (Muller 1991). Various metals, viz. Ag^{2+}, Cd^{2+}, Au^{3+}, Ni^{2+} and Cu^{2+}, can be cathodically recovered through reduction (Eq. 6.2):

$$M^{2+} + 2e^{-} \rightarrow M^{0} \tag{6.2}$$

Though the conventional and electrochemical processes can account for metal recovery to a certain extent (partial), usage of solvents/chemicals as electrolytes and the application of potential using expensive electrode materials are the major economical constraints. Regulation of operational parameters and electrolytes in conventional and electrochemical processes, also adds to the cost. Hence, an alternative and economically viable route/process for metal recovery is required in the current scenario using the renewable resources.

6.3 Bioelectrochemical Systems

Keeping in view the economic viability and sustainability of the process, bioelectrochemical systems have emerged which are similar to electrochemical techniques in terms of redox reactions towards the metal recovery, except for the presence of bacteria as biocatalyst (Venkata Mohan et al. 2014a). Bioelectrochemical systems comprise of an electrode assembly consisting of an anode and a cathode to accomplish the oxidation and reduction reactions at the anode and cathode, respectively (Venkata Mohan et al. 2014b). The electrode assembly present in bioelectrochemical systems acts as a solid electron acceptor in aiding the biological redox reactions.

The biopotential/*in situ* potential developed in bioelectrochemical systems acts as the driving force towards metal removal and recovery (Venkata Mohan et al. 2014a). Some of the metal ions can be recovered by using the *in situ* generated potential, whereas other metal ions can be recovered by the *ex situ* or externally applied potential (Wang et al. 2008, 2011; Tandukar et al. 2009; Huang et al. 2011a; Heijne et al. 2010; Tao et al. 2011a; Zhang et al. 2012a, b; Lefebvre et al. 2012a).

Bioelectrochemical systems can be alternatively termed as “bioelectrochemical treatment systems”, if the treatment or recovery of any metal/product is considered as prime motto (Venkata Mohan et al. 2008a, 2009, 2014b). The treatment/removal/recovery of metals essentially depends on the overall cell potential as well as the individual half-cell potentials of anode and cathode. The coupled reactions occurring at the anode and cathode respectively, help in the overall removal/recovery of the metals. The mechanism of oxidation and reduction reactions towards the recovery of metals at the respective anode and cathode is discussed below.

6.3.1 In situ *Potential Influence on Metal Recovery in the Anodic and Cathodic Chamber*

Most of the bioelectrochemical systems are comprised of a biotic anode and abiotic cathode or a biotic anode and biotic cathode to accomplish the metal recovery. Bacteria play a crucial role in the biotic systems by utilizing the organic substrate and thereby liberate reducing equivalents. The reducing equivalents act as the power source for bioelectrochemical systems in reducing the metal species.

6.3.1.1 Biotic Anode

A bioelectrochemical system commonly employed for metal recovery is a dual chambered system consisting of an individual anode and cathode chamber. The anode chamber resembles a conventional biofactory consisting of a bacterial community that can be capable of degrading the organic substrates (Venkata Mohan et al. 2014a). The anode chamber is usually biotic, consisting of pure/mixed cultures of bacteria as biocatalyst aiding in substrate degradation (Venkata Mohan 2012). More commonly, wastewater consisting of large amounts of organics will be given as substrate in the anode chamber (Velvizhi and Venkata Mohan 2011). Some organic carbon sources, viz. acetate and glucose can be used as electron donors during bioelectrochemical system operation. Bacteria utilise the organic content and will liberate the reducing equivalents, viz. electrons [e^-] and protons [H^+], which act as the redox power in the bioelectrochemical system (Venkata Mohan and Chandrasekhar 2011).

The solid electrode present in the anode chamber acts as an electron acceptor, and will also aid in the development of the bio-potential between the anode and cathode in bioelectrochemical systems (Venkata Mohan and Chandrasekhar 2011). In general, the anode compartment of bioelectrochemical systems looks like an anaerobic bioreactor, which functions similarly to a conventional electrochemical cell that will be used for wastewater treatment. The redox reactions occurring inside the reactor will aid in the degradation of organic matter and toxic pollutants as well as the transformation of metal ions. The electrons liberated by the biocatalyst are passed onto the anode and then finally reach the cathode through the circuit. The electrons are then accepted in the cathode chamber by the terminal electron acceptor.

Various metals, viz. Ag, Au, V, Pb, Cd, Cr and Cu, have been recovered in the bioelectrochemical systems by the action of a biotic anode and abiotic cathode (Wang et al. 2008; Zhang et al. 2012b). Recently, many efforts were made for the recovery and removal of metal wastes, viz. Se(IV), V(V), Ag(I), Cu(II), Mn(IV) and

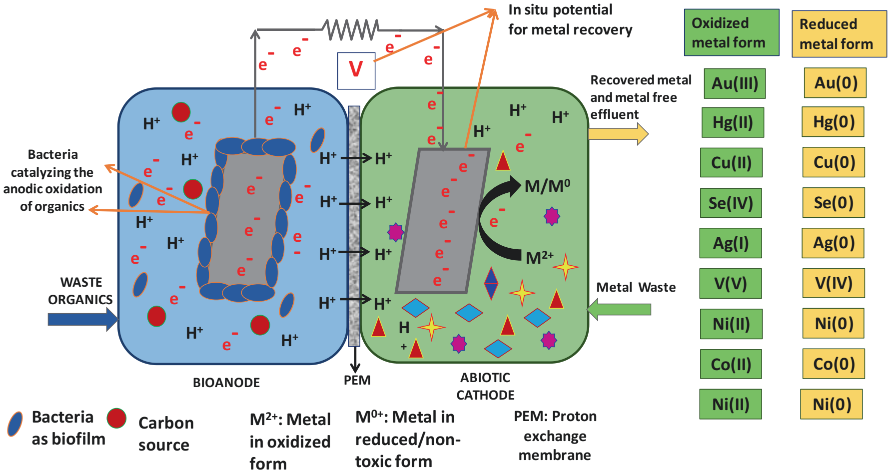

Fig. 6.2 Bioelectrochemical systems operated with biotic anode catalysing the degradation of organic substrates and abiotic cathode consisting of metal laden wastes depicting the influence of the *in situ* potential on metal removal/recovery along with the oxidation and reduction states of metal species

Cr(VI), using a bioelectrochemical system (Nancharaiah et al. 2015c, 2016; Li et al. 2014; Zhang et al. 2009; Rhoads et al. 2005; Tao et al. 2011b, 2012). The *in situ* potential developed between the anode and cathode in bioelectrochemical systems as a combined function of bacterial activity and the organic substrate will aid in the induction of the biopotential that will accomplish the metal recovery at the cathode (Fig. 6.2). More commonly, biotic anode enables the supplementation of redox powers required to carry out reduction of metals/metalloids at cathode. However, use of metals as electrode material/electron acceptor at anode chamber also has been studied which enables high electron transfer and transition in metal oxidation state. Use of metals was also used as a strategy for enriching metal reducing bacteria for high electron transfer which will be discussed in detail in the following sections. Concentration of metal must be optimum, as it causes lethal effects on bacterial growth if the concentration is high. Apart from metal removal/recovery, very high power densities have been reported in bioelectrochemical systems using metal-bearing wastes/wastewaters as substrate (Table 6.2). However, most of the heavy metals are more selectively recovered by using externally applied potentials. The following equation depicts the half-cell reaction at the anode, considering glucose as the substrate delivering electrons and protons (Eq. 6.3):

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \left(\text{Anode}\right) \tag{6.3}$$

Table 6.2 Power densities reported in bioelectrochemical systems using heavy metals and metalloids as substrate

Sl. No	Metal	Power	References
1.	Selenium	12.8 mW/m^2	Yang et al. (2014)
2.	Copper sulphate	314 mW/m^2	Tao et al. (2011b)
3.	Ag ion containing wastewater	4.25 W/m^2	Choi and Cui (2012)
4.	Cr(VI) and V(V)	970 mW/m^2	Zhang et al. (2012a)
5.	Sulfide and vanadium	614 mW/m^2	Zhang et al. (2010)
6.	Oil sand tailings	392 mW/m^2	Jiang et al. (2013)
7.	Tetrachloroaurtae	6.58 W/m^2	Choi and Hu (2013)
8.	Cu	143.6 mW/m^2	Wang et al. (2010)
9.	Cd and Zn	3.6 W/m^2	Abourached et al. (2014)
10	Zn (II)	0.233 mW	Fradler et al. (2014)

6.3.1.2 Abiotic Cathode

The majority of the reduction reactions take place at cathode, which aids in the removal and recovery of metals/degradation of oxidised pollutants (Velvizhi and Venkata Mohan 2011). The cathode chamber is usually abiotic (without bacteria) and aids in the electrochemical reactions (Modin et al. 2012). The compounds, viz. metals, pollutants, or nutrients that are targeted for recovery in bioelectrochemical systems can be placed in the cathode chamber for their reduction (Fig. 6.2). There are a series of bioelectrochemical reactions coupled between the anode and cathode chambers for the reduction of metal compounds. The electrons from the anode chamber reach the cathode and finally get consumed/utilised in the reduction reactions (Rabaey et al. 2004). The metal compounds act as good electron sinks due to their high electronegativity and can be reduced to a different form which can be easily recovered (Kim et al. 2002). Anaerobic micro-environments make the recovery or removal of metals/pollutants easy in bioelectrochemical systems, as the absence of oxygen makes the reduction of the next available higher electronegative compounds (metals) (Rozendal et al. 2006). The *in situ* potential generated in bioelectrochemical systems along with the liberation of higher numbers of reducing equivalents by the biocatalyst will help in the metal recovery (Modin et al. 2012).

The type of electrode material also affects the potential generation in a bioelectrochemical system (Modestra et al. 2016). Hence, non-precious and highly conductive hybrid electrodes can be developed to generate a higher bio-potential in bio-electrochemical systems to recover heavy metals by the *in situ* potential rather than applying external potential. Copper was removed and recovered as deposits on the cathode when the cathode chamber was fed with a fly ash leachate (Tao et al. 2014). Metal laden waste containing copper (Cu^{2+}) (Tao et al. 2011b; Heijne et al. 2010) and hexavalent chromium ($Cr_2O_7^{2-}$) (Huang et al. 2011a; Tandukar et al. 2009) has been used as electron acceptors/sinks at the cathode of bio-electrochemical systems. Both Cu^{2+} and $Cr_2O_7^{2-}$ have high reduction potentials, (0.340 V and 0.365 V, respectively), in which the metal recovery along with electricity generation can be simultaneously achieved. Studies have been carried out using titanium, carbon felt, nickel, graphite felt, graphite plates and activated carbon as electrode materials to recover the metals in bioelectrochemical systems (Nancharaiah et al. 2015c, 2016). The following equation represents the half-cell reaction at the cathode in which copper (II) reduction is observed (terminal electron acceptor) by accepting electrons and protons to form elemental copper (applicable at both biotic and abiotic cathode chambers) (Eq. 6.4):

$$2e^- + 2H^+ + Cu^{2+} \rightarrow Cu^0 \left(\text{Cathode}\right) \tag{6.4}$$

6.3.1.3 Biotic Cathode

The use of biocathodes has been gaining significant attention in the recent past owing to the advantages offered, viz. economic viability and ease of operation (He and Angenent 2006). Biocathode is the use of bacterial community in the cathode chamber for catalysing the reduction reactions (Srikanth and Venkata Mohan 2012a; Kondaveeti et al. 2014). An attractive alternative for abiotic cathodes are the biocathodes that can host a mixed microbial community for effective degradation of specific pollutants like chloramphenicol (CAP) or ferric/ferrous biocatalyzed oxidation/reduction (Sun et al. 2013; Srikanth and Venkata Mohan 2012b; Venkata Mohan and Srikanth 2011; Ter Heijne et al. 2006). The use of biocathode helps in the development of higher biopotential in comparison with abiotic cathode, as there exists a higher potential gradient between both the chambers to accomplish the metal reduction at cathode (Xia et al. 2013; Sun et al. 2012; Huang et al. 2011c). Metal speciation occurs in the presence of an electron donor either from the anode chamber or from the carbon source in the biotic cathode. More specifically, metal speciation occurs from its complex form to a simpler form, viz. cadmium chloride ($CdCl_2$ to $CdCl^+$ and $CdCl^-$) and chromium (Cr^{3+} to $HCrO^{4-}$, $CrOH^{2+}$, Cr_2O_3, $CrO_4{}^{2-}$) (Huang et al. 2011b). This metal speciation occurs via redox reactions in bioelectrochemical systems owing to the electron donation and acceptance by the more reduced metal forms (Fig. 6.2).

The potential of the bioelectrochemical systems for electro-bioremediation of arsenic (As) contaminated (ground) water and reduction to a zero-valent ion (ZVI) has been explored in a recent study (Pousa et al. 2015; Xue et al. 2013). The bacterial catalysed reduction of U(VI) (soluble) to U(IV) (insoluble) has been proposed as a strategy to immobilise/concentrate uranium, after it is extracted from contaminated soils and with the electrode serving as electron donor (Phillips et al. 1995; Holmes et al. 2002; Gregory and Lovley 2005). The heavy metal Cr(VI) is reduced in microbial fuel cells to the less soluble and less toxic Cr(III) by diverse microorganisms (Nancharaiah et al. 2010; Tandukar et al. 2009; Yarlagadda et al. 2012). During biocathode operation in bioelectrochemical systems, various strategies, viz. use of pure cultures as biocatalyst capable of reducing a particular metal, can be employed to recover precious and heavy metals.

Abiotic and biotic cathodic reductions represent a viable route for reducing the metals to a more reduced form by enabling a transition in metal oxidation state. Some abiotic cathodes require catalysts to enable metal reduction, while some do not mandate the catalysts for reduction. Process efficiency for metal reduction is relatively high with abiotic cathodes, as the removal/recovery is easy. In the case of biotic cathodes, recovery of metals is relatively less and requires unit operations. However, the biotic cathodic reduction is eco-friendly and the bacteria employed as biocatalyst is self-regenerative. In addition, bio-cathodes provides the enrichment of novel bacterial species capable of biodegradation of heavy metals and also promote the growth of exo-electrogenic bacteria that could generate high power densities.

6.3.2 Ex situ *Potential for Recovery of Metals in Bioelectrochemical Systems (BES)*

Bioelectrochemical systems provide a flexible platform for both oxidation and reduction reactions for efficient metal recovery (Wang and Ren 2014). Some metals can be reduced to metallic elements or ions with a lower chemical valency in BES due to the *in situ* potential developed. These ions are with positive standard potentials which create a large difference between the anodic and cathodic potentials, and thus get reduced based on the potential developed (Wang et al. 2008, 2011; Wang and Ren 2014). Owing to the thermodynamic limitations, a few metal ions cannot accept electrons spontaneously in the cathode chamber. Hence, they require an externally applied potential source to drive the electrons from the anode to cathode (Fig. 6.3). However, metals like Ni^{2+} ions cannot accept the electrons spontaneously because of the negative standard potential of the Ni^{2+}/Ni^{0} redox couple and according to the Nernst equation, about −0.54 V vs. Standard Hydrogen electrode (SHE) of cathodic potential is required to reduce 1,000 mg/L of Ni^{2+} to Ni^{0} (at 30 °C) (Eq. 6.5):

$$E = E^{\circ} - \frac{RT}{nF} ln\, Qc \tag{6.5}$$

where, E is the cell potential (V) under specific conditions, E^{o} is the cell potential at standard-state condition, R is ideal gas constant, T is temperature in Kelvin, n is number of moles of electrons transferred in the balanced equation, F is the Faraday's constant, and Qc is the reaction quotient.

A high cathode potential creates a more reduced environment, which is more favourable for transfer of electrons from the cathode electrode for Ni^{2+} reduction in the cathode chamber (Qin et al. 2012). Qin et al. (2012) documented that the Ni^{2+} removal efficiency in microbial electrolysis cell (MEC) was three times higher than those with an electrolysis cell and a microbial fuel cell indicating that the *ex situ*

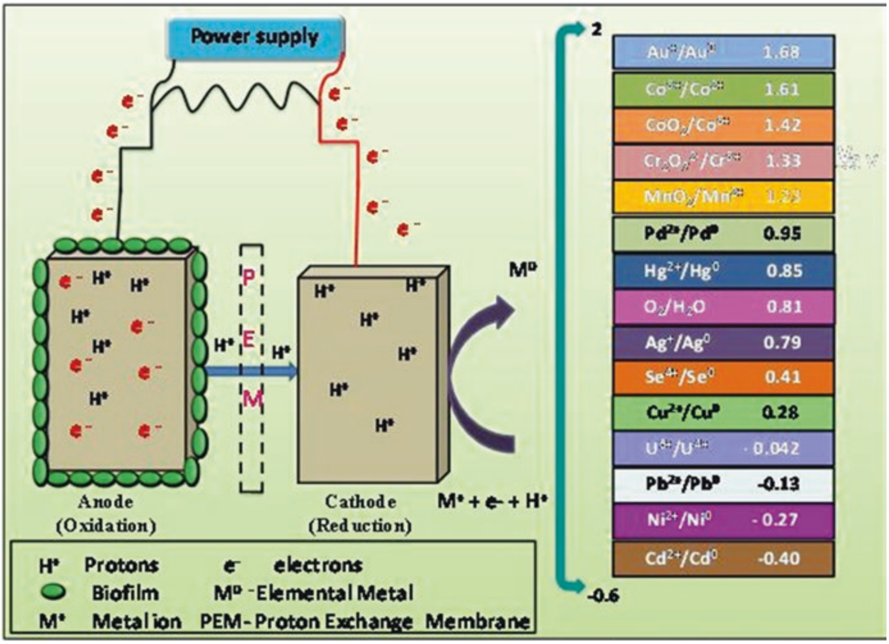

Fig. 6.3 Influence of externally applied (*ex situ*) potential on metal removal/recovery in bioelectrochemical systems operated with biotic anode and abiotic cathode representing the requisite redox potential at the cathode

potential facilitates more reduction of metals than *in situ* potential. Ni^{2+} removal efficiencies decreased from 99 (±0.6) % to 33 (±4.2) % with varying concentrations from 50 to 1,000 mg/L, while the mass removal of Ni^{2+} increased consistently with the initial concentrations. Ni^{2+} removal efficiency varied from 51 % to 67 % with an applied potential ranging from 0.5 to 1.1 V (Qin et al. 2012). With sequential application of the set potential, it is possible to selectively recover metals/metal ions from mixed metal ions from waste streams (Wang and Ren 2014).

Metal ions of Cu(II), Pb(II), Cd(II) and Zn(II) were sequentially recovered with gradual increments of applied voltages from 0.34, 0.52 to 1.7 V from a simulated municipal solid waste (MSW) leachate solution in a two chambered BES system (Modin et al. 2012). Recovery of Cu (77.2 %) was higher than for other metals (Pb(II), Cd(II) and Zn(II); 1.2–5.3 %) owing to the concurrent generation of hydrogen. Hydrogen production in microbial electrolysis cell (MEC) systems, on the other hand, assists in keeping pH balanced, with the accumulation of hydroxyl ions. Additional energy needed for metal reduction should also be considered, based on a cost-benefit analysis and generation of unintended hydrogen gas in some cases, which will reduce the metal-reduction efficiency when the cathode potential drops below −0.6 V vs. NHE (Normal Hydrogen Electrode) (Modin et al. 2012).

A tubular two chambered reactor consisting of graphite fibre as the anode and porous graphite felt as the cathode was operated for removing Co(II) along with the simultaneous formation of methane and acetate by applying potential (Huang et al. 2014). The study concluded that an increase in applied potential from 0.1 to 0.7 V increased the anode potential and decreased the cathode potential. Co(II) reduction increased with the increase in applied voltage from 0.1 to 0.3 V, and thereafter slightly decreased implying the existence of other electron sinks besides Co(II) reduction (Huang et al. 2014). Cobalt leaching was achieved by applying a voltage of 0.2 V at pH 2.0, and the studies documented that higher applied voltages and more acidic pH enhanced cobalt leaching (Mathuriya and Yakhmi 2014). Cu^{2+}, Ni^{2+} and Fe^{2+} were also observed to be removed from artificial acid mine drainage (AMD) with an external potential of 1.0 V (Luo et al. 2014).

Heavy metal exposure to microorganisms at lower concentrations will lead to the development of tolerance and evolution of metal tolerant strains. Hence, biotic processes are favourable for efficient metal reduction and in some cases, resistance develops when there is a gradual increase in metal concentration (Norberg and Molin 1983; Abourached et al. 2014). Metals like cadmium were recovered in a double chamber MFC by combining two cubical two-chambered MFCs connected in series, which worked as a redox-flow battery for recovering metal ions by successfully complementing a sufficient voltage and power. The study revealed that the highest maximum utilisation power density (22.5 W/m^2) of a Cr(VI)-MFC was 11.3 times higher than the highest power density directly supplied to a Cd (II)-MFC (2.0 W/m^2), indicating that there was a tremendous increase of current and power utilisation by installing multiple electron passages (Choi et al. 2014). This amplified phenomenon could be explained by the Le Chatelier's principle that addresses the rate of electron-hole pair formation can be accelerated by quickly removing electrons generated by microorganisms (Choi et al. 2014).

Setting the electrode potential is a viable approach to promote enrichment of biofilm and reduce the start-up time of MFC/MEC system. A tubular two cathode chamber was designed using graphite granules as cathode and graphite brush as anode. Microbial fuel cells were operated at set cathode potentials of −450 mV, −300 mV, −150 mV, −200 mV vs Standard Hydrogen Electrode (SHE) with a fixed resistance of 200 Ω. The study concluded that a set potential of −300 mV improved the subsequent performance of microbial fuel cells for Cr (VI) reduction by higher utilisation of metabolic energy (Huang et al. 2011b). Operating a microbial fuel cell followed by a bioelectrochemical system was effective for Cr(VI) reduction (Huang et al. 2011b). The biofilm developed in the anode in an MFC was used as the cathode in the BES system with a fixed set potential of 0.3 V (Wu et al. 2015). Hence, applying an external potential in a BES systems helps to recover metals from metallurgical waste, municipal solid waste (MSW) and acid mine drainage, etc. with a limited requirement of energy. The type of metal recovered/removed based upon electron donor and acceptor couples in bioelectrochemical systems is given in Table 6.3.

Table 6.3 Removal/recovery of metals and metalloids in bio-electrochemical systems representing the redox potential along with electron donor and acceptor

Metal	Type of reactor	Electron donor	Electron acceptor	Removal/recovery efficiency	Reduction potential	References
Cu $(NH_3)_4^{2+}$	Dual chamber	Acetate	Cu^{2+}	96 %	−0.40 V	Zhang et al. (2012b)
Se^{6+}	Single chamber	Acetate	Se^{6+}	99 %	–	Catal et al. (2009)
Cu^{2+}	Dual chamber	Acetate	Cu^{2+}	84.3 %	0 V	Modin et al. (2012)
Pb^{2+}	Dual chamber	Acetate	Pb^{2+}	47.5 %	0.34 V	Modin et al. (2012)
Cd^{2+}	Dual chamber	Acetate	Cd^{2+}	62.0 %	0.51 V	Modin et al. (2012)
Zn^{2+}	Dual chamber	Acetate	Zn^{2+}	44.2%	1.7 V	Modin et al. (2012)
Ni^{2+}	Dual chamber	Acetate	Ni^{2+}	67 ± 5.3 %	1.1 V	Qin et al. (2012)
Ag^{+}/Ag (I)	Dual chamber	Acetate	Ag^{+}	95 %	–	Tao et al. (2012)
Cu^{2+}	Dual chamber	Acetate	Cu^{2+}	98.5 %	0.568 V	Tao et al. (2014)
Zn^{2+}	Dual chamber	Acetate	Zn^{2+}	95.4 %	−0.550 V	Tao et al. (2014)
Pb^{2+}	Dual chamber	Acetate	Pb^{2+}	98.1 %	0.079 V	Tao et al. (2014)
Cd^{2+}	Single chamber	Acetate	Cd^{2+}	90 %	−0.4 V	Abourached et al. (2014)
Zn^{2+}	Single chamber	Acetate	Zn^{2+}	97 %	−0.764 V	Abourached et al. (2014)
Au^{3+}	Dual chamber	Acetate	Au^{3+}	99.89 %	1.002 V	Choi and Hu (2013)
Cr^{6+}	Dual chamber	Acetate	Cr^{6+}	27.3 %	1.33 V	Wang et al. (2008)
Fe^{3+}	Dual chamber	Acetate	Fe^{3+}	10–99 %	0.77 V	Lefebvre et al. (2012a)
Hg^{2+}	Dual chamber	Acetate	Hg^{2+}	89.5–99.3 % 0.851 V, 0.268 V	0.911 V, 0.796 V,	Wang et al. (2011)
V^{5+}	Dual chamber	Glucose	V^{5+}	67.9 ± 3.1 %	0.991 V	Zhang et al. (2012a)

6.4 Dissimilatory Metal Reduction by Bacteria

Microbial reduction of heavy metals and radionuclides has been represented as a potential strategy for the immobilization of contaminant metal species and radionuclides in waste streams and subsurface polluted environments (Lovley et al. 1993; Liu et al. 2002; Francis and Nancharaiah 2015). The importance of a group of bacteria called dissimilatory metal reducing bacteria (DMRB) on containment and transport of metals and their importance for remediation purposes is well recognized (Kato et al. 2012; Francis and Nancharaiah 2015). They reduce metals during anaerobic respiration through a cell membrane-associated exo-electron transport system (EET) (Richter et al. 2012). Dissimilatory metal reducing bacteria are being exploited in bioelectrochemical systems, viz. biocathode for remediation of minerals, taking advantage of these properties. Dissimilatory metal reducing bacteria like *Geobacter and Shewanella* can reduce various metals like Fe(III), Mn(III/IV), Cr(VI) and Co(III) as well as radio nuclides like uranium (VI) (Gorby and Lovley 1992). Bacterial mediated metal reduction is also important as it controls the fate of environmentally hazardous metals and radionuclides in sediments where the oxygen levels are depleted, like subsurface waters, wetlands and other contaminated environments. As many reduced metal species have a low solubility (e.g., U and Cr), they precipitate as immobilized forms during the microbial reduction process (Nancharaiah et al. 2006, 2010, 2012). This process of metal reduction can be enhanced at a higher rate by using these bacteria in bioelectrochemical systems where the *in situ* potential generated in the system can be effectively used for the metal reduction or additional potential can be applied in certain cases extra reducing power is required (Wang and Ren 2014; Nancharaiah et al. 2006).

6.5 Exo-electron Transport (EET) Mechanisms for Metal Respiration

The ability of bacteria to transfer electrons liberated during oxidative substrate degradation at the anode in different bioelectrochemical systems is under elaborate study. The anode chamber of bio-electrochemical systems can support the growth of both electroactive and non-electroactive bacteria which may or may not have biofilm-forming ability (Patil et al. 2012; Tran et al. 2016; Vamshi Krishna and Venkata Mohan 2016). The various key mechanisms involved in transfer of electrons to electrodes have been established recently. These mechanisms were studied elaborately in metal respiring organisms such as *Shewanella* and *Geobacter sp.* (Gorby and Lovley 1992). The molecular mechanisms of metal respiration in the case of the metal reducers differ depending on their environment or habitat and the minerals involved.

In bioelectrochemical systems, the outer-membrane C-type cytochromes (OMCs) and nanowires made up of pilin (protein complexes) aid in direct electron transfer (DET) to minerals (Mehta et al. 2005; Reguera et al. 2005). In addition, other redox proteins such as multi-copper proteins (OmpB and OmpC), have been shown to be important in exo electron transport by *Geobacter* species (Leung et al. 2013). The role of nanowires in exo-electron transport to the anode has mainly been shown for *G. sulfurreducens.* The nanowires are pilus-like extracellular appendages of bacteria that are electrically conductive. Conductivity across thick biofilms is essential for achieving high current densities, since it allows microbial cells to facilitate electron transfer to distant electrodes and contributes to current generation. The c-type cytochromes present on the outer surface of the nanowires and aromatic amino acids aligned along the nanowires of *G. sulfurreducens* help in conduction of electricity (Vargas et al. 2013).

In a similar way, the participation of cytochromes (c-type) in electron uptake by microorganisms from external electron donors is a common process in natural environments. In addition to these mechanisms, there are a few other ways bacteria transport electrons exocellularly such as redox mediators, the compounds which are also known to transfer electrons between bacteria and an electron acceptor by shuttling between bacteria and acceptor (Brutinel and Gralnick 2012; Marsili et al. 2008; Nancharaiah et al. 2012). In certain cases (like alkalinity) *Shewanella oneidensis MR-1* can use elemental sulphur as an electron shuttle to reduce Fe (III) (Flynn et al. 2014). A direct electron transport pathway called the metal reduction (Mtr respiratory) pathway, consisting of an inner- membrane-associated quinol oxidase (CymA), periplasmic and outer-membrane complex Mtr CAB, OmcA complexes has been identified in *S. oneidensis* MR-1 strain (Pirbadian et al. 2014). In these complexes MtrA, which is a periplasmic protein, and MtrC, which is an outer membrane protein, are multi-heme c-type cytochromes and MtrB is an outer-membrane ß-barrel non-heme protein that connects the two cytochromes. The electrons from the quinone pool are passed to the inner membrane CymA, then to MtrA, and finally exit at MtrC and OmcA (Fig. 6.4). A homologous complex of MtrCAB, one denoted as MtrFDE, has also been reported in *Shewanella* (Teravest et al. 2014; Coursolle et al. 2010). It has also been observed from microarray and proteome analysis that these microorganisms express an array of various proteins to reduce different metal species in the environment while sharing few proteins in common. This indicates that bacteria have various mechanisms to take up various metal species (Aklujkar et al. 2013; Ding et al. 2008).

6.6 Metal Speciation

Metal speciation depends on its physical state, chemical oxidation state and its association with other elements. Factors governing metal speciation at a defined point of time include pH of the associated medium, acidity, alkalinity, quantity and composition of the organic matter with in the surrounding environment, presence of Fe/Mn/Al oxides and hydroxides, redox potential and salt concentration. The mobility and bioavailability of metals depends on their chemical and mineralogical characteristics (Okoro et al. 2012).

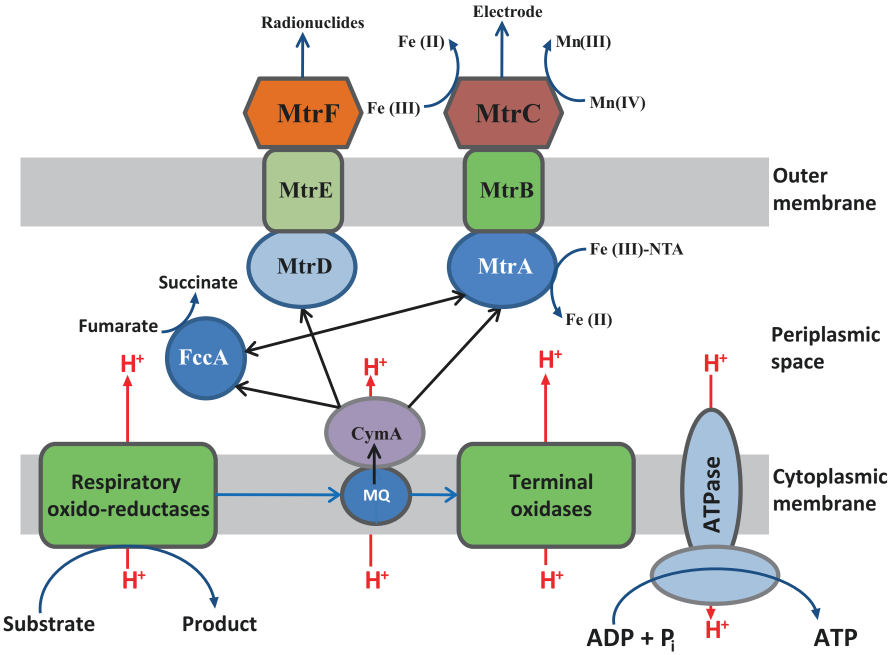

Fig. 6.4 Possible routes for iron (III) and manganese (IV) reduction in bacteria through the metal reducing (Mtr CAB) complex with fumarate as electron donor (*Arrows* indicate the transfer of electrons)

The hydrogen ion concentration is one of the most significant factors governing metal speciation. pH increment generally causes an increase in the specific metal uptake because of the ionic competition for active sites. pH, acidity and alkalinity are inter-dependable factors which are metal specific and control speciation, solubility and mobility of the metals within the medium (Sherene 2010), while the pH and redox potential of water/surrounding environments directly influence the metal species solubility and concentration (Olaniran et al. 2013).

6.6.1 Metal Speciation in Bioelectrochemical Systems and the Redox Mediators

The microbial electron exchange in bioelectrochemical systems in the presence of metals has been suggested through extracellular electron transport capabilities (Harris et al. 2010) and through direct electron transfer mechanisms (Patil et al. 2012). The electron transfer to minerals (metals and their complexes) has been well studied as far as metal reducers are concerned (Lloyd 2003), as depicted in Fig. 6.5. The role of outer-membrane cytochromes (OMCs) and conductive pili or cell

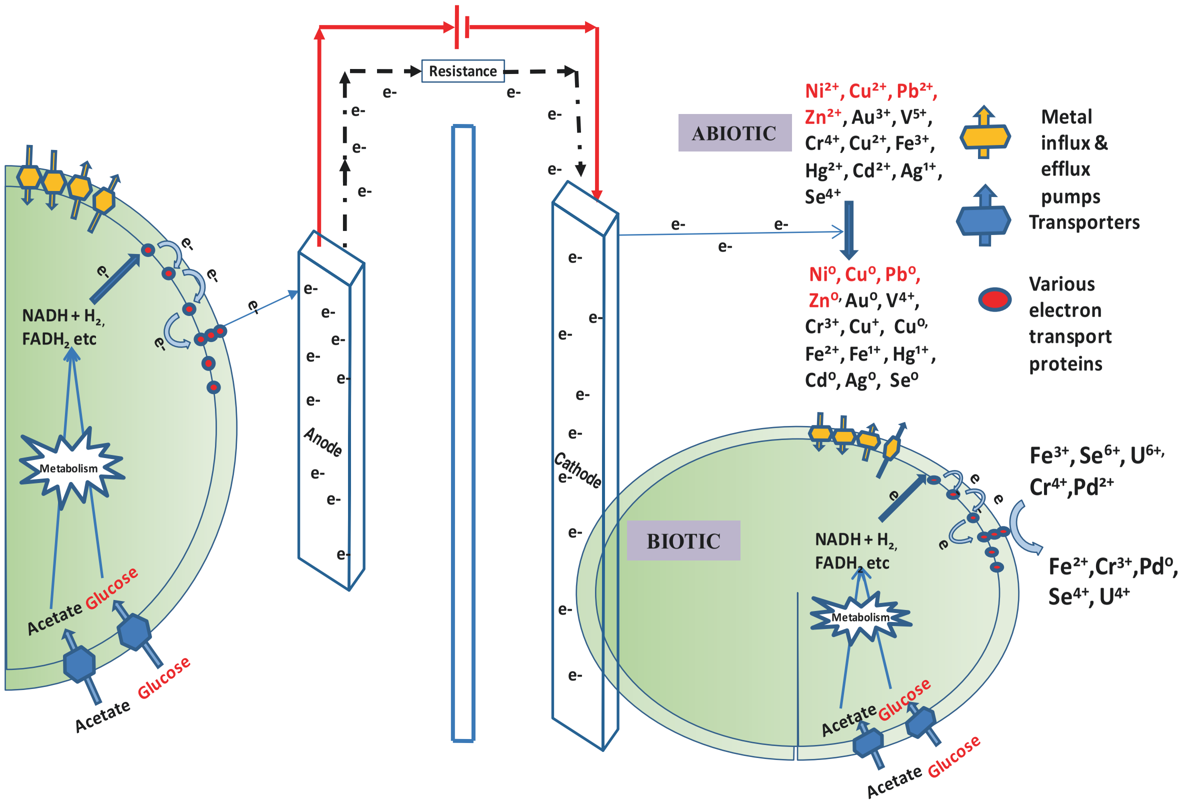

Fig. 6.5 Bacterial metal respiration – schematic illustration of metal reduction and speciation through various exo-electron transport proteins in the presence of acetate/glucose as electron donor and metal as an electron acceptor

appendages (referred to as nanowires) in facilitating direct electron transfer to minerals in both *Geobacter* and *Shewanella* spp. has been explored and reported extensively (Patil et al. 2012). In addition, other redox proteins, such as multi-copper proteins (OmpB and OmpC), play an important role in mediating exo electron transport during reduction of Fe(III) (Liu et al. 2014). The function of outer- membrane complexes in reducing extracellular soluble redox compounds such as anthraquinone-2, 6-disulfonate, humic acid and riboflavins have also been confirmed (Paquete et al. 2014). In addition to direct electron transfer, another major pathway involved in mineral respiration is mediated electron transfer, which involves redox mediators that shuttle electrons between cells and electrodes (Liu et al. 2013). In addition, the role of the Mtr porin protein complex was demonstrated in *Shewanella* spp., indicating the involvement of more than one pathway, or overlapping pathways, in mineral respiration (Richardson et al. 2012). Dissimilatory metal reducing bacteria can use humic acids (heterozygous, soluble, high molecular weight organic compounds) as extracellular electron acceptors and also as redox mediators in the extracellular respiration of iron oxides (Fe (III)).

6.6.2 Redox Reactions and Electron Flux and Salt Concentrations During Metal Speciation

Metal species in their free dissolved ionic state are more bioavailable than in the most complexed state. Mobilisation or immobilisation of metals is catered by the redox reactions depending on the characteristic of metal species and microenvironments (Violante et al. 2010). The electron flow from an electron donor to electron acceptor is the basis for all metabolic functions. Quinones play an essential role in the electron transport systems in microbes. Most of the toxic metals are effectively remediated by (1) making use of metals as part of their electron transport chain, (2) complexing with extracellular secreted materials, (3) internalising them into the cytoplasm, (4) converting them into a non-toxic biochemical form (Gadd 2010) in micro-organisms is widespread (Gadd 2008). Many other metals like silver, aluminium, cadmium, gold, lead, tellurium and mercury do not have biological significance and are potentially toxic to microorganisms. Metals like Cd, Hg, Cr, Pb and As are extremely toxic even at low concentrations. The presence of some of the cations like sodium, iron and aluminium compete with other metals for binding to specific sites. Studies have shown that high sodium levels interfere with copper uptake on biological membranes while iron and aluminium will form strong complexes with organic matter owing to their higher valence (III) (Tipping 1994). This prevents in complexing of metals like copper with dissolved organic matter (DOM) (De Schamphelaere and Janssen 2004).

6.7 Conclusion

This chapter presents the scope and importance of bioelectrochemical systems as an emerging and highly versatile platform for the removal/recovery of precious heavy metals by using bacteria as biocatalyst in driving the redox reactions towards metal recovery. The *in situ* generated bio-potential and *ex situ* applied potential favours in enhancing the redox reactions towards metal removal/recovery. However, research in bioelectrochemical systems on metal recovery should be more focussed in terms of regulating/enhancing the bacterial metabolic capabilities in discharging a higher number of reducing equivalents which in turn will aid in metal reduction. The scope for future research in metal reduction through bioelectrochemical systems includes the strategies on developing efficient cathode materials, optimum fuel cell configurations, circuit design and biocatalyst enrichment to improve the reduction reactions towards metal removal/recovery. Biocathode studies should also be pursued in the future to enrich defined metal reducing bacterial communities towards metal recovery. The exocellular electron transport mechanism needs to be studied to gain insights on metal reduction and recovery using various new bacterial strains. In the future, bioelectrochemical systems are expected to be a viable alternative for the removal/recovery of metals.

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Chapter 7
Bioprecipitation of Metals and Metalloids

Erkan Sahinkaya, Deniz Uçar, and Anna H. Kaksonen

Abstract Heavy metals are toxic, carcinogenic and unlike organic contaminants are not biodegradable, and thus accumulate in organisms. Approximately 60% of the polluted areas in the world, suffer from the harmful effects of metals including Cd, Ni, Cu, Pb, Zn, Hg and Co. Mining, fertilizer, tanneries, paper, batteries and electroplating industries are the main sources of heavy metal containing waters. For example, in China, the annual amount of heavy metal containing electroplating industry wastewater has exceeded 4 billion tons. Up to 1000 mg/kg heavy metal concentration in sediments has been reported due to repeated discharges. We reviewed the sources of heavy metal containing water and metal precipitation techniques including metal sulfide, hydroxide, ferrihydrite, geothite, jarosite as well as schwertmannite precipitation. Metal sulfide precipitation relies on the biological generation of H_2S and near complete metal removal is possible with both organic (i.e. ethanol) and inorganic (i.e. hydrogen) electron donors. The utilization of soluble electron donors provides high rate and dense metal precipitates with metal recovery of over 80% (usually 100%). Additionally, metals can be recovered separately as various metal sulfides by adjusting pH. Biological oxidation/reduction processes facilitate the formation of insoluble metal precipitates for uranium (U^{6+} to U^{4+}); chromium (Cr^{6+} to Cr^{3+}) or iron (Fe^{2+} to Fe^{3+}). The major points extracted from the study are: (1) metal sulfide precipitation is fast, results in low residual metal concentrations and allows for selective recovery of various metals with a wide variety of different reactor configurations, (2) high rate biological metal recovery is possible with cultures which use metals as electron acceptors which eliminates the drawbacks such as chemical costs and huge sludge volume production in chemical reduction, (3) animal manure, leaf mulch, sawdust, wood chips, sewage sludge,

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cellulose could be used in passive treatment systems and therefore operational costs could be optimized, (4) some heavy metals can be precipitated through biological oxidation (i.e. Fe^{2+} to Fe^{3+}) and (5) possible iron precipitates include hematite (Fe_2O_3); geothite (FeOOH); ferric hydroxide $Fe(OH)_3$; jarosite $Fe_3(SO_4)_2(OH)_6$; schwertmannite $Fe_{16}O_{16}(SO_4)_2(OH)12.n(H_2O)$ and scorodite ($FeAsO_4.2H_2O$).

Keywords Acid mine drainage • Biooxidation • Bioprecpitation • Bioreduction • Heavy metal precipitation • Iron oxidation • Metal precipitation • Metal recovery • Metal removal • Oxidative precipitation • Reductive precipitation • Sulfate reduction

Contents

Abbreviations

EC	European Commission
EPA	Environmental Protection Agency
MS	Metal sulfide
SI	Saturation index
WHO	World Health Organization

7.1 Introduction

Bioprecipitation can be defined as the conversion of soluble metals and metalloids into insoluble precipitates by the activity of microorganisms. Microorganisms can facilitate precipitation by catalyzing oxidative and reductive processes that lead to the precipitation of contaminants such as iron, uranium and chromium. Some microorganisms can also liberate phosphate and enhance metal phosphate precipitation. Others may enhance hydroxide or carbonate precipitation by generating alkanity (Kaksonen and Puhakka 2007). Biologically catalyzed precipitation can be utilised to remove metals and metalloids from a range of wastewaters, such as acid mine drainage and effluents from electroplating and tanneries. This chapter reviews antropogenic sources of metal-contaminated wastewaters and discusses various treatment options that are based on bioprecipitation of metals and metalloids. The focus will be on sulfate reduction based treatment and bioprocesses which rely on oxidative and reductive precipitation.

7.2 Major Anthropogenic Sources of Heavy Metals and Metalloids

Heavy metals are toxic or carcinogenic and unlike organic contaminants, they are not biodegradable. Heavy metals also tend to accumulate in organisms, which may lead to a reduction in species diversity (Naser 2013). The source of metal pollution may be anthropogenic or natural. The most important anthropogenic activities are direct or indirect discharges of wastewaters originating from sewage, several industries, such as mining, fertilizer, tanneries, batteries, paper and electroplating (Fu and Wang 2011). Several heavy metals and metalloids are released to the environment from various anthropogenic sources with a particular concern on Zn, Cu, Ni, Hg, Cd, Pb, Cr and As (Fu and Wang 2011; Sahinkaya and Kilic 2014). Heavy-metal (Zn, Cu, Cr, Pb and Mn) contamination has been reported for rivers and harbor sediments with concentrations up to 300–1000 mg/kg owing to repeated discharges over many years. High industrial activities may lead to an increase of Cd and Zn concentrations in sediments over 40 mg/kg and 10,000 mg/kg, respectively (Lors et al. 2004; Fang et al. 2011).

Furthermore, several industrial activities, such as pulp and paper, fermentation, food production, electroplating, tanneries, petrochemical and mining processes produce sulfate-laden wastewaters (Kaksonen and Puhakka 2007; Tang et al. 2009; Hao et al. 2014). Mining and metallurgical industries produce the largest volumes of sulfate and metal containing wastewater (Fu and Wang 2011; Hao et al. 2014). Major anthropogenic sources of sulfate, heavy metals and metalloids are introduced below.

7.2.1 Acid Mine Drainage

Sulfidic mineral exploitation causes the oxidation of reduced sulfide minerals leading to the formation of metal- and sulfate-containing acidic water, which is known as acid mine drainage (Foucher et al. 2001; García et al. 2001; Jong and Parry 2003). Pyrite (FeS_2) is oxidized via the following chemical reaction 7.1 generating acidic iron- and sulfate-containing water (Flege 2001):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+ \tag{7.1}$$

Iron-oxidizing microorganisms can catalyse sulfide mineral oxidation by regenerating ferric iron, which acts as a strong oxidant. Sulfur oxidizing microorganisms oxidise reduced sulfur compounds to sulfuric acid, which decreases pH and attacks acid soluble metal sulfides (Rohwerder et al. 2003). Metals and sulfate may also be released to the aqueous phase owing to the oxidation of other sulfidic minerals, similar to pyrite oxidation. Hence, acid mine drainage may contain elevated concentrations of various metals including Cu, Fe, Zn, Al, Pb, As and Cd (García et al. 2001). As an example, the oxidation of arsenopyrite with oxygen and ferric iron is shown in reactions 7.2 and 7.3, respectively (Gemici et al. 2008; Natarajan 2008):

$$2FeAsS + 7O_2 + 2H_2O \rightarrow 2Fe^{3+} + 2SO_4{}^{2-} + 2H_2AsO_4{}^- \tag{7.2}$$

$$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4{}^{2-} + 13H^+ + H_3AsO_4 \tag{7.3}$$

The characteristics of acid mine drainage show great variation depending on the minerals to which water is exposed, environmental conditions and flow regime. A typical acid mine drainage composition is given in Table 7.1.

Generally, chemical coagulation and flocculation processes are used for metal removal from acid mine drainage. The biological processes such as oxidation and reduction, biosorption, intracellular uptake and accumulation, extracellular precipitation and complexation may also be used for metal removal. Biological processes, such as sulfate reduction, may generate alkalinity and increase the pH of acid mine drainage to neutral levels, which helps the removals of metals as metal-sulfides (Kaksonen and Puhakka 2007). The sulfate reduction bioprocess not only removes sulfate, but also precipitates metals and increases the wastewater pH. Hence, it may be the most promising biological method for treatment of acid mine drainage (Kaksonen and Puhakka 2007).

7.2.2 Electroplating Industries

Electroplating was defined as a thin surface coating of one metal upon another by electrodeposition (EPA-440/1-84/091 1984). Wastewater from electroplating processes has a low pH and contains elevated heavy metal, chloride, nitrate and sulfate

Table 7.1 Acid mine drainage characteristics at a mine site in Turkey

Parameter	Concentration (except pH, mg/L)
Chemical oxygen demand	Lower than 30
pH	3.04
Sulfate	3 360
Al	54.3 ± 3.0
Ca	117 ± 6
Cd	0.01 ± 0.01
Co	8.99 ± 0.48
Cr	0.12 ± 0.03
Cu	44.9 ± 2.8
Fe	391 ± 60
K	19.3 ± 0.9
Mg	342 ± 20
Mn	6.05 ± 1.72
Na	11.2 ± 1.9
Ni	3.78 ± 0.2
Pb	6.90 ± 2.23
Zn	5.90 ± 0.84

Adapted from Sahinkaya et al. (2011)

concentrations. The heavy metal content of electroplating wastewater depends on the metals used for coating (Mazumder et al. 2011). Chang and Kim (2007) reported that an electroplating wastewater contained 1564 mg/L sulfate, 36.5 mg/L Cu, 225 mg/L Cr and 54.5 mg/L Ni together with low concentrations of Fe, Sn, Ag and Zn. Chromium is a common pollutant in electroplating wastewater. It is one of the most toxic metals according to the World Health Organization (WHO) (Tammaro et al. 2014) and is of concern owing to its mutagenicity and carcinogenicity (Chang and Kim 2007). Hexavalent chromium (Cr^{6+}) is highly mobile in the environment (Melitas et al. 2001), whereas trivalent chromium (Cr^{3+}) hydroxide has limited solubility at neutral pH and is thus less available for biological uptake (Alowitz and Scherer 2002). Although Cr^{3+} is less dangerous than the Cr^{6+}, it may cause skeletal and neurological disorders (Tammaro et al. 2014).

Copper may accumulate in the liver and the lenticular nucleus of the brain. Electroplating wastewater may also contain cyanide (Mazumder et al. 2011) and organic compounds that cause high chemical oxygen demand. Liu et al. (2014) reported that acid-nickel-copper line of an electroplating factory may contain chemical oxygen demand (693 mg/L), Ni (20 mg/L), Cu (4 mg/L), NH_3-N (60 mg/L) and P (345 mg/L). Therefore, in addition to heavy metals, chemical oxygen demand and nutrients (N and P) should also be removed from wastewater before discharge.

Since electroplating wastewater contains a high concentration of sulfate, sulfate-reducing bacteria may be used to generate dissolved sulfide to precipitate heavy metals. Hence, bioprecipitation may be an alternative and less expensive way for treating electroplating wastewater (Chang and Kim 2007).

7.2.3 Tannery Industries

Tanning processes transform animal skins into stable leather (Lofrano et al. 2013a). Leather tanning is an important industry in Mediterranean countries, especially in Italy, which has 17% of the world and 62% of the European Union production. Tanneries are also an important economic industry in other countries, like Turkey, Pakistan, India, Brazil, China and Ethiopia (Lofrano et al. 2013b).

The tanning industry is extremely water intensive as approximately 150–200 L wastewater is generated for each kg of leather produced (Fabbricino et al. 2013; Lofrano et al. 2013b). Four sub-processes are required for finished leather production: retanning, finishing, beamhouse operation and tanyard processes. The tanning process varies for each end product and both the amount and the characteristics of wastewater vary accordingly (Lofrano et al. 2013b). Acids, alkalis, chromium salts, tannin solvents and sulfides are used in the production and these chemicals may not be fixed completely by the skin and increase the contaminant concentration in the wastewater (Fabbricino et al. 2013; Lofrano et al. 2013b). Tanning industry wastewaters show a great variation and some typical characteristics are given in Table 7.2.

The presence of high chromium, tannins and other toxic organic/inorganic compounds in tannery wastewater makes their biological treatment difficult. Pretreatment with advanced oxidation process may increase the biodegradability of tannin (Kalyanaraman et al. 2014). Tammaro et al. (2014) compared biological activated carbon and activated sludge processes for tannery wastewater treatment. For soluble chromium and chemical oxygen demand removal, the biologically activated carbon process gave a much higher performance. Chromium may also be removed from wastewater using some other alternative bioprecipitation processes.

Table 7.2 Characteristics of tannery wastewaters

Parameters	Tammaro et al. (2014)	Boshoff et al. (2004)	Kurt et al. (2007)	Ram et al. (1999)	Mandal et al. (2010)
pH	7.5	7.5	7.2	10.5	7.9–9.2
Conductivity, mS/cm	2.25	1.8	20	–	20
Total suspended solids, mg/L	758	5664	1520	1126	1244
Chloride, mg/L	218	3180	6400	8392	6528
Phosphate, mg/L	12.7	Lower than 1	–	–	62
Sulfate, mg/L	570	3190	–	–	–
Total sulfide, mg/L	Over 0.5	13,540	89	55	860
Total Cr, mg/L	49	49	62	83	258

7.3 Sulfide-Based Metal Bioprecipitation

7.3.1 Sulfate-Reducing and Metal Precipitating Bioprocesses

Biological sulfate reduction based metal removal relies on the biological generation of hydrogen sulfide (H_2S) and alkalinity (Reaction 7.4):

$$2CH_2O + SO_4{}^{2-} \rightarrow H_2S + 2HCO_3{}^{-} \tag{7.4}$$

CH_2O in reaction 7.4 represents the electron donor.

The biogenically produced hydrogen sulfide forms metal sulfide precipitates with metals (Reaction 7.5):

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^{+} \tag{7.5}$$

Where M^{2+} represents metal, such as Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} or Fe^{2+}.

Metal precipitation by hydrogen sulfide generates acidity according to reaction 7.5. The acidity can be neutralized by the biogenic alkalinity generated during sulfate reduction (Reaction 7.6):

$$HCO_3{}^{-} + H^{+} \rightarrow CO_2(g) + H_2O \tag{7.6}$$

Biogenic hydrogen sulfide generation for metal removal has several advantages over hydroxide precipitation:

- Hydrogen sulfide readily reacts with heavy metals and the metal sulfides have very low solubility over a broad range of pH values (Table 7.3).
- If acid mine drainage contains complexes and chelating agents, which make hydroxide precipitation difficult, sulfide precipitation by a bioreactor application will be more effective.
- The removal of chromates and dichromates by sulfide precipitation is possible without the requirement of chromium reduction to the trivalent state.
- Metal sulfide sludges are more stable and dense compared to metal-hydroxides sludge (Huisman et al. 2006).

Compared to chemical sulfide precipitation, biological sulfide precipitation has the advantage as sulfate in the water can be used as the sulfur source for H_2S generation.

7.3.2 Suitable Electron Donors for Biological Sulfate Reduction

Hydrogen sulfide is produced as a result of assimilative and dissimilative sulfate reduction of anaerobic microorganisms. In the assimilative sulfate reduction process, reduced sulfur compounds are generated for the biosynthesis of proteins and

Table 7.3 Solubility products of selected metal sulfides and hydroxides

Solubility product (mol^n/L^n)		
	S^{2-}	OH^-
Al	2×10^{-7}	1.3×10^{-33}
Cd	8.0×10^{-27}	7.2×10^{-15}
Co	4.0×10^{-21} (α-CoS)	5.9×10^{-15}
	2.0×10^{-25} (β-CoS)	
Cr		2×10^{-16}
Cu	6.3×10^{-36}	2.2×10^{-20}
Fe	6.3×10^{-18}	4.9×10^{-17}
Mn	2.5×10^{-10} (MnS amorphous)	1.9×10^{-13}
	2.5×10^{-13} (MnS crystalline)	
Ni	3.2×10^{-19} (α-NiS)	5.5×10^{-16}
	1.0×10^{-24} (β-NiS)	
	2.0×10^{-26} (γ-NiS)	
Pb	8.0×10^{-28}	1.4×10^{-15}
Zn	1.6×10^{-24} (α-ZnS)	3×10^{-17}
	2.5×10^{-22} (β-ZnS)	

Adapted from Sahinkaya et al. (2011). Low solubility products indicate low solubility of the metals and, therefore good precipitation properties

amino acids. In the dissimilative pathway, sulfate or sulfur is reduced to hydrogen sulfide for energy generation (Tang et al. 2009). In terms of metabolic functionality, sulfate-reducing bacteria can be classified as complete oxidizers and incomplete oxidizers. Complete oxidizers can oxidize organic compounds completely to carbon dioxide, whereas incomplete oxidizers partially oxidize the organic compounds to CO_2 and acetate, as a result of absence of Acetyl-CoA oxidation (Kaksonen and Puhakka 2007). Among the 40 known genera of sulfate-reducing bacteria, 16 genera are incomplete oxidizers, 22 genera are complete oxidizers and the 2 genera of *Desulfotomaculum* and *Desulfomonile* comprise both complete and incomplete oxidizing species (Hao et al. 2014).

The performance of sulfate reduction-based bioprocesses depends on several factors, including feed composition, microbial community, load and operational conditions (Kaksonen and Puhakka 2007). Acid mine drainage contains very low concentrations of organic carbon and the addition of an external electron source is necessary to promote biogenic H_2S production (Table 7.1). The operational costs of the process are mainly based on the external carbon and electron source. Liquid, solid or gaseous substrates can be used depending on the application. In order to allow passive operation without pumping, solid waste materials or plant residuals are required as a carbon source. However, due to the generally low biodegradability of solid substrates, continuous operation of active-bioreactors necessitates electron sources in liquid or gas forms. The effect of different electron sources on the sulfate reduction bioprocesses is presented below.

7.3.2.1 Low-Cost Electron Donors

In passive treatment systems, solid organic substrates, including animal manure, leaf mulch, sawdust, wood chips, sewage sludge and cellulose, are used as low cost substrates for sulfate-reducing bacteria (see the review by Liamleam and Annachhatre 2007 for more details). Chang et al. (2000) tested spent oak from shiitake farms, oak chips, paper recycling plant waste sludge, spent mushroom compost and organic rich soils as the organic substrates for sulfate-reducing bacteria in column type reactors. The results illustrated that spent mushroom compost, spent oak from shiitake farms and paper-recycling-plant waste sludge were the preferred electron donors by sulfate-reducing bacteria compared to organic rich soils and oak chips. Similarly, Cheong et al. (1998) evaluated the treatment of acid mine drainage at the Dalsung mine, South Korea, using limestone, cow manure and rice stalks packed bioreactor. In this study, 100% Pb, 100% Zn, 100% Cd, 99% Fe, 98% Cu, 97% Al and 61% Mn removals were reported.

Silage was evaluated as a substrate for passive sulfate-reducing systems by Wakeman et al. (2010). In the study, silage supported sulfate reduction up to 87 mg sulfate/gram silage. Sahinkaya (2009) evaluated both mixtures of waste primary and activated sludge and anaerobic digester sludge effluent as carbon and seed sources in batch reactors incubated at 8 °C. Results showed that activated sludge was a much better carbon source as the easily degradable components of anaerobic digester sludge had been already depleted during anaerobic digestion. Activated sludge resulted in more than four times higher sulfate reduction than anaerobic digester sludge. The H_2S produced from 1 g volatile suspended solids/L activated sludge and anaerobic digester sludge precipitated approximately 90 mg and 35 mg Fe^{2+} as FeS, respectively (Sahinkaya 2009).

7.3.2.2 Soluble Electron Sources

When high rate sulfate reduction is desired, soluble electron sources are required. Ethanol, methanol, hydrogen, acetate, propionate, sugar and molasses are the common electron donors used for this purpose (Liamleam and Annachhatre 2007; Sipma et al. 2007). In addition to heterotrophic sulfate-reducing bacteria, autotrophic sulfate-reducing bacteria can be used for sulfate-laden wastewater treatment and the precipitation of metals. Autotrophic sulfate reducers can use CO_2 for carbon source and H_2 as electron donor (Lens and Kuenen 2001).

Lactate is a good growth substrate for many sulfate reducers (Kaksonen et al. 2003a, b, 2004). When simulated acid mine drainage containing 170–230 mg/L Zn and 58 mg/L Fe was supplemented with lactate, Zn and Fe concentrations in the effluent decreased to lower than 0.1 mg/L in both fluidized bed reactor and an upflow anaerobic sludge blanket reactor. The pH of wastewater also increased from 2.5–3 to 7.5–8 owing to the production of alkalinity during sulfate reduction (Kaksonen et al. 2003b).

The synthetic substrate supplementation incurs a significant operational cost for the treatment of acid mine drainage. Bijmans (2008) reported that the cost of ethanol supplementation was approximately 0.24 USD/kg sulfate. The average annual cost of ethanol supplementation to treat an acid mine drainage with a flow rate of 1000 m^3/day and 2000 mg/L sulfate would be $175,200. Therefore, the use of alternative carbon sources, such as wastewater with high carbon content (see Liamleam and Annachhatre (2007) for review), will eliminate or decrease the cost, but the transport cost should also be considered (Sahinkaya et al. 2013).

Boshoff et al. (2004) demonstrated that tannery effluent may be a good organic substrate for sulfate-reducing bacteria in the acid mine drainage treatment (Boshoff et al. 2004). Winery wastewater is also reported as a good organic substrate for acid mine drainage treatment in a down-flow bioreactor (Costa et al. 2009). Lakaniemi et al. (2010) tested acid hydrolyzed *Phalaris arundinacea* as a low-cost substrate for sulfate-reducing bacteria in a fluidized bed reactor operated at 35 °C (Lakaniemi et al. 2010). The sulfate reduction rate was 2.2–3.3 g/(L.d) and Fe and Zn precipitation rates were 0.84 g/(L.d) and 15 mg/(L.d), respectively. Sulfate reduction neutralized the low pH of influent and acetate oxidation limited the fluidized bed reactor performance.

Sahinkaya et al. (2013) used landfill leachate as an alternative organic substrate for sulfate-reducing bacteria in a fluidized bed reactor. In the study, the performances of ethanol and landfill leachate-fed fluidized bed reactor were compared at 35 °C. Significant decrease in sulfate reduction was observed when leachate (0.90 g/(L.d) sulfate) was used instead of ethanol (3.44 g/(L.d) sulfate) while leachate-fed fluidized bed reactor still increased the influent pH to neutral values and removed 82–99.9% of soluble metals and 80–99.9% of total metals. The ratio of electrons consumed for sulfate reduction decreased appreciably in the case of leachate and therefore higher performance may require chemical oxygen demand/sulfate ratios in the feed to be higher than 1.0 to compensate for the decreased electron flow for sulfate reduction.

Theoretically, 0.67 mg of chemical oxygen demand is needed per mg of sulfate reduced. The competition between methanogens and sulfate-reducing bacteria for the same substrates is a significant factor affecting the sulfate reduction and metal precipitation efficiencies. The outcome of this competition may depend on several factors, such as inoculum composition (type of seed, microbial composition, attachment properties, run time), influent composition (acetate concentration, sulfate concentration, sulfide concentration and type of chemical oxygen demand), operational conditions (pH, temperature) and reactor type (Hulshoff Pol et al. 1998).

One of the most significant parameters determining the competition is the chemical oxygen demand/sulfate ratio fed to the anaerobic bioreactor. Anaerobic methanogenic treatment generally proceeds successfully at a chemical oxygen demand/sulfate ratio of greater than 10 and anaerobic reactors may fail at lower ratios. Sulfate-reducing bacteria generally predominate at low chemical oxygen demand/SO_4^{2-} ratios. However, sulfate-reducing bacteria may be outcompeted by methanogens in bioreactors fed with acetate even at low chemical oxygen demand/SO_4^{2-} ratios (Omil et al. 1998). Hydrogen oxidizing sulfate-reducing bacteria produce more energy than hydrogen-utilizing methanogens. Therefore, sulfate-reducing bacteria may outcompete methanogens when hydrogen is supplemented as electron donor if sufficient sulfate is present. Acetate consuming sulfate-reducing bacteria have thermodynamic and kinetic advantages compared to acetate utilizing methanogens. Hence, sulfate-reducing bacteria should outcompete methanogens for acetate in the presence of sufficient amount of sulfate in suspended cell systems such as continuous stirred tank reactor or contact process. However, the winner of the competition in high-rate bioreactors which rely on biomass immobilization is less predictable (Hulshoff Pol et al. 1998). Therefore, the outcome of this competition also depends on the ability of microorganisms to attach to a surface or form granules depending on the immobilization strategy of the high rate bioreactor used. Omil et al. (1998) reported that high pH (approximately 8) and the presence of high concentration of sulfate-reducing bacteria in the inoculum together with a short sludge retention time (lower than 150 days), may significantly reduce the required time of sulfate-reducing bacteria to dominate over methanogens.

7.3.3 Sulfide-Based Arsenic Bioprecipitation

There are a limited number of studies in the literature on arsenic removal from acid mine drainage using sulfate-reducing bacteria (Teclu et al. 2008; Battaglia-Brunet et al. 2012; Altun et al. 2014). Newman et al. (1997a) reported that *Desulfotomaculum auripigmentum* reduced As^{5+} to As^{3+} and sulfate to H_2S in a batch reactor. The As^{3+} precipitated as As_2S_3, which can be removed from water. However, the reaction is highly sensitive to pH and dissolved sulfide concentration. Provided that the medium contains a considerable amount of dissolved sulfide, stable As_2S_3 (orpiment) precipitate is generated, which facilitates the removal of arsenic from water. However, high concentrations of dissolved sulfide and neutral to alkaline pH cause dissolution of orpiment and decrease the efficiency of trivalent arsenic removal (Reaction 7.7):

$$3\mathrm{As_2S_3}\left(\mathrm{amorphous}\right)+3\mathrm{H_2S}\rightarrow 2\mathrm{H_2As_3S_6}^{-}+2\mathrm{H}^{+}\quad \log K=-5.0 \qquad (7.7)$$

In the presence of Fe^{2+}, As^{3+} may precipitate as FeAsS instead of As_2S_3 (Newman et al. 1997a; Altun et al. 2014).

Teclu et al. (2008) stated that sulfate-reducing bacteria can precipitate 1–5 mg/L of arsenic effectively in a batch reactor and biogenic FeS precipitate plays a very important role in arsenic adsorption. Battaglia-Brunet et al. (2012) investigated arsenic removal using a fixed bed sulfidogenic bioreactor which received glycerin or hydrogen as electron sources and 100 mg/L of As^{5+}. When the reactor was fed with glycerin, very low sulfate removal rates were obtained at pH5 and the amount of H_2S produced was just enough to remove arsenic as As_2S_3. In these circumstances, approximately 100% As removal was achieved and yellow colored orpiment pre-

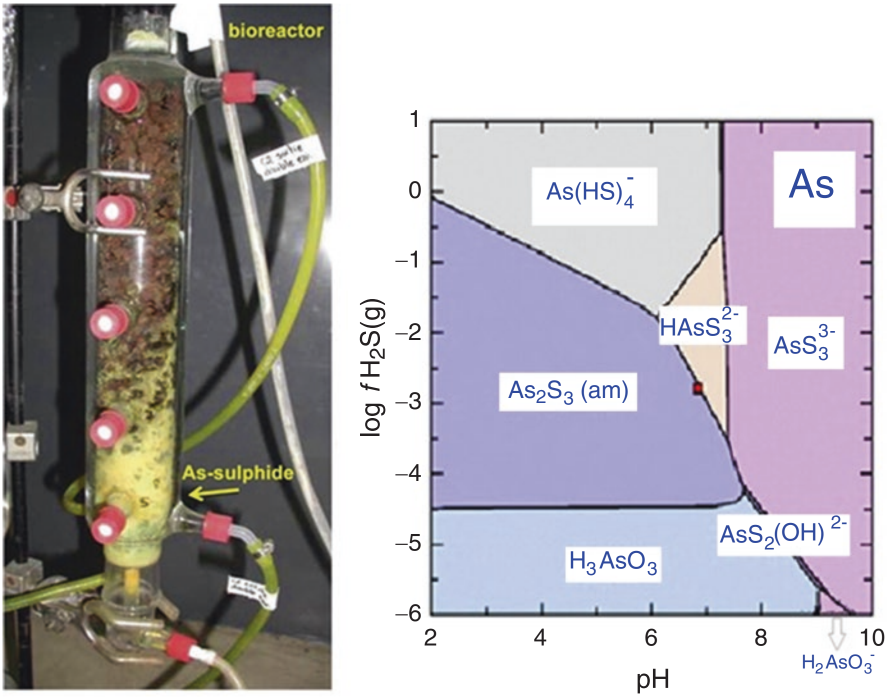

Fig. 7.1 Yellow-colored orpiment (As_2S_3) precipitation in bioreactor and the interrelation between As_2S_3/thioarsenite compounds and pH/sulfide (Reprinted from Battaglia-Brunet et al. 2012, precipitation of arsenic sulfide from acidic water in a fixed-film bioreactor, 46, 2012. with permission from Elsevier)

cipitated within the reactor (Fig. 7.1). In the same study, when hydrogen was used as an electron source, the effluent arsenic concentration increased threefold of the influent since high concentration of dissolved-sulfide resolubilised orpiment resulting in several thioarsenite compounds.

The interrelation between As_2S_3/thioarsenite compounds and pH/H_2S is shown in Fig. 7.1. In the study of Altun et al. (2014a), bioremoval of arsenic from synthetic As^{5+} (5–20 mg/L) and Fe (100–200 mg/L) containing acid mine drainage was studied in an anaerobic upflow fixed-bed column bioreactor. In the absence of Fe, As removal was almost negligible (8%), probably owing to neutral to alkaline pH and high dissolved sulfide concentration in the bioreactor. The addition of 100 and 200 mg/L Fe to the As-containing synthetic acid mine drainage increased the As-removal efficiencies to 63% and 85%, respectively. Decreasing the influent chemical oxygen demand to half to decrease the dissolved-sulfide concentration and keeping influent Fe and As concentrations at 200 mg/L and 20 mg/L, respectively, increased the As removal to 96%. Mineralogical studies showed that As precipitated in the form of As_2S_3 (orpiment) and co-precipitated with ferrous iron as arsenopyrite (FeAsS). In the mixed culture, the dominant sulfate-reducing bacteria were identified as

Desulfomicrobium baculatum, *Desulfovibrio desulfuricans*, D*esulfurovibrio Africanus* and another *Desulfurovibrio* sp.

7.3.4 Selective Metal Recovery with the Control of Sulfide Concentration and pH

The solubilities of various metal-sulfides may differ at different pH values, which can be utilized for the selective recovery of metals. Bijmans et al. (2009a, b) investigated selective nickel recovery from a nickel and iron containing solution keeping pH at 5 in a single-stage sulfate-reducing bioreactor. Nickel can precipitate as NiS at pH lower than 5, whereas iron will remain soluble. Therefore, metals can be recovered selectively with the control of pH and sulfide concentrations from a multi metal containing acid mine drainage. In the experiments conducted by Bijmans et al. (2009b), NiS recovery from a nickel-iron mixture reached over 99.9% with an effluent Ni concentration lower than 0.05 μM. In another study, Ucar et al. (2011) used a three-stage process fed with ethanol at 35 °C to selectively recover Cu and Fe. The process included two settling tanks before a sulfidogenic bioreactor. H_2S was transported from the main bioreactor using N_2 as carrier gas for Cu precipitation and dissolved sulfide and bicarbonate containing water was recirculated for Fe precipitation (Fig. 7.2). In the study, Cu and Fe removal efficiencies were higher than 99%. Also, sulfate and chemical oxygen demand removal efficiencies were 60–90%. Therefore, the use of H_2S for metal precipitation not only allows the production of an effluent with very low metal concentrations, but also provides the possibility of selective precipitation for metal recovery (Sampaio et al. 2009).

Sampaio et al. (2010) investigated selective Cu and Zn precipitation controlling the pS ($pS = -\log(S^{(2-)})$) and pH values at 25 and 3, respectively, using a continuous stirred tank reactor operated at 20 °C. In the study, Cu was selectively precipitated using Na_2S and its concentration was decreased to below 0.3 μg/L when the initial Cu and Zn concentrations were equal to 600 mg/L. The recovery and the purity of Cu were approximately 100% and total dissolved-sulfide concentration was lower than 0.02 mg/L. X-ray diffraction analysis illustrated that Cu precipitated as CuS (covellite) with the mode of particle size distribution of approximately 36 μm. Also, Zn was precipitated with dissolved sulfide as ZnS (sphalerite) at pH 3–4 in batch assays and its final concentration was above 1 mg/L.

Sahinkaya et al. (2009) investigated the separate recovery of copper and zinc from synthetic acid mine drainage simulating a three-stage process similar to that given in Fig. 7.2. In this study, the effluent of a sulfidogenic bioreactor was used as a source of dissolved sulfide. Cu was separately precipitated at pH lower than 2 with H_2S removed from the sulfidogenic bioreactor using N_2 gas. Cu precipitation was completed within less than 1 h in batch assays and during Cu precipitation Zn remained soluble. After selective Cu precipitation, Zn was precipitated with dissolved sulfide and alkalinity containing bioreactor effluent and the

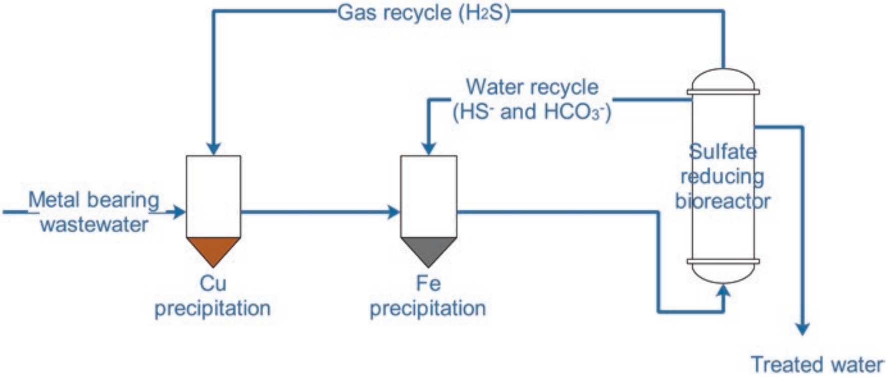

Fig. 7.2 Three-stage process for selective Cu and Fe precipitation (Adapted from Ucar et al. 2011 and Sahinkaya et al. 2009). Note that Cu precipitation is provided only by H_2S recycle to the first precipitation tank where pH is relatively low

removal efficiency was 84–98%. The modes of particle size distributions for ZnS and CuS were 17 μm and 46 μm, respectively. Hence, the CuS particles were larger than the particles of ZnS, although CuS particles formed at very low pH (lower than 2).

7.3.5 *Effect of Dissolved Sulfide Concentration on Metal-Sulfide Formation*

Bijmans et al. (2009) defined saturation index (SI) as shown below (Eq. 7.8):

$$\mathrm{SI} = \log\left[\frac{\left(\mathrm{Zn}^{2+}\right)\left(\mathrm{S}^{2-}\right)}{\mathrm{K}_{\mathrm{SP}}}\right] \tag{7.8}$$

The SI is negative for under-saturation conditions and positive for supersaturation conditions. The (Zn^{2+}) and (S^{2-}) are the concentrations of Zn^{2+} and S^{2-}, respectively and K_{SP} is the solubility product of ZnS. The formation of polysulfides has been investigated by Lewis and Van Hille (2006) in a fluidized bed reactor in which beach sand (SiO_2) (250–500 μm) was used as a biomass support material. The metal-containing feed was introduced to the system together with the recirculation water and Na_2S was introduced to the bottom of the reactor via three inlet points 10 cm apart. The reactor was fed with Ni and Co mixture or Cu and the metal-sulfide formation chemistry was investigated at different super-saturation levels. Under various conditions total metal removal and the fine formation, defined as the difference between total and soluble metal concentrations was investigated. In the fluidized bed reactor, fines formation was observed for all metals studied. The impact of excess sulfide on metal removal and fine formation was also investigated. When the molar metal:sulfide ratios were 1:1 and 1:1.2, high Ni and Co removals were attained. However, metal removal efficiencies, especially for Ni, decreased significantly at a metal/sulfide ratio of 1:2. When excess sulfide was used for Ni removal, the remaining dissolved sulfide concentration was significantly less than expected, which may indicate redissolution of metal sulfides (MS) as aqueous polysulfide complexes according to reaction 7.9 (Lewis and Van Hille 2006):

$$\mathrm{MS}(\mathrm{s}) + \mathrm{HS}^{-}(\mathrm{aq}) \rightarrow \mathrm{MS}(\mathrm{HS})^{-}(\mathrm{aq}) \tag{7.9}$$

Therefore, for metal removal and recovery, sulfide addition should be controlled to avoid local high dissolved sulfide concentrations as the excess dissolved sulfide will redissolve the precipitates and consume excess sulfide for polysulfide complex formation (Lewis and Van Hille 2006). As explained above, high sulfide concentrations may also decrease the sulfidogenic arsenic removal performance (Newman et al. 1997b; Altun et al. 2014).

Bijmans et al. (2009) studied the impact of sulfide concentration on the settling properties of zinc sulfide (sphalerite) precipitates using a gas-lift bioreactor fed with hydrogen and CO_2 gases and operated at pH 5.5. In the study, simultaneous Zn precipitation and sulfate reduction were achieved with 99.9% Zn recovery at a loading rate of 7.2 mmol/(L.d) (or 471 mg/(L.d)). The excess concentration of dissolved sulfide was between 0.26 and 70.4 mg/L. The reuse and the recovery potential of metals depend on their purity and settling characteristics. The zinc particles increased in size and became more homogenous at lower dissolved sulfide concentration. Also, the settling velocity of the precipitates increased at lower dissolved sulfide concentrations, which facilitates dewatering and recovery potential of the sludge.

Villa-Gomez et al. (2011) investigated the effect of dissolved sulfide concentration on the location of the metal sulfide precipitates in mesophilic down-flow fluidized bed reactors. For this purpose, two fluidized bed reactors were operated in parallel, but with different lactate concentrations. Both reactors were fed with 10 mg/L Cu, Pb, Cd and Zn. In one down-flow fluidized bed reactor, the sulfide concentration was kept high at 648 mg/L, while it was only 59 mg/L in the second reactor. When the fluidized bed reactor had high dissolved sulfide concentration, the precipitated metals were mainly as fines and present in the bulk liquid, whereas in the second reactor the metals precipitated mainly in the biofilm (Fig. 7.3) owing to local supersaturation in the biofilm. Therefore, the dissolved sulfide concentrations in the metal removing bioreactors determine the size of metal sulfide precipitates and the precipitates location in the bioreactors.

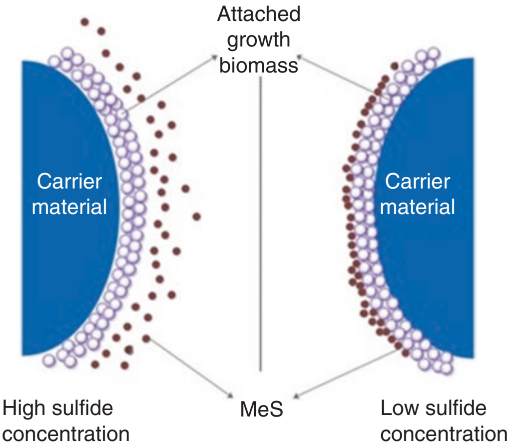

Fig. 7.3 Location of metal sulfide (MS) precipitates depending on the sulfide concentration in down-flow fluidized bed reactors (Adapted from Villa-Gomez et al. 2011)

7.4 Oxidative and Reductive Bioprecipitation

Biological or chemical oxidation (e.g. Fe^{2+}) or reduction (e.g. U^{6+}, Cr^{6+}) of some metals or metalloids may significantly decrease their solubility and cause precipitation. In this section, bioreductive precipitation of Cr^{6+} and U^{6+} will be discussed, followed by the evaluation of Fe^{2+} oxidation and Fe^{3+} precipitation.

7.4.1 Reductive Bioprecipitation of Uranium

Groundwater and surface water may be contaminated with uranium owing to mining activities, especially from the in situ leaching processes (Yi et al. 2007). The concentration of uranium in groundwaters near mining and milling activities may vary from 1 to 210 µM (Luna-Velasco et al. 2010). Uranium contamination is an important environmental problem and may have an adverse effect on human health owing to its toxicity to the kidneys and radioactivity. Because of its toxic effects, the US Environmental Protection Agency (EPA) has set the maximum drinking water uranium concentration as 30 µg/L (0.13 µM) (Luna-Velasco et al. 2010).

Hexavalent uranium (U^{6+}) may be biologically reduced to insoluble tetravalent uranium (U^{4+}) by a wide range of microorganisms. Examples of these include denitrifiers, sulfate-reducing bacteria, e.g. *Desulfovibrio* spp. (Lovley and Phillips 1992), Fe^{3+} reducing bacteria, e.g. *Shewanella* spp. and *Geobacter* spp. (Merroun and Selenska-Pobell 2008), hyperthermophilic archaea (Kashefi and Lovley 2000), thermophilic bacteria (Kieft et al. 1999), fermentative bacteria from the *Clostridium* spp. (Gao and Francis 2008), acidotolerant bacteria (Shelobolina et al. 2004) and myxobacteria (Wu et al. 2006). Other U^{6+} reducing genera include *Tolumonas, Arthrobacter, Dechlomonas* and *Pseudomonas* (Martins et al. 2010). Some organisms may gain energy for growth from U^{6+} reduction when using it as an alternative electron acceptor, whereas others reduce uranium co-metabolically without energy generation (Merroun and Selenska-Pobell 2008). *Geobacter, Shewanella* and *Desulfotomaculum* can grow on U^{6+} reduction, whereas *Desulfovibrio* reduce U^{6+} cometabolically and cannot produce energy for growth from this reduction process (Chabalala and Chirwa 2010).

Mixed cultures have advantages over the pure cultures in bioremediation processes owing to higher metabolic capabilities (Martins et al. 2010). Martins et al. (2010) investigated the mechanism of U^{6+} removal from the waste stream by two anaerobic mixed cultures, one obtained from an uncontaminated site and the other from a uranium mining site. The removal efficiency was 97% at room temperature and pH 7.2 for both cultures. The uranium removal mechanisms for the culture obtained from the uncontaminated site was enzymatic reduction and bioaccumulation, whereas the culture obtained from the uranium-contaminated site removed uranium via an enzymatic process only. Fourier transform infrared spectroscopy (FT-IR) analyses suggested that the reduced U^{4+} attached to carboxyl, phosphate and amide groups in the bacterial cells (Martins et al. 2010).

Chabalala and Chirwa (2010) investigated the removal of U^{6+} under aerobic and anaerobic conditions with the mine consortium obtained from a soil having a background uranium concentration of 168 mg/kg. Studies demonstrated that the anaerobic uranium reduction performance with mixed cultures was much higher than the aerobic reduction performance. This was probably due to the preferential use of oxygen over U^{6+} as terminal electron acceptor under aerobic conditions (Chabalala and Chirwa 2010).

Sulfate-reducing bacteria have the ability to transform soluble U^{6+} enzymatically to highly insoluble uraninite, UO_2 which may be used for bioremediation of uranium contaminated ground water (Suzuki et al. 2005; Yi et al. 2007) and acid mine drainage. Yi et al. (2007) studied the impact of pH, presence of oxyanions (sulfate and nitrate) and Cu and Zn on the uranium bioreduction by sulfate-reducing culture dominated by *Desulfovibrio* spp. In batch bottles, a significant decrease in the U^{6+} concentration was observed and the process efficiency was highly affected by pH. At pH 6, 20 mg/L U^{6+} was almost completely reduced, while at pH 5 the reduction efficiency was approximately 62% and did not change after first 50 h incubation. The presence of sulfate had no adverse effect on the U^{6+} reduction up to 4000 mg/L and Yi et al. (2007) suggested that sulfate reduction and U^{6+} reduction take place in different sites of cells due to different enzyme systems. Sulfate reduction occurs in the cytoplasmic membrane, whereas U^{6+} reduction takes place in the periplasmic space, i.e. outside of the cytoplasmic membrane (Yi et al. 2007).

In the study of Zhou et al. (2014), a hydrogen based membrane biofilm reactor was used for the removal of uranium and the microbial community in the bioreactor was also investigated. The reactor was inoculated with a culture of *Desulfovibrio vulgaris.* When U^{6+} was fed as a sole electron acceptor at 0.5 mM concentration, U^{6+} reduction performance in the reactor increased to higher than 98% in a short time and then, almost complete reduction was attained. In the reactor, nanocrystalline UO_2 aggregates and amorphous U precipitates associated with vegetative cells were observed. Although the reactor was inoculated with *Desulfovibrio vulgaris,* this bacterium was not detected in the biofilm and *Rhodocyclaceae* and *Clostridiaceae* families were abundant in the absence and presence of sulfate, respectively (Zhou et al. 2014).

7.4.2 Reductive Bioprecipitation of Chromium

The worldwide extensive chromium use in several industrial applications, i.e. production of stainless steel and other alloys, leather tanning, wood treatment and metal plating, has led to soil, surface and groundwater contamination (Chang and Kim 2007; Sahinkaya et al. 2012a). The WHO and the European Commission (Water Directive 98/83/EC) set the maximum allowable chromium concentration in drinking water as 50 μg/L. According to the US EPA, chromium is a human carcinogen and the maximum concentration in drinking water should be less than 100 μg/L. The Canadian and Australian Drinking Water Quality Guidelines allow total chromium concentration in water up to 50 μg/L (Sharma et al. 2008).

Cr^{6+} and Cr^{3+} are the most dominant oxidation states of chromium in industrial wastewaters in spite of existing various oxidation states between −2 and +6 (Dogan et al. 2011). Cr^{6+} is considered as acutely toxic, teratogenic and carcinogenic and exhibits high mobility in environmental media (Melitas et al. 2001; Sahinkaya et al. 2012b). On the other hand, trivalent chromium hydroxide has limited solubility at neutral pH and thus is less available for biological uptake. Cr^{3+} is essential for humans as a micronutrient, while at high concentration it is toxic to plants (Chung et al. 2006).

Several processes have been investigated for removing chromium from contaminated environments (Brum et al. 2010; Singh et al. 2011; Sahinkaya et al. 2012a, b). The chemistry and the mechanisms for chromium removal have also been reviewed by Sharma et al. (2008). The chemical and biological reduction of Cr^{6+} followed by immobilization are the most common approaches for removing chromium from water. Iron (zero- and di-valent) and dissolved sulfide have been used for the reduction of chromates (Lee et al. 2008). Although chemical processes are quite efficient, the major disadvantages are associated with the chemical cost and the huge volumes of chemical sludge generation. On the other hand, microbial reduction of Cr^{6+} may be hindered due to its toxicity to microorganisms (Meunier et al. 2006).

Sulfate-reducing bacteria have the ability to reduce sulfate to hydrogen sulfide, which can then induce the reduction of Cr^{6+} to Cr^{3+} (Reaction 7.10) (Sahinkaya et al. 2012a). The production of bicarbonate alkalinity during sulfate reduction (Kaksonen et al. 2003b; Sahinkaya et al. 2009) may increase solution pH and facilitate Cr^{3+} precipitation. Hence, both chromium and sulfate can be concomitantly removed in a single reactor while pH increases from acidic to neutral or alkaline values:

$$3HS^- + 2Cr^{6+} \rightarrow 3S^0 + 2Cr^{3+} + 3H^+ \tag{7.10}$$

Sulfate-reducing bacteria can also reduce Cr^{6+} enzymatically or chemically with the produced H_2S during the dissimilatory sulfate reduction (Dogan et al. 2011). Cr^{6+} is used as an electron acceptor in the absence of sulfate, but the chemical reduction of Cr^{6+} in the presence of H_2S, produced in sulfate reduction, is quite fast and efficient (Smith and Gadd 2000).

Sahinkaya et al. (2012a) investigated the bioreduction of Cr^{6+} from acidic wastewater in the presence and absence of iron using a four-stage sulfidogenic anaerobic baffled reactor. Biotreatment of synthetic acidic wastewater containing

Cr^{6+} (35–200 mg/L), Fe^{3+} (100 mg/L) and sulfate (3500 mg/L) was studied in an ethanol supplemented anaerobic baffled reactor. Very high removal efficiencies for sulfate (over 80%), chemical oxygen demand (over 90%), Cr^{6+} (over 99%) and total Cr (over 98%) were observed in the bioreactor. Also, the alkalinity generated during the sulfate reduction, increased the influent pH from 2.5–3.5 to 7.3–8.0 in the effluent. X-ray diffraction, X-ray fluorescence and scanning electron microscopy studies were conducted to elucidate the removal mechanism of Cr^{6+} in the presence of Fe^{3+}. Sahinkaya et al. (2012a) suggested that Cr^{6+} may precipitate as CrO(OH) and chromium sulfide according to the reactions 7.11–7.13 given below (Sahinkaya et al. 2012a):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \tag{7.11}$$

$$Cr_2O_7{}^{2-} + 2Fe^{2+} + 2HS^- + 3H^+ \rightarrow 2CrO(OH) + FeS_2 + Fe(OH)_3 \tag{7.12}$$

$$Cr_2O_7{}^{2-} + 2Fe^{2+} + 3HS^- + 5H^+ \rightarrow Cr_2S_3 + 2Fe(OH)_3 + H_2O \tag{7.13}$$

Biological reduction of Cr^{6+} is also possible under aerobic conditions. Chirwa and Wang (1997) studied the potential of a fixed-film bioreactor inoculated with *Bacillus* sp. for the bioreduction of Cr^{6+} at 10–200 mg/L. The Cr^{6+} reduction was almost complete and not affected by the varying influent concentration or hydraulic retention time. Although Cr^{6+} reduction was complete, Cr^{3+} remained at the effluent of the reactor and the total chromium removal was almost negligible.

Molokwane et al. (2008) enriched a mixed culture of bacteria that had a high Cr^{6+} reduction rate from a wastewater treatment plant. Three to eight times higher Cr^{6+} reduction rates were observed with the enriched mixed culture compared to the rates observed with pure cultures. Under aerobic conditions, the mixed culture reduced 200 mg/L Cr^{6+} completely within approximately 65 h and 94% removal of 300 mg/L Cr^{6+} was observed in less than 110 h. The reduction rate was slower under anaerobic conditions, although complete removal of Cr^{6+} up to 150 mg/L was achieved, due to low metabolic rates under anaerobic conditions. The enriched mixed culture was also characterized and the members of the Gram-positive *Bacillus (B.)* genus (especially *B. cereus* and *B. thuringiensis*) were observed to be dominant under aerobic conditions, whereas, *Enterococcus*, *Arthrobacter, Paenibacillus* and *Oceanobacillus* species were observed in the cultures grown under anaerobic conditions.

As the maximum allowable chromium concentration set by the authorities considers the total chromium concentration, the bioreduction of Cr^{6+} to Cr^{3+} is not enough and the reduced form of chromium should be removed from the water phase. Although complete Cr^{6+} reduction was observed in many studies, the reduced Cr^{3+} remained in the wastewater without precipitation (Chung et al. 2006). In this context, Chung et al. (2010) combined H_2-based membrane biofilm reactor and membrane processes (reverse osmosis/nanofiltrarion) to further remove soluble Cr^{3+}.

Sahinkaya and Kilic (2014) comparatively evaluated chromate and nitrate removal using heterotrophic and sulfur-packed autotrophic denitrifying column-type bioreactors. Elemental sulfur acted as an electron donor in the sulfur-based autotrophic denitrification process for nitrate and Cr^{6+} reduction and the process did not require any additional carbon source. Complete autotrophic denitrification was attained and Cr^{6+} (up to 0.5 mg/L) did not adversely affect the process performance. Cr^{6+} and total chromium concentrations in the effluent were lower than 50 μg/L when the influent Cr^{6+} concentration was lower than 500 μg/L. In the heterotrophic process, methanol was used as electron source and denitrification was not adversely affected by 20 mg/L Cr^{6+}. Almost complete Cr^{6+} removal was obtained with up to 10 mg/L Cr^{6+} in the influent.

7.4.3 Oxidative Bioprecipitation of Iron

In the mining industry, (bio)hydrometallurgical effluents often contain iron as a result of the dissolution of iron-containing minerals. Excess iron removal is required as a high iron concentration in the recirculation of the leach liquors decreases the process kinetics because of precipitate formation. Oxidative precipitation is a widespread method utilized for the removal of iron from acidic effluents in active treatment processes involving the supplementation of chemical-neutralizing agents (Coulton et al. 2003).

Fe^{3+} may form various precipitates, such as ferric hydroxide or ferrihydrite, jarosite, schwertmannite, goethite, hematite and scorodite depending on pH, temperature and solution composition (Fig. 7.4). The theoretical contents of various iron precipitates are shown in Table 7.4 (Kaksonen et al. 2014b).

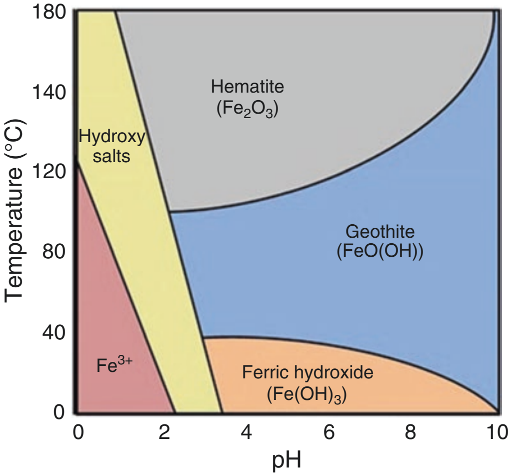

Fig. 7.4 Proposed conditions for the precipitation of hematite, goethite, ferric hydroxide and hydroxy salts, including jarosites and schwertmannite from 0.5 M ferric sulfate solutions (Adapted from Claassen et al. 2002)

Table 7.4 Theoretical contents (weight-%) of Fe, S and other monovalent cations in jarosites, schwertmannite, goethite, hematite and scorodite

Mineral	Chemical formula	Fe (%)	S (%)	Cation (%)	Cation
Potassium jarosite	$KFe_3(SO_4)_2(OH)_6$	33.5	12.8	7.8	K^+
Ammonium jarosite	$NH_4Fe_3(SO_4)_2(OH)_6$	34.9	13.4	3.8	NH_4^+ (2.9% N)
Sodium jarosite	$NaFe_3(SO_4)_2(OH)_6$	34.6	13.2	4.7	Na^+
Hydronium jarosite	$H_3OFe_3(SO_4)_2(OH)_6$	34.9	13.3	4.0	H_3O^+
Schwertmannite	$Fe_{16}O_{16}(SO_4)_2(OH)_{12}\cdot nH_2O$ (n = 10–12)	50.7–51.8	3.6–3.7	–	–
Goethite	FeOOH	62.9	0	–	–
Hematite	Fe_2O_3	69.9	0	–	–
Scorodite	$FeAsO_4\cdot 2H_2O$	24.1	0	32.5	As^{5+}

Adapted from Kaksonen et al. (2014b)

7.4.3.1 Ferric Hydroxide, Ferrihydrite and Goethite Precipitation

Ferric iron has often been suggested to hydrolyze according to reaction 7.14 at pH values above 3:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\ (\text{yellow boy}) + 3H^+ \tag{7.14}$$

However, the formation of $Fe(OH)_3$ has been questioned by some authors owing to the difficulty in characterization. It has been suggested that ferrihydrite or schwertmannite has often been mistakenly designated as $Fe(OH)_3$ under various pseudonyms (Jambor and Dutrizac 1998).

Ferrihydrite is present widely in natural waters, sediments, soils, sulfide oxidation products and in the acid mine drainage precipitates. Ferrihydrite has also been suggested as the dominant constituent in some metallurgical residues (Jambor and Dutrizac 1998). Ferrihydrite and goethite (α-FeOOH) are known to precipitate at a wide range of pH values (Bigham and Nordstrom 2000) (Fig. 7.4). Goethite formation is shown in reaction 7.15 (Nurmi 2009):

$$Fe^{3+} + 2H_2O \rightarrow \alpha - FeOOH + 3H^+ \tag{7.15}$$

In the zinc industry, goethite precipitation is carried out at a temperature of 70–90 °C and at pH 2.8–3. The acid generated requires neutralization, but no other reagents are required (Nurmi 2009).

7.4.3.2 Jarosite Precipitation

Iron can also be removed from aqueous solutions as ammonium, potassium, sodium, silver or hydronium jarosites at pH lower than 2–3 at high SO_4^{2-} concentrations (Bigham et al. 2010; Nurmi et al. 2010). The formation of jarosites with the formula of $MFe_3(SO_4)_2(OH)_6$ is shown in reaction 7.16, where M = K^+, Na^+, NH_4^+, Ag^+ or H_3O^+ (Zhu et al. 2013). Generally, K^+ jarosite is preferentially precipitated followed by NH_4^+ and Na^+ jarosites and the K^+ jarosite is more stable than the other forms (Kaksonen et al. 2014a, b).

$$3Fe^{3+} + M^+ + 2HSO_4^- + 6H_2O \rightarrow MFe_3\left(SO_4\right)_2\left(OH\right)_6 + 8H^+ \tag{7.16}$$

Factors affecting the properties of jarosites are the Fe concentration in solution, temperature, precipitation rate, solution chemistry and pH (Drouet and Navrotsky 2006). Mineral salts, base additions or solubilization of accessory minerals are the source of monovalent cations needed for jarosite formation. There are very different threshold levels of NH_4^+, K^+ and Na^+ needed for the jarosite precipitation. Jarosite seed addition increases the rate of jarosite formation and precipitation (Dutrizac 1999).

Jarosites are found in acid sulfate soils, oxidized zones of sulfidic deposits, acid mine drainage and hydrometallurgical and bioleaching systems (Bigham and Nordstrom 2000). Jarosite precipitation has been extensively used in the zinc industry for the removal of iron in the processing circuits (Dutrizac 1999). The formation of jarosite is favorable at elevated temperatures (Nurmi et al. 2010). In abiotic systems the precipitation of jarosite at an appreciable rate requires temperatures above 75 °C. However, in iron-oxidizing bioreactors jarosite precipitation can be achieved at ambient temperature (Kaksonen et al. 2014b). Jarosite has good settling and filtering characteristics and various metals may also co-precipitate together with iron (Nurmi et al. 2010; Kaksonen et al. 2014b).

Ozkaya et al. (2007) studied Fe^{2+} oxidation in a heap-leaching water containing (as g/L) Fe^{2+} (20), Mn^{2+} (3) and Al^{3+} (0.1) using a fluidized bed reactor dominated with *Leptospirillum ferriphilum* at 37 °C. The impacts of initial pH and the presence of inorganic cations on the Fe^{2+} oxidation rate were also studied in batch experiments at 25 °C. Batch experiments showed that the oxidation efficiencies of Fe^{2+} were almost 100% in both the presence and absence of cations although the presence of cations significantly reduced the iron oxidation rates from 6.3 to 2.2 g Fe^{2+}/(L.d). At various pH values, Fe^{2+} oxidation was almost complete and the rates were not notably affected by the studied pH range. The settling velocity of the formed precipitates increased with increasing pH, i.e. from 2.2 cm/h at pH 1.5 to 2.9 cm/h at pH 3. The formation of jarosite caused clogging of the fluidized bed reactor and decreased Fe oxidation performance even at pH values 1.5–2. After the addition of a settling tank, the performance was recovered as jarosite clogging of the bioreactor was eliminated. When the influent pH was 1.5, the effluent pH increased to 1.6–1.9 owing to iron oxidation. However, when the influent pH was increased to 2.5, the effluent pH decreased to approximately 2.0 due to the increased formation of jarosite, which produced acid. Therefore, iron oxidation is an acid consuming reaction, whereas the Fe^{3+} precipitation generates acid and the combined impact of these reactions determines the final pH. The maximum Fe^{2+} oxidation rate in the fluidized bed reactor was 10 g/(L.h) at a loading rate of 10.7 g/(L.d) and at hydraulic retention time of 2 h.

In another study, the influence of H^+, Fe^{2+}, Fe^{3+} and Cu^{2+} and combinations of these cations on the iron oxidation of *L. ferriphilum* were investigated. The rate of iron oxidation was not adversely affected in the pH range from 0.9 to 1.5 and slightly decreased at pH 0.7 (Kinnunen and Puhakka 2005).

Nurmi et al. (2010) developed a highly effective iron oxidizing and jarosite-precipitating process. In the study, the effluent of an iron oxidizing fluidized-bed reactor was partially neutralized using KOH or $CaCO_3$ to precipitate Fe^{3+} and sulfate from the reactor effluent. The rate of iron oxidation was 3.7 g/(L.h) at an influent Fe^{2+} concentration of 6.0 (±1.5) g/L and approximately 99% of iron was precipitated when pH was adjusted to 3.5 with KOH. Similar efficiencies were also obtained when $CaCO_3$ was used as the neutralizing agent and sulfate removal increased owing to the formation of gypsum ($CaSO_4{\cdot}2H_2O$). In addition to jarosite, goethite or gypsum were observed in the precipitate when KOH or $CaCO_3$ was used for neutralization, respectively.

Kaksonen et al. (2014b) proposed the process shown in Fig. 7.5 for the excess iron removal from leach liquors. In the process, base-metal sulfides are leached using acid and ferric iron and the excess iron is precipitated from the liquor as jarosite after biological iron oxidation. The jarosite may also be converted to hematite and sulfuric acid at elevated temperatures (220–250 °C) (Dutrizac 1990) and the

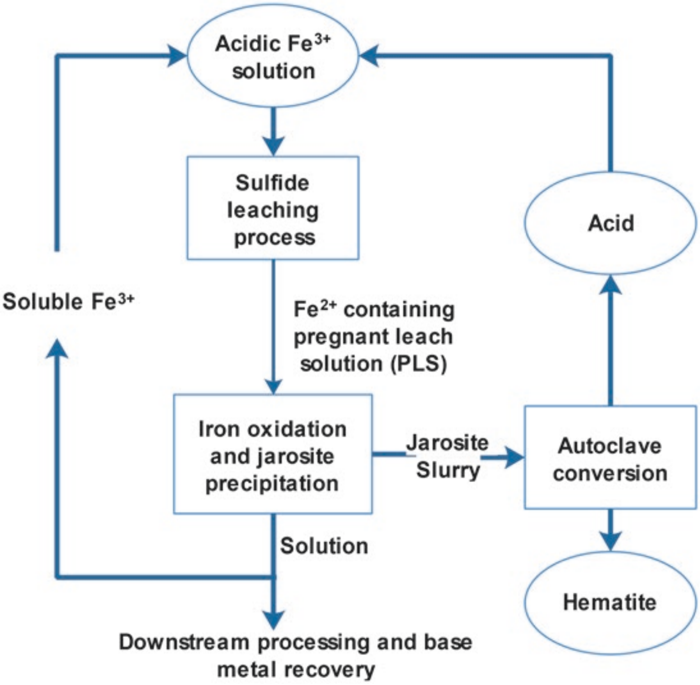

Fig. 7.5 Application of iron oxidation and jarosite precipitation and conversion of jarosite to hematite (Adapted from Kaksonen et al. 2014b)

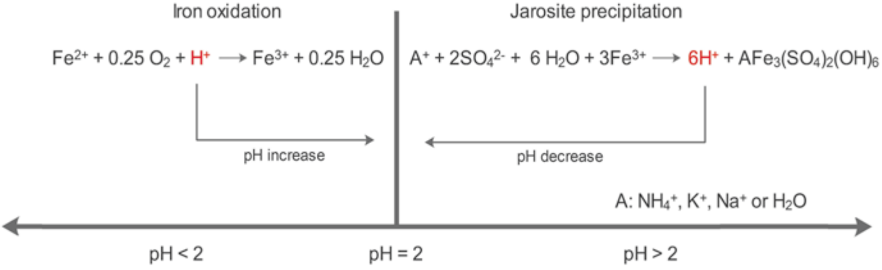

Fig. 7.6 Conceptual diagram on the effects of ferrous-iron oxidation and ferric-iron precipitation on pH (Adapted from Kaksonen et al. 2014c)

generated acid can be reused in the leaching process together with ferric iron (Kaksonen et al. 2014b).

Generally, ferric iron removal from solution is preferred at low pH values without using neutralizing agents. Depending on the form of the precipitate and the extent of precipitation, the overall reaction of biological Fe^{2+} oxidation and Fe^{3+} precipitation may be acid producing or consuming and the conceptual diagram showing this process is given in Fig. 7.6.

Kaksonen et al. (2014c) investigated Fe^{2+} oxidation and precipitation using a two-stage continuous stirred tank reactor system (Fig. 7.7) and the impact of influent pH on the iron oxidation and precipitation rates. Although the influent pH of the two stage continuous stirred tank reactor processes varied between 1.9 and 2.2, the effluent pH remained almost constant at 2.05–2.06 (close to the buffer pH of HSO_4^-/SO_4^{2-}) owing to the balance between acid utilizing iron oxidation and acid generating iron precipitation reactions. With influent pH values of 1.1 and 1.5, the effluent pH increased to approximately 1.5 and 1.9, respectively. Hence, iron oxidation and precipitation caused a net pH increase with influent pH values below pH 2.05–2.06 and a net pH decrease at influent pH values above 2.05–2.06. Depending on the influent pH, the precipitation of Fe and S was 8.2–54% and 3.7–33%. Cu and Ni losses owing to co-precipitation were very low, only 0.25–2.5% and 0.01–0.26%, respectively (Kaksonen et al. 2014c).

The prediction of effluent pH of an iron-oxidizing bioreactor may be difficult owing to the occurrence of both acid consuming and acid producing reactions (Ozkaya et al. 2007; Nurmi et al. 2010; Kaksonen et al. 2014c). Kaksonen et al. (2014c) developed an empirical model to predict the pH of an iron oxidizing bioreactor as (Eq. 7.17 and 7.18):

$$\mathrm{pH} = 2.06 + \frac{\mathrm{pH}^0 - 2.06}{1 + \left(\frac{\mathrm{Fe}^{2+}{}_{\mathrm{ox}}}{\mathrm{c}}\right)^2} \tag{7.17}$$

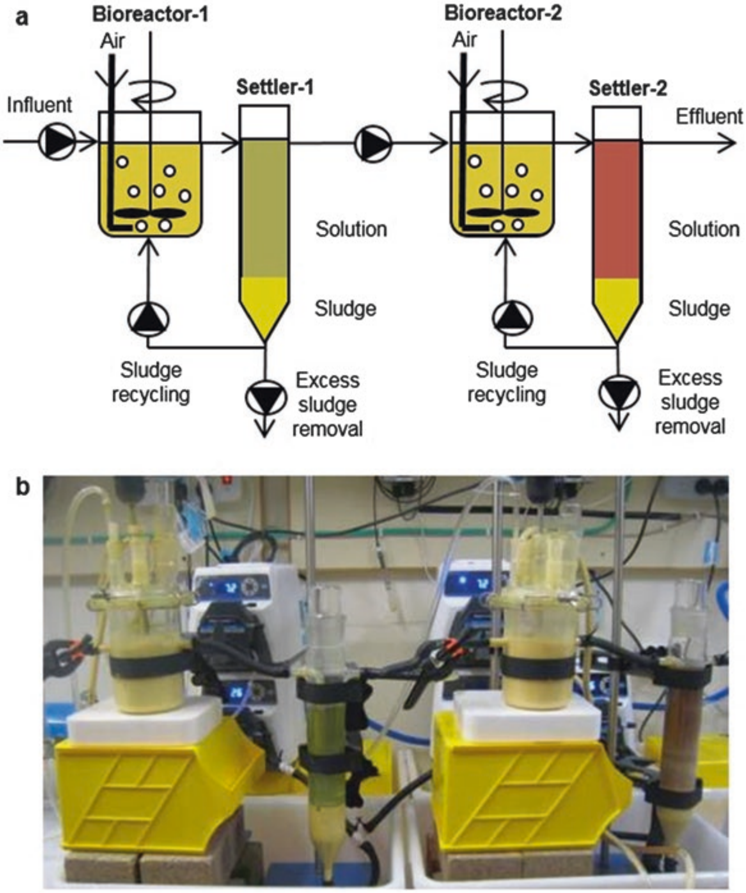

Fig. 7.7 (**a**) A schematic diagram and (**b**) a photo of a Lab-scale two-stage continuous stirred tank reactor process for biological iron oxidation and precipitation (Reprinted from Kaksonen et al. 2014c, Biohydrometallurgical iron oxidation and precipitation: part I – effect of pH on process performance, Hydrometallurgy, 147, 2014, with permission from Elsevier)

$$c = \frac{Fe^{2+0}}{1+\left(\frac{pH^{0}}{1.7}\right)^{9}} \tag{7.18}$$

Where
$Fe^{2+}{}_{OX}$ = Concentration of Fe^{2+} oxidized within the bioreactor (g/L)
Fe^{2+0} = Concentration of Fe^{2+} in the influent (g/L)

Scanning electron microscopic images of jarosite precipitates and cells in an iron-oxidizing culture from a two-stage airlift bioreactor used for iron oxidation and precipitation are illustrated in Fig. 7.8 (Kaksonen et al. 2014a). The morphologies

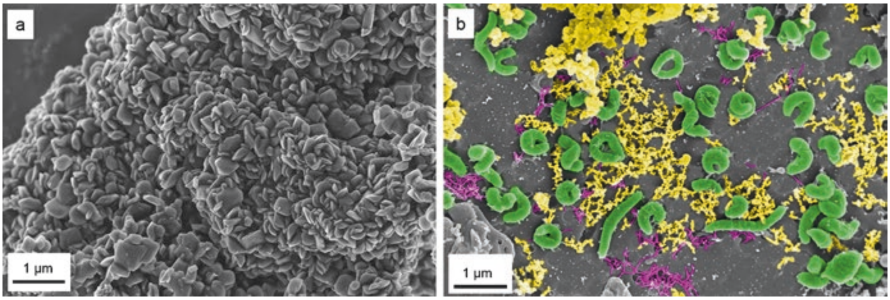

Fig. 7.8 Scanning electron microscopic images of precipitates (**a**) and microbial cells (**b**) obtained from iron oxidizing airlift bioreactor. Cells, extracellular polymeric substances and precipitates are artificially colored as *green, purple* and *yellow*, respectively (Reprinted from Kaksonen et al. 2014a, iron oxidation and jarosite precipitation in a two-stage airlift bioreactor, Hydrometallurgy, 150, 2014, with permission from Elsevier)

of the precipitated particles resembled jarosite and quantitative X-ray diffraction analysis confirmed that the precipitates predominantly (higher than 95w-%) comprised jarosite. In the scanning electron microscopic images, extracellular polymeric substances were also covered with precipitates, indicating that the extracellular polymeric substances may not only change the chemistry of the solution, but also affect the initiation and the location of precipitation (Kaksonen et al. 2014a).

7.4.3.3 Schwertmannite Precipitation

Schwertmannite is a ferric-oxyhydroxysulfate with the general formula of $Fe_8O_8(OH)_6(SO_4)$ (Bigham et al. 2010). Schwertmannite occurs commonly at pH 2.0–4.0 (Reaction 7.19) (Wang et al. 2006).

$$8Fe^{3+} + SO_4^{\;2-} + 14H_2O \rightarrow Fe_8O_8\left(OH\right)_6\left(SO_4\right) + 22H^+ \qquad (7.19)$$

Schwertmannite is the most common Fe precipitate at pH values between 3 and 4, though traces of goethite are also often present. Schwertmannite may be converted to goethite (Bigham et al. 1996) or jarosite with decomposition and ageing (Wang et al. 2006).

In addition to hydrometallurgical residues, schwertmannite formation can also be encountered in acidic (pH 2–3) sulfate-rich waters and soils, and in particular acid mine drainage (Schwertmann et al. 1995). Hedrich and Johnson (2012) investigated selective iron removal from acidic (pH 2) metal-containing water by selectively precipitating the oxidized iron as schwertmannite. The aim was to selectively remove iron from a metal mixture containing aluminum, copper, manganese, zinc and iron. After oxidization of iron with *Ferrovum myxofaciens*, the produced ferric iron was precipitated as schwertmannite at varying pH values of 2.75, 3.0 or 3.5 to allow the precipitation of iron and avoiding the co-precipitation of other metals. At pH 2.75, only 27% of the ferric iron precipitated within 200 h. At pH 3.0, the precipitation efficiency (higher than 80%) and the rate (1.9 mg Fe^{3+}/(L.min)) increased, while a much faster rate of 27 mg Fe^{3+}/(L.min) with almost complete precipitation was observed at pH 3.5. The addition of the flocculent FLOCCIN 1105 increased the sedimentation efficiency of the precipitates. Although almost complete iron removal was attained by bacterial oxidation and schwertmannite precipitation, little or no co-precipitation of other metals was observed (Hedrich and Johnson 2012).

7.5 Conclusions

Contamination of soil and groundwater with heavy metals is a worldwide environmental concern. In this chapter, the sources of heavy metal pollution (i.e. acid mine drainage, electroplating and tannery industries) and various bioprecipitation processes were reviewed. Metal sulfides have very low solubility over a broad range of pH values and in some cases selective recovery of metals such as Fe and Cu is possible. Soluble organic compounds (i.e., ethanol and lactate) can be externally supplied to high rate metal precipitating bioreactors as carbon and energy sources for sulfate reducers. However, the operational costs of the bioreactor processes may be prohibitive. Alternatively, passive treatment systems utilizing low cost natural organic waste materials can be used, but metal recovery may become more difficult and the process efficiency is less predictable. Additionally, biological oxidation (i.e., Fe^{2+}) or reduction (i.e. Cr^{6+} or U^{6+}) of some metals or metalloids may significantly decrease their solubility and induce metal precipitation. In low pH environments, bacterial Fe^{2+} oxidation may lead to the formation of various Fe-based precipitates depending on pH, temperature and the presence of other ions.

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Chapter 8
Biosolubilisation of Metals and Metalloids

Anna H. Kaksonen, Naomi J. Boxall, Kayley M. Usher, Deniz Ucar, and Erkan Sahinkaya

Abstract The solubilisation of metals and metalloids is catalysed by a variety of microorganisms in natural and engineered environments. Biosolubilisation has a number of undesired implications, such as the generation of acid mine drainage and the formation of acid sulfate soils, which have harmful environmental impacts. Biosolubilisation also contributes to the corrosion of man-made structures causing significant economic losses. On the other hand biosolubilisation has been harnessed by the mining industry to recover valuable metals and uranium from low-grade ores and concentrates in large scale. This allows the utilisation of ores the processing of which would not be economically feasible through traditional mining methods. Biosolubilisation holds also potential for the recovery of resources from waste and clean-up of metal contaminated environments. This chapter reviews the role that microorganisms have in the solubilisation of various metals and metalloids, the mechanisms through which biosolubilisation occurs and microbial groups mediating the solubilisation. The environmental implications and industrial applications of biosolubilisation are also discussed. Microorganisms can catalyse biosolubilisation through oxidative and reductive dissolution, mediated by the oxidation and reduction of ferrous and ferric iron, respectively. Moreover, biosolubilisation can be achieved through the production of biogenic acids, alkali and ligands, such as cyanide, thiosulfate, organic acids and iodide. Mechanisms contributing to microbially influenced corrosion of metallic iron and steel include differential aeration cells, galvanic cells, attack by microbial oxidants, acids, sulfides and other metabolites, cathodic depolarisation and direct microbial extraction of electrons from steel. A wide range of microorganisms are able to facilitate solubilisation reactions, including bacteria, archaea and eukaryotes. Bioleaching has been explored for recovering metals from e.g. a variety of sulfide ores, metallurgical waste, electronic scrap,

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sludge from municipal and industrial wastewater treatment, municipal solid waste incineration fly ash and contaminated sites. Large-scale biosolubilisation has been mainly used for copper-, cobalt-, nickel-, zinc-, uranium- and gold-containing sulfidic ores through oxidative bioleaching, whereas reductive bioleaching is yet to be implemented at industrial scale.

Keywords Acid mine drainage • Acid sulfate soil • Biocorrosion • Biohydrometallurgy • Bioleaching • Biooxidation • Bioreduction • Biosolubilisation • Iron oxidation • Iron reduction • Mineral • Steel • Sulfate reduction • Sulfur oxidation

Contents

8.1 Introduction

Microorganisms play an important role in driving the biogeochemical cycling of elements in various environments. Microorganisms influence the changes in speciation and mobility of elements, such as metals, carbon, sulfur, phosphorus, and nitrogen, with implications for primary productivity and ecosystem health (Gadd 2004). Some elements, such as carbon, sulfur, phosphorus, and nitrogen, are essential for microbial nutrition and some ions act as electron donors or acceptors in energy-yielding catabolic reactions. The solubility and mobility of metals are impacted by microorganisms, e.g. by their effect on pH and redox conditions, chemical transformation, production of complexing ligands, sorption, uptake and bioaccumulation (Gadd 2004; Reith et al. 2007a).

Biosolubilisation of metals and other elements can have profound environmental impacts, as evident, e.g. in acid mine drainage (Jarvis and Younger 2000) and acid sulfate soils (Vahedian et al. 2014). Some of the impacts, such as biocorrosion, can also have considerable economic impacts due to the damage to man-made structures. On the other hand, biosolubilisation can be exploited in environmental biotechnology for the removal of contaminants from soils, sediments and industrial wastes (Bosecker 1999; Gadd 2004). Moreover, biosolubilisation has been commercially utilised for recovering valuable metals and uranium through bioleaching and biooxidation of low-grade ores, concentrates and metal-containing waste materials (Brandl 2001; Olson et al. 2003; Watling 2006; Vestola et al. 2010; Kaksonen et al. 2011, 2014).

This chapter reviews the role of microorganisms in the solubilisation of metals and other elements, the various mechanisms through which biosolubilisation occurs, environmental implications and the utilisation of biosolubilisation for environmental and industrial applications.

8.2 Oxidative Biosolubilisation of Sulfide Minerals

8.2.1 Role of Iron- and Sulfur-Oxidising Microbes in Solubilising Metal Sulfides

The oxidation of sulfide minerals is predominantly the result of the activity of acidophilic chemolithotrophic iron- and sulfur-oxidising microorganisms. These microorganisms gain energy from oxidising ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) (Reaction 8.1) and/or elemental sulfur (S^0) and other reduced sulfur compounds to sulfuric acid (H_2SO_4) (Reaction 8.2) (Sand et al. 1995):

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O \quad (\text{under aerobic conditions}) \tag{8.1}$$

$$2\,S^0 + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4 \quad (\text{under aerobic conditions}) \tag{8.2}$$

The rate of biological Fe^{2+} oxidation is considerably faster (approximately 10^5–10^6 times) compared to chemical oxidation, especially at low pH values (pH <2) (Rao et al. 1995; Bosecker 1997; Tuovinen and Bhatti 1999; Meruane and Vargas 2003). The Fe^{3+} and H^+ ions attack the valence bonds of sulfide minerals leading to the breakdown of the sulfide matrix (Nagpal et al. 1994; Morin 1995; Rawlings and Silver 1995; Sand et al. 1995; Belzile et al. 2004). Below are some examples of this process for pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$) and other metal sulfides (MS) (Reactions 8.3, 8.4, 8.5, 8.6, 8.7, and 8.8):

$$FeS_2 + 2\,Fe^{3+} \rightarrow 3\,Fe^{2+} + 2\,S^0 \tag{8.3}$$

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ \tag{8.4}$$

$$Fe_{1-x}S + (2-2x)Fe^{3+} \rightarrow (3-3x)Fe^{2+} + S^0 \tag{8.5}$$

$$Fe_{1-x}S + (8-2x)Fe^{3+} + 4\,H_2O \rightarrow (9-3x)Fe^{2+} + SO_4^{2-} + 8\,H^+ \tag{8.6}$$

$$2\,Fe_{1-x}S + 4(1-x)H^+ + (1-x)O_2 \rightarrow 2(1-x)Fe^{2+} + 2\,S^0 + 2(1-x)H_2O \tag{8.7}$$

$$MS + 2\,Fe^{3+} \rightarrow M^{2+} + S^0 + 2\,Fe^{2+} \tag{8.8}$$

The solubilisation of sulfide minerals is thought to be hindered by the formation of passivating layers of elemental sulfur, polysulfides, and jarosite (Stott et al. 2000). Microorganisms can enhance solubilisation by removing passivating layers from mineral surfaces. *Acidithiobacillus* (*At.*) *ferrooxidans* and some other acidophilic microorganisms are also capable of oxidising sulfur in anaerobic environments with Fe^{3+} as the terminal electron acceptor (Reaction 8.9) (Pronk et al. 1992):

$$S^0 + 6\,Fe^{3+} + 4\,H_2O \rightarrow SO_4^{2-} + 6\,Fe^{2+} + 8\,H^+ \ (\text{under anaerobic conditions}) \tag{8.9}$$

This process decreases pH and reduces the precipitation of ferric iron as passivating iron hydroxyl compounds (Nurmi 2009). In addition to *At. ferrooxidans*, several other acidophilic microorganisms can also reduce ferric iron, including *At. ferrivorans*, *Acidiferrobacter thiooxydans*, *Ferrimicrobium acidiphilum*, *Acidimicrobium ferrooxidans*, *Ferrithrix thermotolerans*, several *Acidiphilum* spp., *Acidocella* spp., *Acidobacterium* spp., *Alicyclobacillus* spp., *Sulfobacillus* spp., *Acidiplasma* spp. and *Ferroplasma* spp. (Johnson et al. 2012).

8.2.2 Biosolubilisation Pathways for Sulfide Minerals

Metal sulfide oxidation can proceed via the thiosulfate or the polysulfide pathway. The leaching process differs for acid soluble and acid insoluble minerals as reactivity of the mineral sulfides with protons (H^+) varies (Rohwerder et al. 2003; Sand and

Gehrke 2006). Acid soluble metal sulfides are leached by both Fe^{3+} and H^+ via the polysulfide pathway, whereas acid-insoluble metal sulfides are leached by ferric ions alone via the thiosulfate pathway (Hansford and Vargas 2001; Schippers 2007). This difference in mechanisms explains why sulfur-oxidising microorganisms are able to assist the leaching of some minerals, but not others.

8.2.2.1 The Thiosulfate Pathway

The oxidation of acid-insoluble minerals, e.g. pyrite (FeS_2), tungstenite (WS_2) and molybdenite (MoS_2) proceeds via the thiosulfate pathway (Fig. 8.1). The breakage of the chemical bonds between sulfur and the metal moiety leads to the liberation of thiosulfate (Rohwerder et al. 2003). Thiosulfate degradation to tetrathionate by the microorganisms produces sulfate and protons. However, if abiotically driven, higher polythionates and elemental sulfur are produced. In the case of acid mine drainage, it is preferable that the reactions are mainly abiotic so further acid is not produced (Hallberg 2010). On the other hand, when sulfidic-refractory gold ore is bioleached to release entrapped/enclosed gold, it is preferable that the process is enzymatically driven, as this will limit the amount of elemental sulfur produced. This is because cyanide is used to dissolve the gold from solid residues and elemental sulfur is highly consumptive of cyanide (Sand and Gehrke 2006).

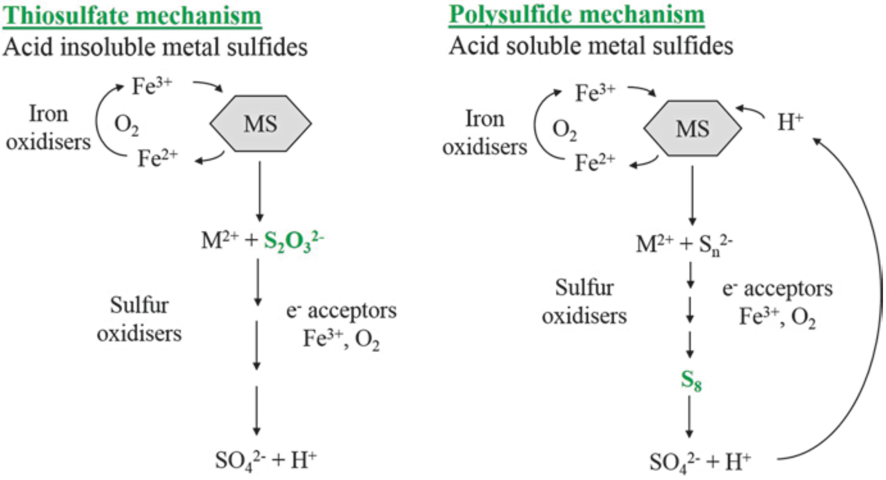


Fig. 8.1 The two mineral sulfide oxidation pathways. Acid-insoluble minerals are oxidised via the thiosulfate pathway, whereas acid soluble metal sulfides are oxidised via the polysulfide pathway. MS: metal sulfide (Adapted from Rohwerder et al. 2003)

8.2.2.2 The Polysulfide Pathway

The oxidation of acid soluble sulfide minerals, such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), covellite (CuS), sphalerite (ZnS), cadmium sulfide (CdS), millerite (NiS) and cobalt sulfide (CoS) proceeds via the polysulfide pathway (Fig. 8.1). Proton attack and concomitant oxidation of acid soluble sulfide minerals by ferric iron liberates sulfur compounds such as H_2S^+. This dimerizes to H_2S_2 which in turn is oxidised to various polysulfides, eventually oxidising to elemental sulfur (Rohwerder et al. 2003). Sulfur-oxidising microorganisms like *At. thiooxidans* can oxidise the reduced sulfur compounds and produce sulfate (Sand and Gehrke 2006).

8.2.3 Contact, Non-contact and Cooperative Leaching

Bioleaching mechanisms have been further divided into contact, non-contact and cooperative leaching mechanisms (Silverman 1967; Sand et al. 2001; Crundwell 2003). In non-contact leaching (Fig. 8.2), planktonic microbial cells generate Fe^{3+} and/or H^+ which attack the sulfide minerals directly. In the contact mechanism, the bioleaching reactions take place in the extracellular polymeric substances at the interface between attached microbial cells and the sulfide mineral (Fig. 8.2) (Sand et al. 1995, 2001; Rohwerder et al. 2003). In cooperative leaching (Fig. 8.2), attached microorganisms release mineral particles and soluble forms of sulfur, including reduced intermediate sulfur compounds and sulfur globules (colloidal forms of sulfur) which are utilised by the planktonic microorganisms (Ceskova et al. 2002). Figure 8.3a, b show scanning electron microscope images of *At. ferrooxidans* and *Leptospirillum ferrooxidans* cells, respectively, growing on chalcopyrite demonstrating contact leaching.

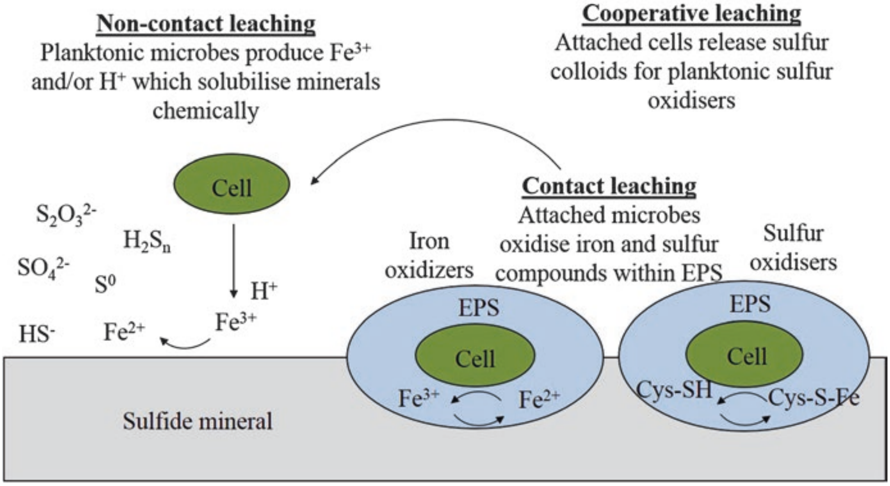


Fig. 8.2 Non-contact, contact and cooperative leaching of metals from minerals (Rawlings 2002). EPS: extracellular polymeric substances

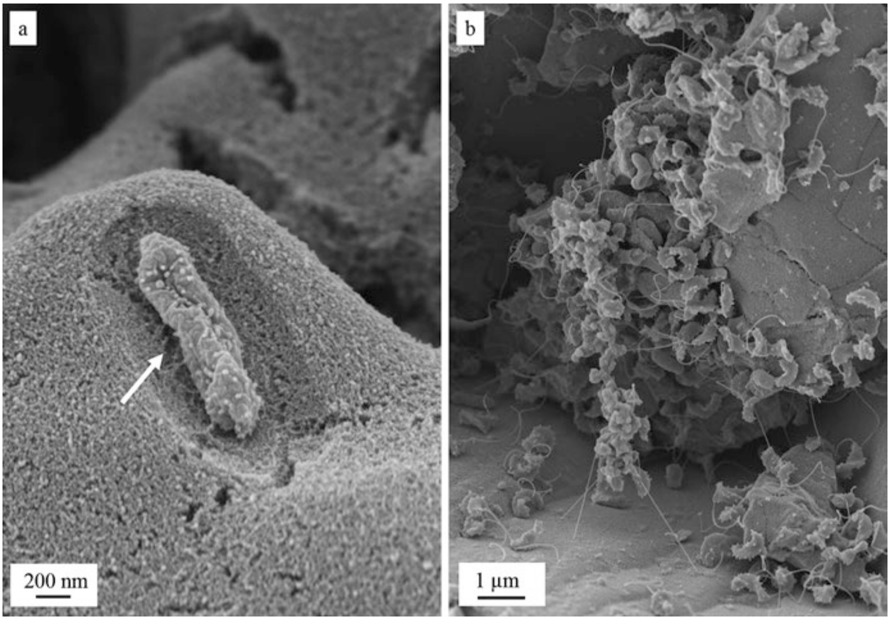


Fig. 8.3 Scanning electron microscopic images of **a** an *At. ferrooxidans* cell (pointed out with an *arrow*); and **b** *L. ferrooxidans* cells growing on chalcopyrite (Photos: Kayley Usher; Copyright: CSIRO)

8.2.4 Modelling Bioleaching

A number of mathematical models have been developed to describe biosolubilisation in the context of sulfide mineral leaching. A number of sub-processes, such as chemistry, microbiology, and hydrodynamics, require consideration (Watling 2006). Moreover, one needs to consider processes at various scales, such as grain, particle, cluster and unit process scale (Petersen and Dixon 2007). Chemical factors relevant for leaching include solution speciation, leaching reaction kinetics, gangue interactions, precipitation, adsorption, pore diffusion kinetics and liquid-solid and gas-liquid mass transfer kinetics. Microbiological factors relevant for modelling biosolubilisation are e.g. microbial activity, growth rates and yields, maintenance and death rates, effects of temperature, pH, substrate and inhibitors on growth and activity, microbial speciation, microbial inoculation, mobility and attachment (Watling 2006). Solute, gas and heat transport are affected by factors such as advection, convection, conduction, diffusion, evaporation and condensation (Watling 2006). A holistic model is required that accounts for as many as possible of the complex micro- and macro-scale processes and their interactions (Watling 2006) and the equations for each process are beyond this chapter.

A shrinking core model was described by Kargi (1989) for bioleaching lead sulfide. The model considered the deposition of insoluble biooxidation products on metal sulfide particle surfaces and the effects of variations in particle size on diffusion limitations. Several authors have employed fluid models to investigate the hydrodynamic behaviour of leaching heaps (McBride et al. 2015). Dixon and Petersen (2003) and Watling (2006) have reviewed various models used for heap and dump leaching. The HeapSim© model (Dixon and Petersen 2003, 2004) includes a systematic conceptual and mathematic description of many of the processes relevant for heap leaching combined with a comprehensive simulation engine. Multidimensional models, such as the Phelps Dodge copper stockpile model (Bennett et al. 2003) and the CSIRO Heap model (Leahy et al. 2007), enable the simulation of two phases (gas and liquid) (Watling 2006).

8.3 Biosolubilisation of Uranium

Uranium occurs largely as oxide minerals in association with many different metals in the Earth's crust (Tuovinen and DiSpirito 1984). Uranium also exists in nature in various other mineral forms such as silicates, phosphates, carbonates and vanadates (Francis 1994), as well as in organic and inorganic aqueous complexes (Gadd and Fomina 2011). The aqueous chemistry of uranium is affected by several factors, including pH, redox reactions, hydrolysis, precipitation/dissolution, complexation and sorption (Gadd and Fomina 2011).

Microorganisms can contribute to the solubilisation of uranium through oxidation reactions, changes in pH and redox potential as well as complexation by excreted metabolites (Gadd and Fomina 2011). Dilute acid can chemically solubilise hexavalent uranium (U^{6+}) in uranium trioxide (UO_3) from its mineral matrices (Muñoz et al. 1995) (Reaction 8.10):

$$UO_3 + 2\,H^+ \rightarrow UO_2^{2+} + H_2O \tag{8.10}$$

However, tetravalent uranium (U^{4+}) in uranous oxide (UO_2) (i.e. uraninite) is not easily solubilised in acidic solutions without being first oxidised to U^{6+}, i.e. to the uranyl ion (UO_2^{2+}), by O_2 and/or Fe^{3+} (DiSpirito and Tuovinen 1982b). Acidophilic sulfur- and iron-oxidising microorganisms can catalyse uranium leaching by generating sulfuric acid and soluble ferric iron from sulfide minerals (DiSpirito and Tuovinen 1982a). Sulfuric acid solubilises UO_3 (Reaction 8.10) and Fe^{3+} oxidises U^{4+} in UO_2 leading to the formation of soluble UO_2^{2+} (U^{6+}) (Rawlings and Silver 1995; Tuovinen and Bhatti 1999) (Reaction 8.11):

$$UO_2 + 2\,Fe^{3+} \rightarrow UO_2^{2+} + 2\,Fe^{2+} \tag{8.11}$$

Microorganisms play a role in the solubilisation of uranium in acidic systems by oxidising Fe^{2+} to Fe^{3+} and S^0 to sulfuric acid (Pronk et al. 1992; Tuovinen and Bhatti 1999) (Reactions 8.1, 8.2 and 8.9). A high Fe^{3+}/Fe^{2+} ratio and thus redox potential improves uranium solubilisation (Muñoz et al. 1995). Sulfuric acid (H_2SO_4) forms soluble uranyl sulfate complexes [$H_4[UO_2(SO_4)_3]$] with U^{6+} (Tuovinen and Bhatti 1999) (Reaction 8.12):

$$UO_3 + 3H_2SO_4 \rightarrow H_4\left[UO_2\left(SO_4\right)_3\right] + H_2O \tag{8.12}$$

Hexavalent uranium can also form complexes with carbonate and phosphate (Tuovinen and DiSpirito 1984). In the absence of complexing agents, uranium tends to precipitate through hydrolysis (Muñoz et al. 1995) (Reaction 8.13):

$$UO_2^{2+} + 3H_2O \rightarrow UO_2\left(OH\right)_2 \cdot H_2O + 2H^+ \tag{8.13}$$

Oxygen produced by some algal species such as *Scenedesmus quadricauda* and *Nostoc linkia* may oxidise U^{4+} to U^{6+} (Reaction 8.14) (Calmoi and Cecal 2007):

$$2UO_2 + O_2 + 4H^+ \rightarrow 2UO_2^{2+} + 2H_2O \tag{8.14}$$

Calmoi and Cecal (2007) investigated the bioleaching of uranium with algae at 30 °C in the presence of continuous illumination and achieved 20 % bioleaching in 10 days. Heterotrophic fungi and bacteria can also solubilise uranium (Hefnawy et al. 2002) by producing complex-forming organic acids and decreasing pH. Mishra et al. (2009) compared the capability of various fungal cultures to solubilise uranium from Turamdih (Jharkhand, India) low-grade, predominantly oxidic uranium ore. In 10 days, *Curvulria clavata*, *Spergillus flavus* and *Cladosporium* exhibited 50 %, 59 % and 71 % uranium recovery, respectively (Mishra et al. 2009). Examples of organic acids involved in uranium biosolubilisation are small carboxylic (e.g. oxalic, citric and iso-citric) and phenolic (Berthelin and Munier-Lamy 1983) acids. Uranium forms very stable uranium-citrate complexes with stability constants that are considerably higher than those of the complexes of uranium with acetate, ascorbate, lactate and ethylenediaminetetraacetic acid (EDTA) (Borkowski et al. 1996). However, the stability of uranium complexes may be lower under extreme conditions. In the presence of phosphate, uranium-citrate complexes dissociate in hypersaline conditions, generating citric acid and a uranium precipitate that is predominantly $K(UO_2)_5(PO_4)_3(OH)_2.nH_2O$ (Francis et al. 1992).

8.4 Biosolubilisation of Oxide Minerals

Dissimilatory ferric iron-reducing microorganisms can catalyse reductive biosolubilisation of iron hydroxy compounds that contain ferric iron, such as jarosite, goethite, or schwertmannite (Johnson and Hallberg 2008). Reaction 8.15 shows the reductive dissolution of schwertmannite with glucose as an electron donor (Coupland and Johnson 2008):

$$3Fe_8O_8\left(OH\right)_6\left(SO_4\right) + C_6H_{12}O_6 + 6H_2O \rightarrow 24Fe^{2+} + 6CO_2 + 3SO_4^{2-} + 42OH^- \tag{8.15}$$

In addition to ferric iron reducers, other heterotrophic microorganisms (particularly fungi) can also play a role in biosolubilisation of oxide ores due to the excretion of organic acids, which dissolve heavy metals from lateritic ores by forming salts and chelates (Le et al. 2006; Mohapatra et al. 2008). The bioreduction of ferric iron requires a suitable electron donor, such as organic compounds, hydrogen, or elemental sulfur for the microorganisms (Hallberg et al. 2011). Acidophilic microorganisms that can use ferric iron for respiration include *At. ferrooxidans* (Pronk et al. 1992; Hallberg et al. 2011), *Sulfobacillus* spp. (Brock and Gustafson 1976; Bridge and Johnson 1998; Johnson et al. 2008), *Acidiphilum* spp. (Bridge and Johnson 2000), *Acidiplasma aeolicum* (Golyshina et al. 2009), *Ferrimicrobium acidiphilum* (Johnson et al. 2009), *Ferrithrix thermotolerans* (Johnson et al. 2009), *Acidiferrobacter thiooxidans* (Hallberg et al. 2011) and *Alicyclobacillus*-like microorganisms (Yahya et al. 2008).

Soluble ferric iron is preferentially reduced by the microorganisms, followed by insoluble ferric iron minerals where the rate of dissolution depends on the degree of crystallisation (Hallberg et al. 2011). Hallberg et al. (2011) showed that *At. ferrooxidans* could solubilise over 70 % of the nickel in a nickel laterite ore (<6 mm, nickel grade 0.5 %) in 14 days by reducing goethite, the main ferric iron mineral present in the ore.

In addition to acidophilic microorganisms, some neutrophilic microbes can also reduce Fe^{3+} to Fe^{2+}. These include strict anaerobes such as *Desulfovibrio* (*Dv.*) spp. and *Desulfuromonas* (*Dm.*) spp. (Li et al. 2006; Papassiopi et al. 2010) and facultative anaerobes such as *Shewanella* spp. (Venkateswaran et al. 1999) and *Paenibacillus* spp. (Munch and Ottow 1983). The anaerobic sulfate-reducing species *Dv. desulfuricans* strain G-20 reduced ferrihydrite, goethite, and hematite in the absence of sulfate (4.6 %, 5.3 % and 3.7 % of total iron reduced, respectively). In the presence of sulfate, however, the total iron reduced was greatly enhanced for these minerals (100 %, 73.9 %, and 64.3 %, respectively) due to a combination of microbial iron reduction and the biogenic H_2S produced (Li et al. 2006). Microorganisms can generally reduce naturally occurring goethite and hematite more easily than synthesized compounds. Microbial reduction of goethite by *Dm. palmitatis* in bauxite samples corresponded to 8 mM Fe^{2+} in solution compared to 1.2 mM Fe^{2+} for synthetic goethite (Papassiopi et al. 2010). Zachara et al. (1998) also reported that *Shewanella oneidensis* strain CN32 was able to reduce natural oxides far more readily than their synthetic counterparts.

Many *Shewanella* (*Sh.*) spp. can reduce amorphous Fe^{3+}-oxides and some can reduce crystalline iron oxides such as hematite and goethite (Roden and Zachara 1996; Bose et al. 2009). The more crystalline iron Fe^{3+}-oxides are less bioavailable for microorganisms to reduce. The facultative anaerobe *Sh. alga* strain BrY reduced 44 % of the amorphous ferrihydrite iron oxide ($FeOOH{\cdot}4H_2O$) compared to 0.6 % of hematite (Fe_2O_3) and 1.5–3.0 % of goethite (Roden and Zachara 1996). Similar results for goethite and hematite reduction were found by Papassiopi et al. (2010) using the strict anaerobe *Dm. palmitatis*. The maximum level of reduction observed was directly correlated to the surface area of the oxides.

8.5 Biosolubilisation of Gold

Microorganisms can facilitate the solubilisation of gold by catalysing the oxidation of sulfides in refractory gold minerals, thus making the gold more accessible for leaching (for a review, see Kaksonen et al. 2014). The sulfide oxidation mechanisms are similar to those described in Sect. 8.8.2 and are facilitated by acidophilic iron- and sulfur-oxidising microorganisms. Some microorganisms can also prevent carbonaceous content in the ore from robbing already dissolved gold from solution (Brierley and Kulpa 1993) by producing microbial metabolites which adsorb to the carbonaceous content or by degrading carbonaceous material to carbon dioxide (Brierley and Kulpa 1993; Yen et al. 2009). The carbonaceous content comprises of activated carbon-type material, long-chain hydrocarbons, and organic acids, such as humic acid (Brierley and Kulpa 1993). Microorganisms reported to be involved in these processes include bacteria, such as *Pseudomonas maltophila*, *P. oryzihabitans, P. putida, P. fluorescens, P. stutzeri, Achromobacter* spp., *Arthrobacter* spp. and *Rhodococcus* spp. and fungi, such as *Trametes* spp., *Phanerochaete* spp., *Phlebia* spp., *Cyathus* spp. and *Tyromyces* spp. (Brierley and Kulpa 1993; Yen et al. 2009; Kaksonen et al. 2014).

Microorganisms can also excrete ligands that can stabilise gold through formation of gold-rich colloids and/or complexes. The solubilisation of gold can be facilitated by biologically produced amino acids, cyanide, and thiosulfate (Reith et al. 2007a; Kaksonen et al. 2014). Moreover, microorganisms can participate in the redox cycling of iodine (Amachi 2008), which may also solubilise gold (Kaksonen et al. 2014).

8.5.1 *Thiosulfate*

Thiosulfate can solubilise gold in the presence of oxidants (e.g. Cu^{2+}) and complexing ligands (e.g. ammonia) (Aylmore and Muir 2001; Wan and LeVier 2003; Reith et al. 2007b) (Reaction 8.16):

$$\mathrm{Au} + 5\,\mathrm{S_2O_3^{2-}} + \mathrm{Cu(NH_3)_4^{2+}} \rightarrow \left[\mathrm{Au(S_2O_3)_2^{3-}}\right] + \mathrm{Cu(S_2O_3)_3^{5-}} + 4\,\mathrm{NH_3} \quad (8.16)$$

The Au^+ thiosulfate complex is stable in the pH range 5–10 and from reducing to moderately oxidising environments (Redox potential −0.17–0.76 V against standard hydrogen potential) (Reith 2003).

Ammonium and thiosulfate are produced and excreted by microorganisms during a number of metabolic reactions (Reith et al. 2007b). Ammonium is a common product of the hydrolysis of urea, which is produced by many bacteria and yeasts, including many alkaliphilic *Bacillus* spp. (Schmidt Mumm and Reith 2007; Reith et al. 2007b). A common soil actinomycete, *Streptomycetes fradiae*, produces thiosulfate when metabolising sulfur from cysteine (Kunert and Stránský 1988; Reith et al. 2007a). Sulfate-reducing microorganisms form thiosulfate under certain conditions, e.g. when reducing sulfite with formate or H_2 (Fitz and Cypionka 1990; Reith et al. 2007a, b; Kaksonen et al. 2014).

Thiosulfate mediated biosolubilisation of gold is likely in environments that are poor in organic carbon, for example in primary sulfide bearing deposits (Reith et al. 2007a). Reith and McPhail (2006) studied the solubilisation of sub-microscopic gold in carbon-limited quartz vein materials with pyrite and arsenopyrite from the Tomakin Park Gold Mine (Australia). Reith et al. (2007a) proposed that the gold solubilisation was mediated by microbially produced thiosulfate. Up to 550 ng of gold per gram of quartz vein material (dry weight, particle size <200 μm, equivalent to 550 mg gold t^{-1} dry weight) was solubilised in a biologically active agitated slurry after 35 days of incubation and the concentration decreased thereafter. In contrast, a sterile control system showed solubilised gold concentrations that were ten times lower than the biotic tests (Reith and McPhail 2006; Reith et al. 2007a).

8.5.2 *Biogenic Cyanide*

Cyanide can complex Au^+ as a dicyanoaurate complex (Reaction 8.17), which is stable in a wide redox and pH range (Reith et al. 2007a):

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \rightarrow 4\left[Au\left(CN\right)_2\right]^- + 4\,OH^- \tag{8.17}$$

Many soil bacteria (such as *Pseudomonas* spp. and *Bacillus megaterium*), fungi, and plants can produce and excrete cyanide (Reith et al. 2007a). Cyanide is not known to have any function in primary microbial metabolism and its production is optimal when growth is limited. Cyanide producers are often tolerant to cyanide and may gain a competitive advantage by causing toxicity to other microorganisms (Castric 1975; Bakker and Schippers 1987; Reith et al. 2007a). Cyanide has a pKa value of 9.3, and it therefore mainly occurs as volatile hydrogen cyanide (HCN) at neutral pH. Biogenic cyanide may contribute to gold solubilisation (Faramarzi and Brandl 2006; Reith et al. 2007a). Cyanide mediated gold biosolubilisation may occur in the rhizosphere, where organic compounds excreted by plants may directly solubilise gold or provide nutrients for cyanide excreting microorganisms (Bakker and Schippers 1987; Reith et al. 2007a).

Chromobacterium violaceum, which is able to produce cyanide, has been shown to solubilise 100 % of the gold from glass slides in 17 days, resulting in soluble cyanide and gold concentrations of 14.4 and 35 mg L^{-1}, respectively (Campbell et al. 2001). In the presence of bio-oxidised gold concentrate, the species generated a maximum of 9 mg L^{-1} CN^- and 0.34 mg L^{-1} gold was solubilised in 10 days (Campbell et al. 2001). Fairbrother et al. (2009) examined the effect of cyanide production by *C. violaceum* on ultra-flat gold foil by incubating the bacteria and foil in peptone meat extract for up to 56 days. The total concentrations of solubilised gold increased throughout the experiment and after 56 days 74.3 μg L^{-1} of gold was detected in solution and 51.3 μg L^{-1} was reversibly or irreversibly bound to cells.

8.5.3 Organic Acids

Various researchers have reported that amino acids generated by heterotrophic microorganisms, such as *Bacillus* spp., *Pseudomonas* spp. and *Bacterium nitrificans* can enhance gold solubilisation by forming gold-amino acid complexes (Korobushkina et al. 1974; Reith et al. 2007a). According to Korobushkina et al. (1983), the redox potential of gold-amino acid complexes influences their stability. The complex forming capacity of amino acids may be ranked according to the redox potentials as follows: cysteine > histidine > asparagine > methionine > glycine ≈ alanine ≈ valine ≈ phenylalanine (Korobushkina et al. 1983). Electron donor elements, e.g. N, S, and O, are usually involved in the interaction between organic matter and gold (Reith et al. 2007a). Jingrong et al. (1996) suggested that the oxygen atom in the carboxyl group (COO^-) and the nitrogen atom in the amino group ($-NH_2$) play a role in the gold complexation. Vlassopoulos et al. (1990) reported gold being complexed with organic O in oxidising environments and binding preferentially to organic S under reducing environments. Jingrong et al. (1996) reported that the solubilisation of gold by amino acids also depends on pH and temperature.

Gold solubilisation via complexation with organic acids may happen in the rhizosphere and top soils which are rich in organic matter and where organic acids excreted by plants may directly solubilise gold or support the growth of organic acid-excreting microorganisms (Reith et al. 2007a). According to Korobushkina et al. (1974), aspartic acid, histidine, serine, alanine, and glycine play a substantial role in gold dissolution by cultures isolated from gold-bearing deposits. Amino acid production by the strains was increased by mutagenic factors (ultraviolet rays and ethylenimine) and the solubility of gold increased in the presence of an oxidising agent (2 g L^{-1} sodium peroxide) under alkaline conditions (pH 9–10). Dissolution of gold by purified amino acid fractions yielded solutions with up to 14–15 mg L^{-1} of gold in 20 days (Korobushkina et al. 1974).

In a study by Reith and McPhail (2006) with gold-containing soils rich in organic matter, samples with biological activity showed up to 80 wt% gold solubilisation within 45 days of incubation under aerobic conditions. The original gold concentration was 1.45 μg g^{-1} dry weight soil; equivalent to 1.45 g t^{-1} dry weight soil. The microbial community produced up to 64.2 μM free amino acids within the first 20 days of incubation, leading to gold complexation and solubilisation. However, later the microbial community metabolised the gold-complexing ligands as free amino acid concentration decreased to approximately 8 μM by day 50. Simultaneously, the soluble gold concentration declined likely due to adsorption to the soil. The structure of the microbial community shifted from one that uses polymers and carbohydrates to one that utilises amino and carboxylic acids when soluble gold concentrations decreased (Reith and McPhail 2006).

Some amino acids are also precursors for the microbial production of other gold-complexing ligands. For example, cysteine is a precursor for thiosulfate (Kunert and Stránský 1988; Reith et al. 2007b) and glycine is a precursor for cyanide (Rodgers and Knowles 1978; Reith et al. 2007a, b; Fairbrother et al. 2009).

8.5.4 Iodide

Iodide (I^-) can solubilise gold according to Reactions 8.18 and 8.19 (Davis and Tran 1991; Angelidis et al. 1993):

$$2\,Au + I^- + I_3^- \rightarrow 2\,AuI_2^- \tag{8.18}$$

$$2\,Au + 3\,I_3^- \rightarrow 2\,AuI_4^- + I^- \tag{8.19}$$

In aqueous environments, iodide can occur as several species: I_2, HIO, I^-, I_3^-, and IO^- which exist in equilibrium (Reactions 8.20, 8.21, and 8.22; Davis and Tran 1991):

$$HIO \leftarrow\rightarrow H^+ + IO^- \tag{8.20}$$

$$I_2 + H_2O \leftarrow\rightarrow H^+ + I^- + HIO \tag{8.21}$$

$$I_2 + I^- \leftarrow\rightarrow I_3^- \tag{8.22}$$

The reaction equilibria are influenced by pH, temperature and soluble I^- and I_2 concentrations (Davis and Tran 1991). Considerable geochemical evidence has indicated that microorganisms contribute to the reduction and oxidation of inorganic iodine species and the volatilisation of organic iodine compounds into the atmosphere, although the mechanisms are not well known (Amachi 2008). Thus, microorganisms may contribute to gold solubilisation by oxidising I^- to I_2 (Kaksonen et al. 2014). Some microorganisms can also reduce iodate (IO_3^-) to I^- (for a review, see Amachi 2008; Kaksonen et al. 2014).

A number of bacteria have been shown to oxidise I^-. In 1968, Gozlan reported the isolation of an I^--oxidising heterotrophic bacterium from experimental seawater in an aquaria. The isolate, later invalidly named as "*Pseudomonas iodooxidans*", oxidised I^- to I_2 using an extracellular peroxidise with hydrogen peroxide (H_2O_2) as an electron acceptor (Reaction 8.23) (Gozlan and Margalith 1973, 1974):

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow I_2 + 2\,H_2O \tag{8.23}$$

More recently, Fuse et al. (2003) and Amachi et al. (2005) isolated I^--oxidising bacteria from marine environmental samples. The bacteria were affiliated with the *Alfaproteobacteria.* Some of the strains were most closely related to *Roseovarius tolerans* (94–98 % 16S rRNA gene sequence similarity) and others were related to *Rhodothalassium salexigens* (89–91 % 16S rRNA gene sequence similarity). The I^- oxidation reaction was facilitated by oxygen-requiring extracellular oxidase (Reaction 8.24) (Amachi et al. 2005):

$$4\,I^- + O_2 + 4\,H^+ \rightarrow 2\,I_2 + 2\,H_2O \tag{8.24}$$

Although the oxidation of I^- by oxygen as an electron acceptor is energetically favourable ($\Delta G^{0'} = -56$ kJ reaction^{-1}), the extracellular nature of the enzyme implies that energy conservation by this reaction is not possible (Amachi et al. 2005). However, I^--oxidising bacteria seem to prefer I^--rich environments (Amachi et al. 2005). I^- may enhance the competitive advantage of I^--oxidising bacteria over competing microbial species (Amachi 2008). I_2 produced by I^--oxidising bacteria is a strong oxidant and can act as bactericide and fungicide (Mcdonnell and Russell 1999).

Microbial IO_3^- reduction to I^- is still not well understood because of few IO_3^--reducing isolates available for experimental analysis and the limited data on enzymes catalysing IO_3^- reduction. It has been proposed that microbial remineralisation of organic iodine compounds and microbial reduction of IO_3^- are likely to be important processes to maintain reduced forms of iodine in deep waters (Nakayama et al. 1989), anoxic basins (Wong and Brewer 1977; Farrenkopf et al. 1997) and pore waters of marine sediments (Muramatsu et al. 2007), where I^- is often highly enriched to concentrations of over 1 mM (Amachi 2008), whereas in seawater the average dissolved iodine concentration is 0.45 μM (Kaksonen et al. 2014).

A marine IO_3^--reducing *Pseudomonas* sp. strain SCT was reported to reduce 200 μM IO_3^- to I^- in 12 h under anaerobic conditions in the presence of 10 mM nitrate, but the strain was not able to grow with 5 or 10 mM IO_3^- as the only electron acceptor in the absence of nitrate (Amachi et al. 2007). However, the strain grew well at 2, 3, and 4 mM IO_3^- as the only electron acceptor. The growth increased with increasing IO_3^- concentrations. The strain used malate, glycerol, lactate, succinate, acetate, and citrate as electron donors (Amachi et al. 2007).

Direct microbial reduction of IO_3^- has also been shown for the sulfate-reducing bacterium *Desulfovibrio desulfuricans* and the dissimilatory Fe^{3+}-reducing bacterium *Shewanella putrefaciens* (Councell et al. 1997). Soluble Fe^{2+}, sulfide, and iron sulfide (FeS) were reported to abiotically reduce IO_3^- to I^-. The study indicated that sulfate-reducing bacteria and Fe^{3+}-reducing bacteria can facilitate both direct enzymatic and abiotic IO_3^- reduction under anaerobic conditions (Councell et al. 1997).

8.6 Biosolubilisation of Silicate

8.6.1 Si-Containing Minerals

Some microorganisms can enhance the dissolution of silicate and aluminosilicate minerals (Kaksonen et al. 2014) by non-enzymatic mechanisms (Ehrlich 1996). The dissolution mechanisms may involve the production of alkalinity in the form of NH_3, acid polysaccharides or organic acids which act as ligands (Ehrlich 1996). Among the organic acids, citric and oxalic acid formed by some fungi and 2-ketogluconic acid formed by some bacteria, are effective in the dissolution of silicates (Duff et al. 1963; Vandevivere et al. 1994; Ehrlich 1996). The organic acids help to break Al–O and Si–O bonds via protonation. Some organic acids can also act as ligands that pull cations from the framework of the crystal lattice, leading to the breakage of framework bonds. Bacterial acid polysaccharide slimes can complex silicate, leading to silicate dissolution (Malinovskaya et al. 1990; Ehrlich 1996; Liu et al. 2006).

Quartz (SiO_2) comprises 20 % of the volume of the exposed Earth's crust and is among the most resistant rock minerals (White and Brantley 1995; Brehm et al. 2005). It solubilises slowly in pure water at a rate of approximately 10^{-17} mol cm^{-2} s^{-1} at 40 °C, neutral pH, because the breaking of Si–O bonds requires a lot of energy (Brehm et al. 2005). As a component of rocks (e.g. gneiss, granite, and sandstone), quartz crystals and grains have a higher resistance to weathering processes than many other common minerals such as feldspar and mica, which also contain silicate (Brehm et al. 2005). Quartz dissolution is minimal at a pH below 3.5 and increases significantly in alkaline conditions of above pH 9 (Brehm et al. 2005). Various biological processes can consume acidity or generate alkalinity and, therefore, have the potential to increase pH and quartz dissolution. These include: denitrification (Kalin et al. 1991; Johnson 1995); hydrolysis of urea (Fujita et al. 2000); photosynthesis (Robb and Robinson 1995; Van Hille et al. 1999; Johnson 2000; Brehm et al. 2005); methanogenesis, ammonification, and iron and sulfate reduction (Kalin et al. 1991; Johnson 1995, 2000; White et al. 1997) (Table 8.1).

8.6.2 Si-Containing Materials

Natural biofilms composed of cyanobacteria, diatoms (eukaryotic algae) and heterotrophic bacteria have been reported to actively attack quartz and glass (Brehm et al. 2005). The analysis of a quartz crystal from a mountain in South America revealed that the associated biofilms can shift the localised pH from 3.4 (pH of the water at the site) to over 9 (which is required for solubilising quartz). The biofilm covered quartz was perforated to over 4 mm depth. The resident microbial community was estimated to have been solubilising the quartz for over 10 years (Brehm et al. 2005).

A consortium of diatoms and heterotrophic bacteria covered in abundant extracellular polymeric substances created depressions or pitted zones in window glass in a 9 months study (Brehm et al. 2005). Brehm et al. (2005) suggested that bacterial leaching provided silicon ions for diatoms, whereas the diatoms produced polysaccharides utilised by the bacteria. Quartz often contains iron as an impurity (Štyriaková et al. 2003). Štyriaková et al. (2003) studied the biodestruction and deferrisation of quartz sands by *Bacillus* spp. The bioleaching experiments showed that *Bacillus* spp. can solubilise iron, silica, and aluminium from quartz sands and reduce the iron oxyhydroxide concentrations present as impurities.

Table 8.1 Alkalinity generating microbially catalysed bioprocesses (Kaksonen et al. 2014)

Process	Reaction	Comments	Reference(s)
Photosynthesis	$H_2O + CO_2 + hv \rightarrow O_2 + CH_2O$	Requires light	Robb and Robinson (1995), Van Hille et al. (1999), Johnson (2000), and Brehm et al. (2005)
Ammonification	$\text{Organic} - N \rightarrow NH_3$	Requires organic N	Kalin et al. (1991), Johnson (1995, 2000), and White et al. (1997)
Urea hydrolysis	$CO(NH_2)_2 + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}$	Requires aerobic conditions and urea	Fujita et al. (2000)
Methanogenesis	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	Requires anaerobic conditions and an electron donor	Kalin et al. (1991), Johnson (1995), 2000), and White et al. (1997)
Sulfate reduction	$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$	Requires anaerobic conditions, sulfate and an electron donor	Kalin et al. (1991), Johnson (1995, 2000), and White et al. (1997)
Denitrification	$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^-$	Requires anoxic conditions, nitrate or nitrite and an electron donor	Kalin et al. (1991) and Johnson (1995)
Ferric iron reduction with organic electron donors	$4\ Fe(OH)_3 + CH_2O \rightarrow 4\ Fe^{2+} + H_2CO_3 + 2\ H_2O + 8\ OH^-$	Requires anaerobic conditions, Fe^{3+} compounds and an electron donor	Kalin et al. (1991), Johnson (1995, 2000), and White et al. (1997)

8.7 Biosolubilisation of Metallic Iron and Steel

In addition to various minerals, microorganisms can also biosolubilise elemental iron (Fe^0) and steel, thus contributing to microbially influenced corrosion of man-made structures. Various mechanisms have been proposed for biosolubilisation of metallic iron and steel, the major mechanisms are summarized in Fig. 8.4.

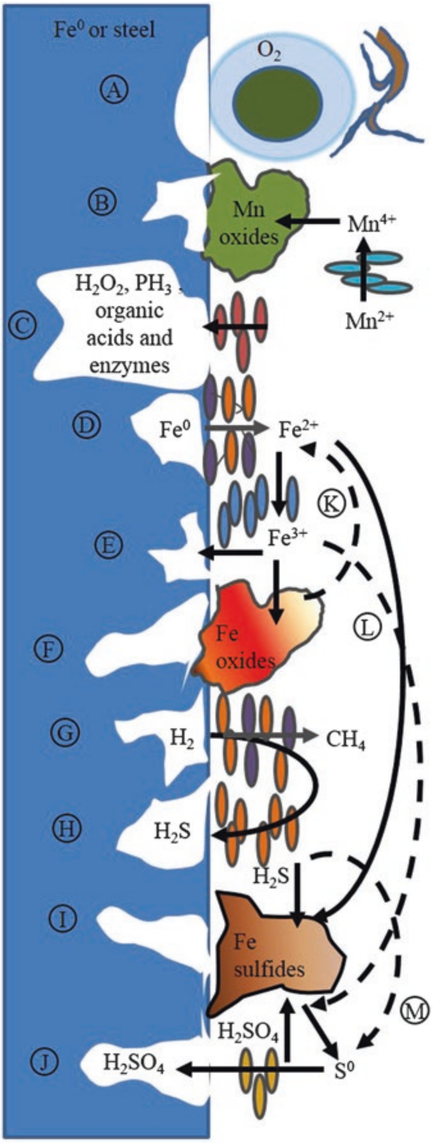
8.7.1 Differential Aeration Cells

The formation of differential aeration cells over short distances has been proposed as one of the mechanisms causing metal solubilisation (Ferguson and Nicholas 1992). Differential aeration cells may result from biogenic generation of oxygen by photosynthetic cyanobacteria, diatoms, and plant roots, or alternatively the oxygen consumption by respiring microorganisms (Little et al. 1991; Stewart and Franklin 2008) and limited diffusion of oxygen in biofilms (Little et al. 1991) and biogenic mineral deposits (Gu 2009; Usher et al. 2014). The steel surface becomes cathodic and the regions under the biofilms and deposits act as anodes, facilitating electron flow towards the cathode and causing corrosion (Gu 2009; Usher et al. 2014).

However, the activity of photosynthetic microorganisms is limited by light penetration. Cyanobacteria are able to photosynthesise even when the light level is only 1 % of surface sunlight (Furnas and Crosbie 1999; Usher et al. 2014). Soils commonly harbour diatoms (Van de Vijver and Beyens 1999) which are usually photosynthetic, although some are able to be active at a very low light intensity or in the dark (Furnas and Crosbie 1999; Landoulsi et al. 2011). Oxygen is released by the roots of some plants into the rhizosphere, increasing the redox potential by 750 mV at the surface of the root (Stottmeister et al. 2003). Oxygen release is affected by factors such as initial redox potential, pH, and the type, size, and growth stage of the plants (Sorrell et al. 1994; Stottmeister et al. 2003). Organic matter generated through photosynthesis can be utilised by various heterotrophic microorganisms which consume oxygen for aerobic respiration (Das et al. 2009; Usher et al. 2014).

8.7.2 Attack of Metal Surfaces by Microbial Oxidants

Hydrogen peroxide is a strong microbially produced oxidant which can enhance metal corrosion (Landoulsi et al. 2011). It is secreted by photosynthetic diatoms and a number of aerobic microorganisms, many of which grow in soil (Landoulsi et al. 2011; Li et al. 2012). Soil compounds can stabilise hydrogen peroxide enabling it to be transported from the illuminated soil surface to the deeper layers, while remaining reactive (Watts et al. 2007).



(A) Differential aeration cells created by oxygen generated by diatoms, cyanobacteria, and plant roots

(B) Precipitation of biologically generated Mn^{4+} as manganese oxides, which oxidise metal

(C) Attack by H_2O_2, PH_3, organic acids and enzymes generated by microorganisms

(D) Direct extraction of electrons and Fe^{2+} release from steel by anaerobic methanogens and sulfate-reducing microorganisms. Connecting lines indicate nanowires

(E) Attack by Fe^{3+} oxidant generated by aerobic Fe^{2+}-oxidising microorganisms

(F) Precipitation of biologically generated Fe^{3+} as iron oxides, which form a mat forming galvanic cells and differential aeration cells

(G) Cathodic depolarisation due to consumption of H_2 by anaerobic microorganisms, such as sulfate-reducers and methanogens

(H) Attack by H_2S generated by sulfate-reducers

(I) Precipitation of Fe sulfides with biogenic H_2S, creating differential aeration cells and galvanic cells

(J) Attack of Fe^0 steel and sulfides by sulfuric acid generated by sulfur-oxidising microorganisms

(K) Biological reduction of Fe^{3+} oxides generating Fe^{2+}

(L) Oxidation of sulfides with biogenic Fe^{3+} generating S^0

(M) Biological oxidation of H_2S to S^0

Fig. 8.4 Simplified schematic of mechanisms by which microorganisms facilitate solubilisation of Fe^0 and steel (Adapted from Usher et al. 2014). See the legend for each of the processes A-M

Iron-oxidising microorganisms oxidise Fe^{2+} to Fe^{3+} (Reaction 8.1), which can act as an oxidant in redox reactions. Additionally, biologically generated Fe^{3+} can together with Cl^- form a very corrosive solution (Videla and Herrera 2004; Javaherdashti 2008) which may be concentrated underneath corrosion products (Tatnall 1981). Ferric chloride ($FeCl_3$) can hydrolyse in water generating H^+, Cl^- and $Fe(OH)_3$ and forming an acidic and corrosive solution (Usher et al. 2014).

Iron-oxidising microorganisms usually oxidise Fe^{2+}, although Xu et al. (2013) have recently reported that nitrate-reducers catalyse Fe^0 oxidation (Xu et al. 2013). Neutrophilic iron oxidisers such as *Gallionella* and *Leptothrix* often live in zones where anoxic and oxic conditions transition (Emerson and Revsbech 1994; Weber et al. 2006; Usher et al. 2014) allowing them to compete with abiotic Fe^{2+} oxidation, which is rapid at circumneutral pH (Emerson et al. 2010). At high concentrations of soluble iron, the cells of the neutrophilic iron oxidisers usually become coated with iron precipitates, leading to the formation of mats rich in iron oxides (Emerson and Revsbech 1994; Emerson et al. 2010; Usher et al. 2014).

Although most iron oxidisers use oxygen as terminal electron acceptor, some can also utilise Mn^{4+} or NO_3^- in anoxic conditions (Chaudhuri et al. 2001; Weber et al. 2001, 2006; Miot et al. 2009; Usher et al. 2014). In addition, electrons can be carried by redox couples from anoxic areas to regions which are aerated and where oxygen is the final electron acceptor (Brown et al. 1994; Hamilton 2003; Usher et al. 2014). Electrons can also be transferred between species by electron shuttles, such as cysteine, formate, hydrogen, and possibly sulfur compounds (Stams et al. 2006).

Contrary to Fe^{2+} oxidation, abiotic Mn^{2+} oxidation does not occur at neutral pH values, which enables microorganisms to oxidise Mn^{2+} to Mn^{4+} in aerobic conditions (Usher et al. 2014). Manganese oxidisers are found in a number of microbial groups, including fungi and Gram-positive bacteria as well as *Alfa*-, *Beta*-, and *Gammaproteobacteria* (Hamilton 2003; Miyata et al. 2006; Usher et al. 2014). Additionally, several iron oxidisers are also able to oxidise Mn^{2+} (Usher et al. 2014). The electron acceptor is oxygen (O_2) or hydrogen peroxide (H_2O_2) and the Mn^{4+} precipitates quickly as MnO_2 (Hamilton 2003). Manganese oxides, which are among the strongest natural oxidants (Landoulsi et al. 2008), accept electrons (Huang et al. 2008) and participate in many interfacial and redox reactions (Hamilton 2003; Usher et al. 2014). Electrons released during metal dissolution reduce MnO_2 to Mn^{2+} (Gu et al. 2009). The presence of MnO_2 enhances corrosion by oxidising ferrous oxides, thus creating differential aeration cells (Dickinson and Lewandowski 1996; Usher et al. 2014).

8.7.3 Acid Attack

Acid attack causes corrosion (Gu et al. 2009) and decreasing pH has been reported to increase Fe^0 leaching (Barker et al. 1998; Usher et al. 2014). Microorganisms can generate various inorganic and organic acids that cause localised corrosion (Campaignolle and Crolet 1997; Rajasekar et al. 2010). Barker et al. (1998) noted bacterial colonies which grow in mineral cracks can locally decrease the solution pH from 7 to 3–4. Biofilm growing on corroding metal in a marine environment had pH values <3 (Barker et al. 1998). Carbonic acid generated from carbon dioxide released during organic matter degradation or respiration can acidify inner regions of biofilms even in aerobic environments when oxygen diffusion through the biofilm is limited (Suflita et al. 2008). Sulfur-oxidising microorganisms generate sulfuric acid (H_2SO_4) (Reaction 8.2) and H_2S-oxidising microorganisms convert biologically generated H_2S to S^0 (Sahinkaya et al. 2011). Microorganisms also produce various organic acids, such as citric, isocitric, coumaric, hydroxybenzoic, oxalic, and succinic acids, which can enhance metal solubilisation (Francis 1998). Microbially generated hydrogen ions (H^+), fulvic and humic acids also cause localised acidification (Gadd 2010). Mineral dissolution rates can be two to four times higher due to organic acids than by rainwater (Kurek 2002). However, except for the impact of acidity, the way in which various metabolites affect steel corrosion rates are not fully understood. In addition to bacteria, fungi also contribute to the acidification of soils (Gadd 2010). Fungi excrete siderophores as well as citric and oxalic acids, which act as chelators (Leake et al. 2004).

8.7.4 Attack by Sulfides

Dissimilatory sulfate reduction by sulfate-reducing microorganisms generates H_2S, which is excreted from the cells into the environment (Lee et al. 1995; de Romero et al. 2005). H_2S readily oxidises Fe^0 to generate FeS, according to Reaction 8.25 (Dinh et al. 2004; Sun and Nesic 2007; Enning and Garrelfs 2014):

$$H_2S + Fe^0 \rightarrow FeS + H_2 \tag{8.25}$$

The H_2 generated from H_2S causes penetration of steel by hydrogen and embrittlement, i.e. cracking corrosion (Biezma 2001; Koh et al. 2004).

Biogenic H_2S also contributes to the formation of iron sulfides, such as greigite (Fe_3S_4), pyrite (FeS_2), and pyrrhotite ($Fe_{(1-x)}S(x = 0 \text{ to } 0.2)$) (Lee et al. 1995; Enning and Garrelfs 2014). Protective FeS films can theoretically decrease corrosion (Sun and Nesic 2007); however, their impacts remain controversial (Gu 2012). Sulfide films are not effective in preventing corrosion (Little et al. 2000; Xu et al. 2011) because of the cracking caused by the growing film and the porous films that are formed (Sun and Nesic 2007; AlAbbas et al. 2013). Sulfate-reducers facilitate the transformation of FeS to Fe_3S_4 or FeS_2, which easily flakes of the surface, thus increasing the corrosion rate (Bourdoiseau et al. 2011).

8.7.5 Biosolubilisation by Other Microbial Metabolites

Microorganisms can generate and excrete a variety of metabolites that can enhance the solubilisation of iron and steel. Examples of such metabolites include ammonia (NH_3), phosphine (PH_3), and enzymes that can attack metals (Beech and Gaylarde

1999; Usher et al. 2014). Various microbes, such as sulfate-reducers and many soil bacteria, can reduce phosphate (PO_4^{3-}) to PH_3, which causes aggressive chemical corrosion (King and Miller 1971; Glindemann et al. 1998; Roels and Verstraete 2001).

Microorganisms excrete enzymes, such as catalases, esterases, hydrogenases, lyases, oxidoreductases, and phosphatases (Beech and Gaylarde 1999; Little et al. 2000; Busalmen et al. 2002; Beech and Sunner 2007; Usher et al. 2014). Some enzymes may facilitate oxygen reduction, catalyse cathodic reactions and thus increase corrosion, but the impacts are not fully understood (Beech et al. 2002, 2005). Hydrogenases, which have Fe-active sites, catalyse H^+ reduction and/or H_2 oxidation and may enhance corrosion by facilitating the transfer of electrons from steel (Da Silva et al. 2002; Gu 2012) or by removing hydrogen causing cathodic depolarisation (Beech and Coutinho 2003). However, the second process has been recently discredited (Usher et al. 2014). Extracellular polymeric substances have been reported to significantly increase solubilisation of minerals (Barker et al. 1998). Figure 8.5 shows a cryo-scanning electron microscopic image of cells and extracellular polymeric substances present on mild steel washers.

Some electrically active proteins promote the reduction of oxygen in biofilms, increasing corrosion (Busalmen et al. 2002; Landoulsi et al. 2008; Erable et al. 2010). Cell wall cytochromes (proteins) of many bacteria facilitate the use of metal ions or oxides as electron donors or acceptors for energy generation (Gu 2012). For example, ferric iron can be used as electron acceptor by some sulfate-reducers (Park et al. 2011) which impact corrosion rates (Burkhardt et al. 2011).

8.7.6 Galvanic Cells

The generation of metal rich phases in biofilms near metal surfaces may form a galvanic cell between the biofilm and the metal surface (Konhauser 2007) moving the corrosion potential to negative or positive direction (Little et al. 1998) and

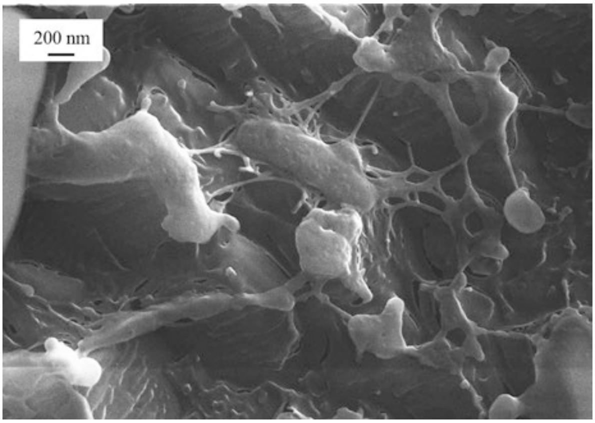


Fig. 8.5 Cryo-scanning electron microscopic image of extracellular polymeric substances and microorganisms growing on mild steel washers (Photo: Kayley Usher; Copyright: CSIRO)

increasing corrosion (Lee and Characklis 1993; McLean et al. 2002; Javaherdashti 2008). The metal-rich phases can be formed through the sorption of metals to cells and extracellular polymeric substances (Barkay and Schaefer 2001; Usher et al. 2014) and bioprecipitation of metals as sulfides or oxides (Beveridge et al. 1983; McLean et al. 2002). Iron- and manganese-oxidising bacteria can form stalks and sheaths with encrusted oxides of iron and manganese (Ghiorse 1984).

Sulfate-reducing microorganisms generate H_2S in the dissimilatory reduction of sulfate, while the biogenic H_2S precipitates metals (M^{2+}) as metal sulfides (MS) (Reactions 8.26 and 8.27):

$$SO_4^{2-} + 2\,CH_2O \rightarrow H_2S + 2\,HCO_3^- \tag{8.26}$$

$$H_2S + M^{2+} \rightarrow MS + 2\,H^+ \tag{8.27}$$

The activity of sulfate-reducers is required to maintain the electrochemical activity of iron sulfides (Li et al. 2001). The sulfate-reducers affect the conductivity, structure, and composition of corrosion products (AlAbbas et al. 2013). Sulfate-reducing microorganisms may reduce sulfate with electrons derived from iron sulfides, thus maintaining electron flow from steel (King and Miller 1971; Jack et al. 1996; Vuković et al. 2009; Usher et al. 2014). The mechanisms are not fully understood and corrosion may be facilitated by the dissociation of H_2S, the formation of hydrogen, or the direct transfer of electrons (Jack 2002). Anaerobic microorganisms can generate magnetite (Fe_3O_4) (Konhauser 1997), which is semi-conductive and may act as an electron acceptor (Zegeye et al. 2007), forming galvanic couples on steel and resulting in galvanic corrosion (Chan 2011).

8.7.7 Cathodic Depolarisation

Researchers have proposed that some sulfate-reducers utilise cathodic H_2 (generated in chemical iron oxidation) as an electron donor, resulting in cathodic depolarisation and increasing corrosion rates at the anode (Lappin Scott and Costerton 1989; Lee et al. 1995; Little et al. 2000; Park et al. 2011; Venzlaff et al. 2013; Enning and Garrelfs 2014). Methanogens may also increase corrosion by using cathodic H_2 (Daniels et al. 1987; Boopathy and Daniels 1991). However, the importance of cathodic depolarisation due to H_2 consumption remains controversial (Dinh et al. 2004; de Romero et al. 2005; Uchiyama et al. 2010). Recent studies have reported that the significant corrosion caused by some sulfate-reducers cannot be explained by biological H_2 consumption and cathodic depolarisation (Dinh et al. 2004; de Romero et al. 2005; Uchiyama et al. 2010; Enning et al. 2012; Venzlaff et al. 2013), although some studies still occasionally site the hypothesis (Usher et al. 2014).

8.7.8 Direct Microbial Extraction of Electrons from Steel

Some sulfate-reducers and methanogens are able to oxidise Fe^0 to Fe^{2+} and use Fe^0 as sole electron and energy source (Daniels et al. 1987; Dinh et al. 2004; Uchiyama et al. 2010; Enning et al. 2012; Venzlaff et al. 2013; Usher et al. 2014). Some microorganisms can cause significant steel corrosion and increase iron solubilisation by nearly ten times (Uchiyama et al. 2010). This is often called as electrical microbially influenced corrosion (Enning et al. 2012; Usher et al. 2014) and is likely a widespread microbial ability in phylogenetically diverse microbial groups in various environments (Uchiyama et al. 2010; Enning and Garrelfs 2014).

It is not well understood how various microbial species extract electrons from solid materials (Rosenbaum et al. 2011; Bose et al. 2014). The extraction of electrons may be facilitated by redox proteins located in the outer membrane (Dinh et al. 2004). Uchiyama et al. (2010) suggested a hydrogenase enzyme secreted by *Methanococcus maripaludis* to catalyse Fe^0 oxidation, while Venzlaff et al. (2013) proposed that the cathodic reaction may be driven by the extraction of electrons by electrical microbially influenced corrosion microorganisms.

In earlier studies, the growth of microorganisms with Fe^0 as sole electron donor was assumed to be facilitated by the indirect electron consumption through the utilisation of the H_2 generated during corrosion rather than direct electron utilisation (Daniels et al. 1987; Belay and Daniels 1990; Usher et al. 2014). Figure 8.6a shows corroded low carbon steel coupons in anaerobic tubes with a microbial community growing on minimal medium. The steel coupon is the only electron source and the scanning electron microscopic image in Fig. 8.6b shows the community making holes in the corrosion products. Raman spectroscopy and X-ray diffraction analysis showed that siderite and magnetite were produced by the anaerobic microbial oxidation of steel (Usher et al. 2015). The direct electron consumption would require microbial attachment to the steel surface or to conductive corrosion products (Enning et al. 2012; Usher et al. 2014). Electrons may also be transferred through nanowires, i.e. nano-scale protein-containing electrically conductive filaments, from steel to microbial cells (Erable et al. 2010; Malvankar et al. 2011; Gu 2012; Lovley 2012). Microbial cells can transfer electrons via nanowires to suitable electron acceptors such as iron oxides, which may be even 1 cm distance away from the cell (Malvankar et al. 2011). Nanowires may be used for energy extraction and distribution by a variety of microbes and they may facilitate electron transfer between various taxonomic groups (Gorby et al. 2006; Lovley 2012). For example, species of the bacterial genus *Geobacter* have been shown to donate electrons via nanowires to species of the archaeal genus *Methanosaeta* (Rotaru et al. 2014). However, not all microbial filaments can conduct electrons (Lovley 2012; Vargas et al. 2013; Usher et al. 2014). More research is required to understand the potential role of nanowires in metal solubilisation.

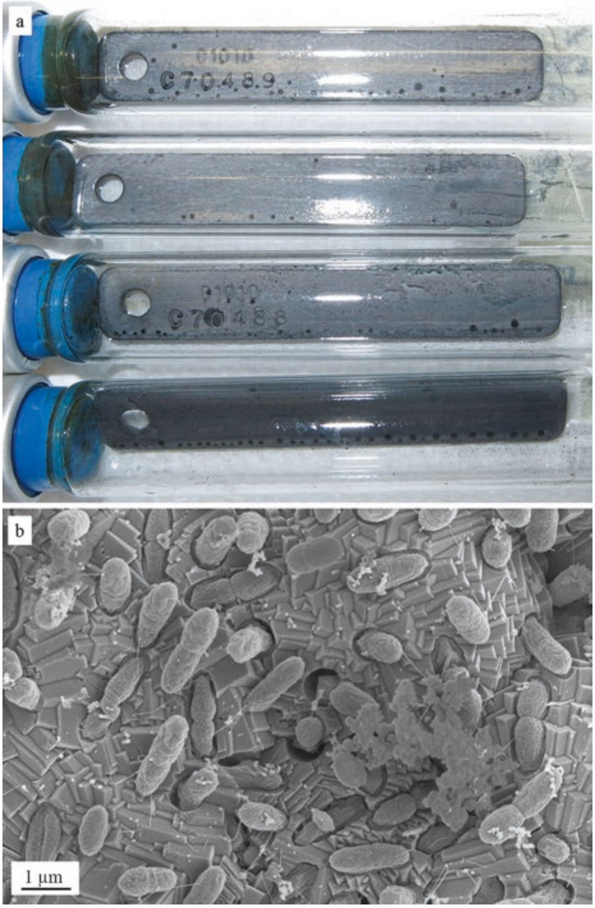


Fig. 8.6 (**a**) Biocorroded low carbon steel coupons in anaerobic tubes with a microbial community cultured on minimal medium with steel coupons as the sole electron donor and (**b**) a scanning electron microscopic image of the community making holes in the corrosion products. The community was composed of sulfate-reducing bacteria, sulfur reducing bacteria, and acetogens likely growing in a syntrophic relationship (Usher et al. 2015) (Photos: Kayley Usher; Copyright: CSIRO)

8.8 Environmental Impacts

8.8.1 *Acid Mine Drainage*

As a consequence of mining activities, reduced sulfide minerals are exposed to oxygen and water resulting in the oxidation and biosolubilisation of the minerals (Christensen et al. 1996; Banks et al. 1997). This leads to the generation of acidic sulfate- and metal-containing waters, i.e. acid mine drainage or acid rock drainage. Under favourable conditions, the formation of acid mine drainage can continue hundreds of years after the ceasing of mining activities (Béchard et al. 1994; Szczepanska and Twardowska 1999). The quality of the mine waters may vary depending on the local conditions and over time (Clarke 1995). Examples of the chemical characteristics of waters at Finnish mine sites are presented in Table 8.2. Acidic metal-containing wastewaters are not only formed in mine shafts, heaps, and tailings, but also at metallurgical mills processing sulfide minerals.

Table 8.2 Examples of the chemical characteristics of waters at Finnish mine sites (Kaksonen 2004). All units (except for pH) are in mg L^{-1}

	Surface waters					Ground water
	Paroistenjärvi mine	Hitura mine	Ruostesuo mine	Kangasjärvi mine	Otravaara mine	Hitura mine
pH	3.1–5.8	6.3–6.6	3.0	3.7	2.2–2.3	5.4–8.3
SO_4^{2-}	168–872	1,400–3,680	4,885	900	6,260–9,440	3,900–17,250
Cl	1–6.7	450–840	NR	NR	NR	23–1,760
Fe	0.5–74	0.02–0.11	233	20	2,130–2,650	0.02–4.6
Al	NR	0.01	NR	NR	267–395	0.01
As	0.01–0.39	NR	NR	NR	NR	NR
Cd	NR	0.09	NR	NR	NR	0.0002–0.0003
Co	NR	0.15–0.29	NR	NR	0.99–1.16	0.03–2610
Cu	0.5–20	0.01–0.02	2	2.5	2.8–3.3	0.01–0.21
Mn	0.3–7.6	0.78–2.67	55	6	8.5–14	1.7–5.4
Ni	NR	1.57–1.88	NR	NR	1.3–1.6	0.02–2860
Zn	0.1–3.2	0.1–0.38	557	45	9.2–10.7	0.05–760
References	Carlson et al. (2002)	Heikkinen et al. (2002)	Mustikkamäki (2000)	Mustikkamäki (2000)	Räisänen et al. (2001)	Heikkinen et al. (2002)

NR: not reported

In the presence of bicarbonate or mineral alkalinity, pyrite oxidation may not cause significant acidification (Banks et al. 1997). However, these alkalinity sources are not always present in significant quantities (Banks et al. 1997). The acidity of the mine waters results from both proton and mineral acidity (soluble metals) (Clarke 1995). The most significant metals for causing mineral acidity are Fe, Al, and to some extent Mn. The acidity of metals is due to their hydrolysis (Reactions 8.28, 8.29, and 8.30), which in the case of Fe^{2+} and Mn^{2+} is preceded by oxidation (Johnson 2000):

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{8.28}$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{8.29}$$

$$Mn^{4+} + 2H_2O \rightarrow MnOOH + 3H^+ \tag{8.30}$$

In addition to metal mining, acid mine drainage formation may also occur in coal mines (Fig. 8.7a, b). Coal contains organic sulfur (mostly sulfides, thiophenes, sulfones, and sulfoxides) and inorganic sulfur (mostly sulfate and pyrite). The sulfur-content of coal is usually 1–10 % (Johnson 2000).

Acid mine drainage has caused severe environmental impacts in a number of countries. In the UK alone, over 700 km of rivers and streams have been reported to be affected by mine waters (Jarvis and Younger 2000). Rio Tinto River (Red River) (Fig. 8.7c) in Spain near the Rio Tinto mine was named after the red colour of the water imparted by the high Fe^{3+} concentration of up to approximately 10 g L^{-1} (Cánovas et al. 2014) present in the acid mine drainage impacted river (Rawlings 2002). This acid mine drainage from the mines along the river has existed for at least 2000 years and continues to persist (LPSDP 2007).

The major acid mine drainage impacted areas are lakes, rivers, coastal waters and estuaries (Gray 1997), although mine waters can also contaminate groundwater resources (Barnes et al. 1991a, b) and arable land (Clemente et al. 2003) as well as damage man-made constructions (Jarvis and Younger 2000). Mine pit lakes are permanent legacies with often poor water quality and overflow due to gradual groundwater rebound or rainstorm events negatively impacting down-gradient surface waters and groundwater (Davis and Ashenberg 1989; Castro and Moore 2000; Blodau 2006; Geller et al. 2012).

Acid mine drainage can have various chemical, physical, biological, ecological, and socioeconomic impacts on the affected environments (Table 8.3) (Gray 1997; Jarvis and Younger 2000). Acid mine drainage affects aquatic ecosystems through various direct and indirect mechanisms (Gray 1997). The acidity of the wastewaters can cause direct toxic effects (e.g. harm fish gills) or have an indirect influence by increasing the solubility of toxic metals (Johnson 2000). Iron-rich precipitates hamper fish spawning (Clarke 1995) and smother river sediments, impeding oxygen diffusion and killing benthic organisms (Robb 1994; Johnson 2000). The precipitation of iron can also increase the turbidity of the receiving stream and reduce light penetration, thus impacting primary production (Robb 1994; Johnson 2000). This may have a

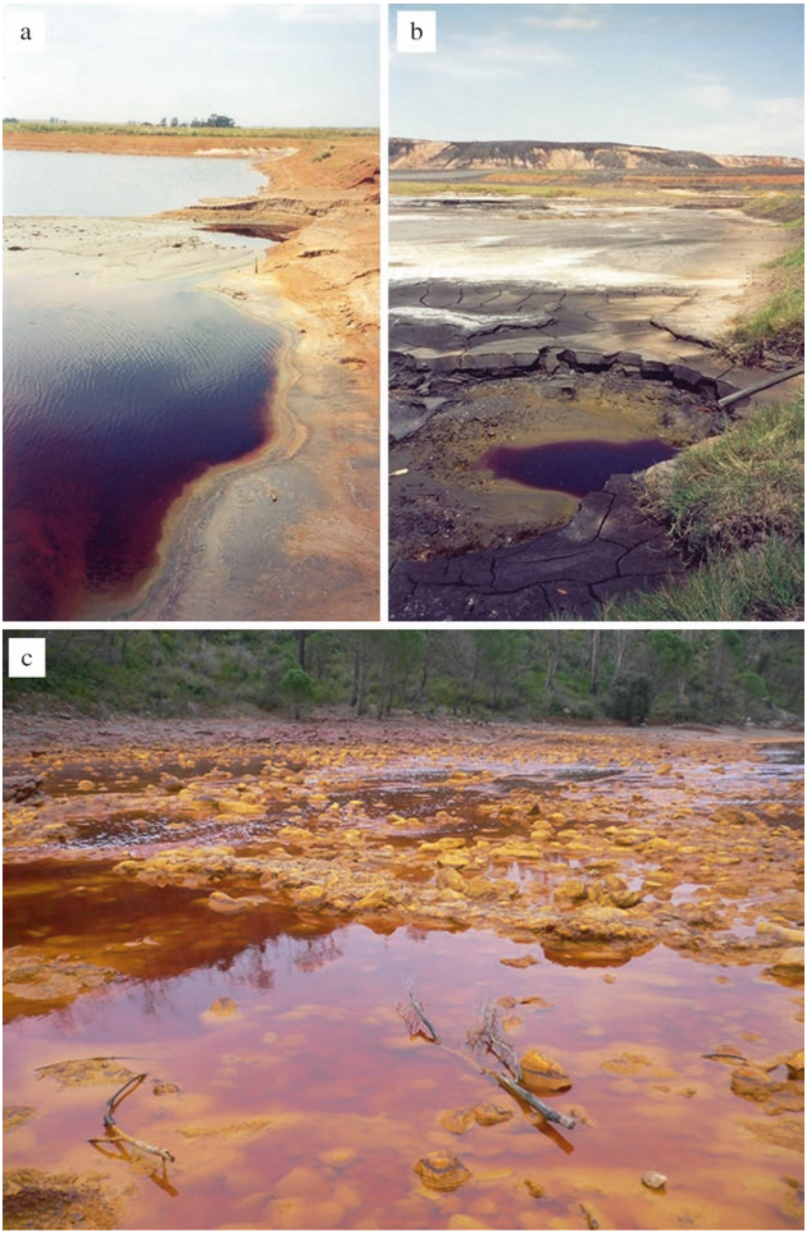


Fig. 8.7 (**a**–**b**) Acid mine drainage waters at a South African coal mine and (**c**) Rio Tinto river coloured red by acid mine drainage in Spain (Photos and copyright: Anna Kaksonen)

Table 8.3 Major effects of acid mine drainage (Kaksonen 2004; Gray 1997; Jarvis and Younger 2000)

Physical	Chemical	Biological	Ecological	Socioeconomic
Increased turbidity	Salinisation	Acute and chronic toxicity	Reduction in primary productivity	Flooding
Sedimentation	Increased acidity	Acid-base balance failure in organisms	Niche loss	Subsidence
Decrease in light penetration	Destruction of bicarbonate buffering	Osmoregulation	Habitat modification	Corrosion
Adsorption of metals into sediments and organisms	Increase in soluble and particulate metal concentrations	Death of sensitive species	Loss of food source or prey	Aesthetic loss
		Respiratory	Food chain modification	Decrease of drinking, agricultural, industrial and recreational water quality
		Reproduction	Bioaccumulation in the food chain	Decrease in catch of fish
		Behavioural		Health effects
		Migration or avoidance		

dramatic effect on the food chain in contaminated waters (Johnson 2000). Acid mine drainage impacted water courses tend to be devoid of fish and have lower biodiversity in planktonic and benthic organisms than non-polluted waters (Johnson 2000). Also, the microbial community structure and function in acid mine drainage impacted waters are very different from those of non-polluted waters (Mills and Mallory 1987).

Rising underground mine waters in deep mines may cause flooding, corrosion, and subsidence of foundations following mine closure (Jarvis and Younger 2000). Acidic waters are also corrosive to bridges, dams, and plumbing (Dugan 1975) and severe mine water discharges may pollute potable water supplies (Jarvis and Younger 2000). In addition, orange iron precipitates can decrease the aesthetic value of water bodies (Jarvis and Younger 2000). Due to increased toxicity and hardness, the recipient waters of the acid mine drainage discharge may be unusable for agriculture and industry as well as for recreational purposes (Dugan 1975; Clarke 1995). For example, fish farming was ceased in the Finnish Kangasjärvi-lake due to the acidic, Zn-containing waters flowing from the nearby Kangasjärvi open pit mine in Keitele, Finland (Mustikkamäki 2000). Near another Finnish mine in the village of Antskog, the pollution from historical Fe and Cu works resulted in a crop failure when sediment material dredged downstream of the metal works was spread out on a nearby farmland (Åström and Nylund 2000). The concentrations of Cu, Pb, and Zn in the dredged sediment were over five times higher than in other contaminated soils in Finland (Åström and Nylund 2000). High chloride concentrations, which are often associated with chloride-containing minerals, are also harmful to crops and cause corrosion of metal devices (Clarke 1995).

The most drastic environmental effects of wastewaters originating from mining and metallurgy have been caused by sudden accidents, such as the catastrophic spill of approximately 50,000 m^3 of acid mine drainage from the former Wheal Jane tin mine (Cornwall, UK) in 1992 (Banks et al. 1997). The acid mine drainage was released into the Carnon River resulting in an iron-hydroxide deposition in the Fal Estuary (Hallberg and Johnson 2003). Another major accident took place in 1998, when a dam wall enclosing acidic pyritic mine sludge was broken at Aznalcóllar (Seville, Spain). Approximately 5,000,000 m^3 of pyrite waste spread along the Guadiamar River and covered 45 km^2 of the nearby arable land (Clemente et al. 2003). Even though most of the waste and surface soil was removed, the soil in some areas was still toxic to plants due to high concentrations of heavy metal (Cd, Cu, and Zn). Additionally, the oxidation of the remaining sulfides to sulfuric acid led to further acidification of the soil (Clemente et al. 2003). Another accident occurred at the Baia Mare gold mine in Romania, where a wastewater dam was broken causing 100,000 m^3 of cyanide- and heavy metal-containing wastewater to flow into the Szamos River, a tributary river of the Danube in 2000 (Järvinen 2000; Hallberg and Johnson 2003). The toxic plume killed tons of fish and the harmful effects were seen as far as Hungary and former Yugoslavia (Järvinen 2000).

8.8.2 Acid Sulfate Soils

Acid sulfate soils are characterised as soils with iron sulfide rich horizons, the disturbance and oxidation of which causes the generation of acidity and the mobilisation of metals and contaminants to adjacent soils and sediments. The sulfide minerals are predominately in the form of pyrite (FeS_2, cubic crystal structure) and less commonly, marcasite (FeS_2, orthorhombic crystal structure) and iron monosulfide (FeS) (Ward et al. 2004; Powell and Martens 2005; Fitzpatrick et al. 2009; Wu et al. 2013).

The formation of pyritic minerals within acid sulfate soils results from biological sulfate reduction activity and requires the presence of organic carbon, high concentrations of sulfate and dissolved iron or iron minerals in a saturated, anoxic environment (i.e. waterlogged soils and sediments) (Van Breemen 1982; Van Breemen et al. 1983; King et al. 1985; Fitzpatrick et al. 2009). Sulfate reducers anaerobically oxidise organic carbon to bicarbonate and reduce sulfate to produce H_2S (Reaction 8.26). The biogenic H_2S subsequently reacts with iron to produce iron sulfides (Berner 1984; Smith and Melville 2004). The biogenic bicarbonate is removed by tidal turbulence or diffusion into overlaying water (Van Breemen et al. 1983). This leads to a permanent separation of the neutralising bicarbonate and acid phases of the soil, and decreases the capacity of the soil to neutralise acid following pyrite oxidation.

The amount of pyrite that can be formed by sulfate reducers largely depends on the amount of organic carbon available as an energy source and the availability of iron and dissolved sulfate within the soil (Fitzpatrick et al. 2009). Seawater comprises of an endless supply of sulfate. Hence, acid sulfate soils are most commonly associated with coastal and floodplain areas, but have also been identified in inland areas such as wetlands and permanently waterlogged ecosystems (Jones 2014; Virtanen et al. 2014) and even sandy soils with small amounts of pyrite but poor buffering capacity (Clohessy et al. 2013).

The pyritic minerals can accumulate over time and are generally benign whilst protected within the anoxic, waterlogged environment in which they were formed (Sammut et al. 1996; Ward et al. 2004). However, the iron sulfide minerals are oxidised when they become exposed to oxygen due to tidal activity, lowering of the groundwater table due to e.g. drought, clearing of native vegetation or subsurface excavation. Climate change is also expected to result in longer periods of drought, which will lower the groundwater table (Okkonen and Kløve 2010) and further facilitate the penetration of oxygen deeper into the subsoil, promoting the oxidation of iron sulfides at increasing depths in the soil profile.

The oxidation of iron sulfides is initiated by molecular oxygen until the pH of the soil falls below 4, at which time the activity of acidophilic iron- and sulfur-oxidising microorganisms, such as *At. thiooxidans* and *At. ferrooxidans*, is promoted (Van Breemen 1982; Sammut et al. 1996; Ward et al. 2004; Wu et al. 2013). These microorganisms significantly increase the sulfide mineral oxidation rate by the regeneration of ferric iron (Fe^{3+}), which acts as a stronger oxidant than molecular oxygen at low pH, and by the generation of sulfuric acid from oxidation of reduced sulfur compounds (Reactions 8.1 and 8.2).

Mineral sulfide oxidation results in the release of acidity, an increase in the mobility of metals and other contaminants from the surrounding sediments and the formation of ferric iron precipitates. The complete oxidation of one mole of pyrite generates two moles of sulfuric acid, which then reacts with soils and clays to release silica and metals including aluminium, iron, magnesium, potassium and sodium, as well as other trace heavy metals that are toxic in low levels to most gilled organisms and other aquatic life (Sammut et al. 1996; Fitzpatrick et al. 2009). In addition, the oxidation of ferrous iron consumes oxygen resulting in the deoxygenation of the water, and the resulting iron oxyhydroxide and hydroxide precipitates cover stream beds and sediments (Sammut et al. 1996). The acidic waters from acid sulfate soils can detrimentally affect water quality, the health of aquatic ecosystems, agriculture production, and human health (see e.g. Dent and Pons 1995; Roos and Åström 2006).

In Europe, the largest acid sulfate soil areas are located along the Baltic Sea coast (Andriesse and Van Mensvoort 2006). The formation of acidity in that area is expected to continue, in association with post-glacial isostatic land uplift occurring in the area (Johansson et al. 2004). Acid sulfate soils have also been identified in the United States, Thailand, Senegal, Gambia, Vietnam and a range of other coastal regions (Jones 2014). In Australia, acid sulfate soils occupy an estimated total land area of 215,000 km^2, with 58,000 km^2 identified along the coastline and 157,000 km^2 identified inland (Fitzpatrick et al. 2009). An example of the impact of inland acid sulfate soils in the Wheatbelt of Western Australia is shown in Fig. 8.8. In this inland acid sulfate soil area, the clearing of native vegetation has resulted in salinisation and rising of the acidic groundwater table which promoted the formation of sulfidic soils. To manage the rising saline groundwater, drainage ways were constructed to intersect the saline groundwater table and direct water to discharge lakes. However,

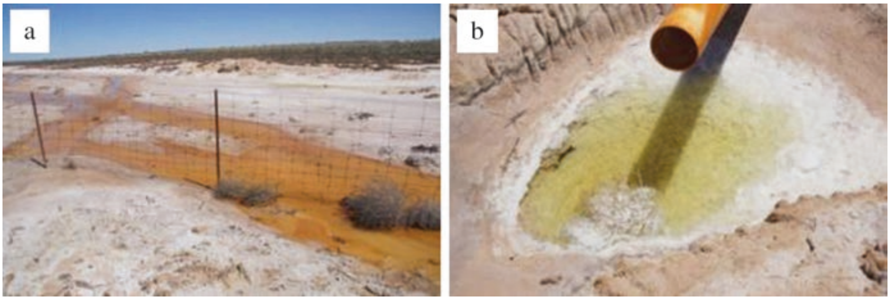


Fig. 8.8 The impact of disturbing acid sulfate soils in the Western Australian Wheatbelt has resulted in the generation of (**a**) acidic, metal containing and (**b**) saline waters. Clearing of native vegetation and rising of the acid groundwater table has promoted the formation of acid sulfate soils and an ongoing environmental impact in this area. The pH at both sites was below pH 2, which is a direct result of the generation of acidity by the oxidation of pyritic materials contained in the soil profile following exposure to the atmosphere. Similarly, the rust coloured sediments and water are a direct result of the oxidation of ferrous iron to ferric iron by iron-oxidising microorganisms. Salinisation of the sediment and water is also evident (Photos: Naomi Boxall and Michael Siebert; Copyright: CSIRO)

in recent years, further acidification of the drainage ways and discharge lakes has occurred due to the oxidation of pyritic minerals, causing mobility of metals and other contaminants (Shand and Degens 2008; Environment Protection and Heritage Council and the Natural Resource Management Ministerial Council 2011). Similar scenarios of inland acid sulfate soils are described for the Murray-Darling Basin (Victoria) and in South Australia. Ongoing management of these acid sulfate soil regions is required to minimise the impacts associated with acidification, deoxygenation, and corrosion (Environment Protection and Heritage Council and the Natural Resource Management Ministerial Council 2011).

8.8.3 Biocorrosion

Biocorrosion can cause severe damage of man-made structures, such as pipes, bridges, pumps and equipment. The consequences of pipe failure can include difficult and expensive repairs, loss of production, environmental contamination and suspension of critical services (Usher et al. 2014). Figure 8.9 shows a scanning electron microscopic image of microorganisms in rust lumps on low carbon steel in a marine environment and Fig. 8.10 shows scanning electron microscopic images of biofilms attached to low carbon steel that has been submersed in the ocean for 2 months. Biocorroded low carbon steel coupons that have been exposed to natural soil for 2 months are shown in Fig. 8.11 along with a scanning electron microscopic image of the microorganisms attached to a coupon. Biocorrosion can cause significant economic loss to industries and utilities worldwide. The estimated costs of metal corrosion across various industries in developed countries range between 2 % and 3 % of the gross domestic product (Koch et al. 2002; Kruger 2011; Enning and

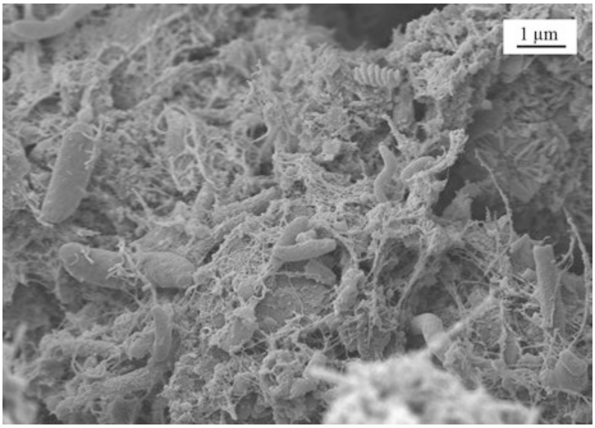


Fig. 8.9 Scanning electron microscopic image of microorganisms in rust lumps on low carbon steel in a marine environment (Photos: Kayley Usher; Copyright: CSIRO)

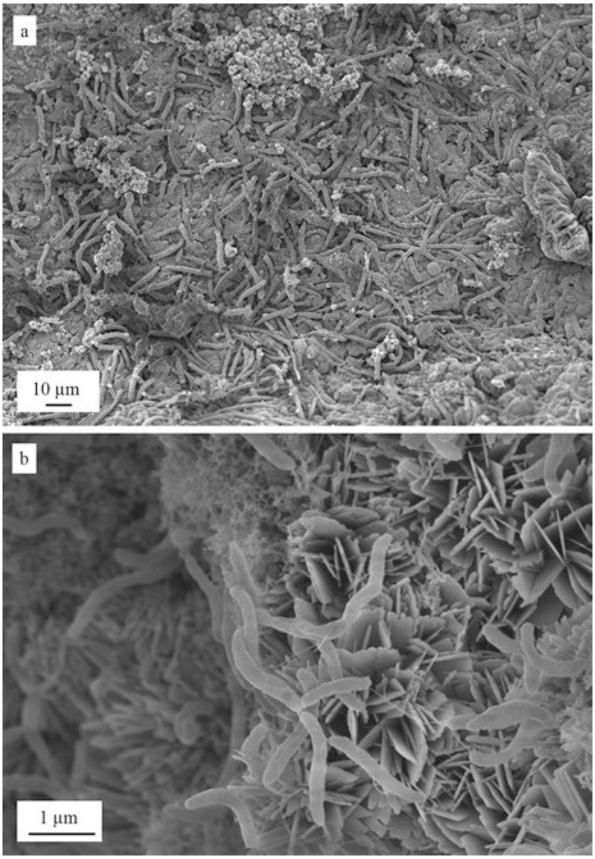


Fig. 8.10 Scanning electron microscopic images, (**a**) broader view and (**b**) close-up view of biofilms attached to low carbon steel that has been submersed in the ocean for 2 months (Photos: Kayley Usher; Copyright: CSIRO)

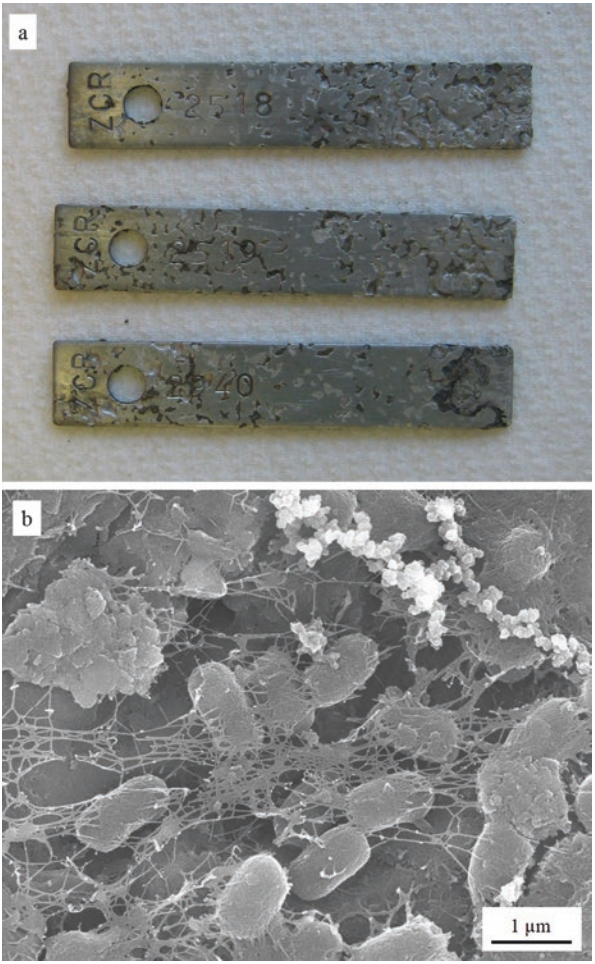


Fig. 8.11 (**a**) Corroded low carbon steel coupons exposed to natural soil for 2 months and (**b**) a scanning electron microscopic image of microorganisms attached to one of the coupons (Photos: Kayley Usher; Copyright: CSIRO)

Garrelfs 2014). The majority of the costs are caused by corrosion of iron which is used abundantly and is susceptible to oxidative damage. The estimates of the costs that can be attributed to biocorrosion vary (Enning and Garrelfs 2014). However, biocorrosion likely accounts for a large portion of the overall costs (Booth 1964; Flemming 1994, 1996; Beaver and Thompson 2006; Beech and Sunner 2007; Enning and Garrelfs 2014). Annual biocorrosion-related costs of replacement and repair of piping material used in various services in the USA in the 1950s were approximately \$0.5–2 billion (Beech and Gaylarde 1999). Annual costs for replacing biocorroded gas mains in the UK were £250 million (Beech and Gaylarde 1999). More recently the cost of corrosion to the global oil and gas industry has been estimated to exceed \$60 billion annually (Papavinasam 2014).

8.9 Industrial Applications: Utilisation of Biosolubilisation in Biohydrometallurgy

Copper was widely recovered from mine drainage waters in the Mediterranean basin as early as 1000 B.C. (Brierley 1982). Pre-Romans and Romans recovered silver and copper, respectively, from a deposit located in the Seville province in the south of Spain, which later became known as the Rio Tinto mine (Rawlings 2002). Large-scale leaching of copper was practiced at the Tharsis and Rio Tinto mines in Spain by the eighteenth century, but the miners were not aware of the microbiological involvement in the solubilisation of metals (for a review, see Brandl 2001). It was only approximately 70 years ago that it began to be understood that microorganisms are the principle causative agents for the leaching of metals from mines and ore deposits. The identification of *At. ferrooxidans* (which was formerly known as *Thiobacillus ferrooxidans*) in the 1940s (Colmer and Hinkle 1947; Kelly and Wood 2000) and its role in copper extraction led to the Kennecott Mining Company filing a patent titled "Cyclic leaching process employing iron-oxidising bacteria" (Zimmerley et al. 1958). The patent detailed copper recovery from low-grade copper ore in run-of-mine with blasted, but uncrushed rock dumps from the Bingham Canyon Mine near Salt Lake City, USA. In the 1970s, this was the largest dump leaching operation and approximately 200 tonnes of copper were recovered daily (Bosecker 1997), even though it was not designed to promote microbial activity (Olson et al. 2003).

Bioleaching can be a feasible process for low-grade ores which are too expensive to process using traditional methods and where smelters charge penalties due to hazardous emissions, e.g. ≥0.15 % arsenic in feed intake (du Plessis et al. 2007; Kaksonen et al. 2014). The relatively low capital and operational costs of bioleaching make it a good alternative for low-grade ores which contain <0.5 % of valuable metals (Bosecker 1997).

Bioleaching has been explored for recovering metals from a variety of sulfide ores, metallurgical wastes (Vestola et al. 2010; Kaksonen et al. 2011), electronic scrap (Brandl 2001; Vestola et al. 2010), municipal and industrial sludge from waste water treatment (Blais et al. 1992; Solisio et al. 2002), municipal solid waste incineration fly ash (Yang et al. 2009), and contaminated sites (Bosecker 1999). Large-scale bioleaching applications have been mainly used for copper (Watling 2006), but to some extent also for cobalt, nickel (Brandl 2001), zinc (Riekkola-vanhanen 2010), and uranium (Olson et al. 2003). In addition, biooxidation of refractory gold concentrates has been established as a commercial technology since 1986 (Morin 1995; Bosecker 1997). The share of bioleached copper has been estimated to be 15–20 % of the total global copper production (Brierley and Brierley 2013; Schippers et al. 2013). According to Schippers et al. (2013), at least 14 active gold biooxidation projects existed in 2013. These projects produced at least 84 t of gold and 161 t of silver in 2010. The share of biooxidised gold has been estimated to be approximately 3–5 % of the total global gold production (Brierley and Brierley 2013; Schippers et al. 2013). Large-scale bioleaching applications have mainly used oxidative bioleaching processes for sulfide-containing minerals. Reductive bioleaching has been explored at laboratory scale, but is yet to be implemented at industrial scale (Hallberg et al. 2011).

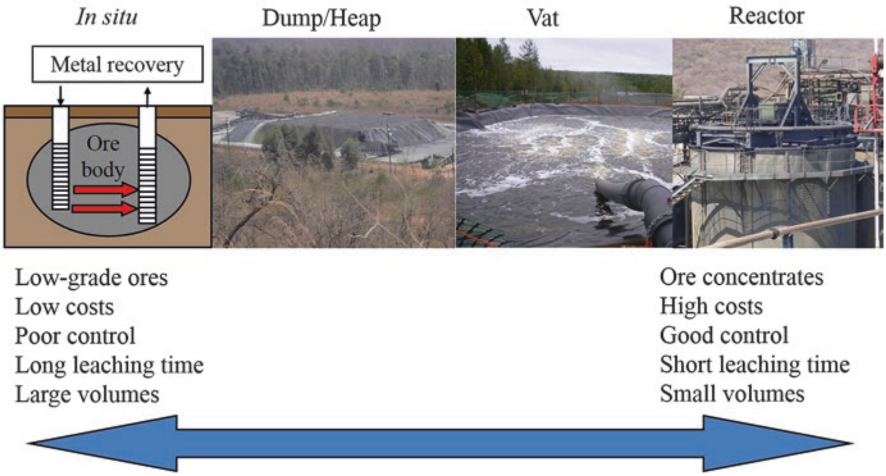


Fig. 8.12 Engineering approaches that can be used for biosolubilisation in biohydrometallurgical processes (Adapted from Kinnunen 2004; Kaksonen et al. 2014) (Photos and copyright: Anna Kaksonen)

The main engineering approaches used for leaching are reactor, vat, heap, dump, stope, in situ and in place leaching (Fig. 8.12). In reactor leaching, several aerated, mixed and often cooled bioreactors are operated in continuous mode in parallel or in series for processing of concentrates (for a review see Rawlings et al. 2003). In vat leaching, the ore is crushed and leached in a series of vats lined with acid-proof material and sometimes equipped with agitators (Cope 1999). In heap leaching, the ore is crushed, pre-conditioned with H_2SO_4 and piled on a water-impermeable leach pad. The heaps are aerated from the bottom; leach liquor is applied on top and allowed to percolate to the bottom of the heap where it is collected for the recovery of valuable metals (for a review see Rawlings et al. 2003). Dump leaching is similar to heap leaching, but the dumps are not aerated and the process is less controlled (Bosecker 1997). In stope leaching, a stope is sealed with concrete bulkheads and filled with broken ore. The stope is flooded with acidic liquor, immediately drained and allowed to rest. Flooding, draining and rest cycles are repeated until leaching has been completed (Chien et al. 1990). In the in situ leaching process, the ore remains in the underground ore body. The acidic liquor is injected into the ore body and pregnant leach solution is collected from production wells for the recovery of metals (Bosecker 1997). In place leaching is similar to in situ leaching, but the ore body is additionally fractured, e.g. by blasting, to enhance the permeability before the leaching (Wadden and Gallant 1985).

Reactor leaching is most commonly used for concentrates whereas heap, dump, stope and in situ leaching methods are more feasible for lower grade ores (Fig. 8.12) (for reviews see Bosecker 1997; Kinnunen 2004). In situ leaching is especially suitable for ore bodies that are not economic to mine by conventional underground or open-pit methods. In situ leaching does not generally require extensive mine infrastructure and the visual impact of the mining operation is likely to remain low.

However, in situ leaching requires relatively long leaching times and good reservoir permeability. Additionally, extensive knowledge is required of the hydrology and geology of the area and the leaching solutions need to be controlled carefully to prevent groundwater contamination (Kinnunen 2004; Nurmi 2009).

8.10 Conclusions

Microorganisms facilitate the solubilisation of various metals and other elements from reduced and oxidised minerals through various mechanisms such as oxidative and reductive dissolution and solubilisation through the production of biogenic acids, alkali or ligands, such as cyanide, thiosulfate, organic acids and iodide. Moreover, microorganisms can biosolubilise metallic iron and steel by creating differential aeration cells, galvanic cells, cathodic depolarisation, generating oxidants, acids, sulfides and other microbial metabolites or by directly extracting electrons from steel. Biosolubilisation has profound environmental and economic impacts due to the generation of acid mine drainage and acid sulfate soils and biocorrosion of various man-made structures. On the other hand, biosolubilisation is commercially utilised for large scale extraction of valuable metals from ores and concentrates. It holds potential for resource recovery from waste and clean-up of metal contaminated environments.

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