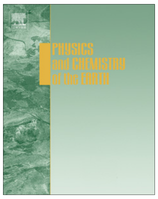
Physics and Chemistry of the Earth xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce



Implication of plants and microbial metalloproteins in the bioremediation of polluted waters: A review

E. Fosso-Kankeu [a,b,*], A.F. Mulaba-Bafubiandi [a]

[a] Minerals Processing and Technology Research Centre, Department of Extraction Metallurgy, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, South Africa
[b] School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Potchefstroom Campus, Potchefstroom, South Africa

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Bioremediation
Toxic heavy metals
Water pollution
Plants
Microorganisms
Metal-binding proteins

ABSTRACT

Traditional approaches to municipal water monitoring barely includes procedures for toxic heavy metals testing. However, the presence of such contaminants in water sources is expected in South African surface and ground waters as a result of dispersion of effluents from acid mine drainage sites. Cheap and eco-friendly methods using microorganisms and plants are discussed in this review. Metal uptake mechanisms involving special proteins namely metalloproteins or metal-binding proteins and peptides, are elaborated and supported with some examples. The potential of phytochelatins and metallothioneins as metal chelating ligands in plants and microorganisms are reviewed and suggestion made to engineer these peptides in microbial sorbents for improved metal uptake. This review covers a number of approaches in the bioremediation of metal polluted effluents and systematically explains the mechanisms involved in the bio-uptake of metals, while highlighting the contribution of metal-binding proteins.

1. Introduction

The release of heavy metals into the environment by industrial and artisanal activities is one of the major causes of pollution and destabilisation of the ecosystem. For a sustainable solution to this problem, there is a need to shift from the conventional ways to new approaches requiring biological resources, which are eco-friendly. Several works have been carried out in this direction using plants or microorganisms for the uptake of heavy metal from solutions (Ghosh and Singh, 2005; Fosso-Kankeu et al., 2011). Although the mechanism of metal biosorption by plants and microorganisms may not be entirely identical, both are however, reported to contain metalloproteins which play an important role in the uptake of metals by these biosorbents (Shah and Nongkynrih, 2007; Sriprang and Murooka, 2007). Microorganisms and plants have potential for metal adsorption, accumulation or resistance that are depending on the synthesis of metal binding proteins such as metallothioneins or phytochelatins (Mejare and Bulow, 2001; Sriprang and Murooka, 2007).

Metal binding proteins or metalloproteins are a large group of proteins which play an important role in many aspects of the cell life and generally contribute in regulating the amount of metals within the cells through import and/or export transport as well as storage of metal ions (Ma et al., 2009). In microorganisms and plants, metal binding proteins at the outer membrane, interact with environmental metal ions ensuring their transport in the cytosol, where metallochaperones (specialized proteins chelators) transfer metals to the appropriate receptor protein. Metal binding to proteins is site specific and it has been reported that hard metals preferentially bind to Asp and Glu (Vallee and Auld, 1989, 1990) rich proteins, while soft metals tend to bind to Cys and His rich proteins (Yamashita et al., 1990). Although naturally abundant in some proteins, these specific binding sites have also been engineered in other proteins. Some researchers have developed heterologous metalloproteins with higher affinity, higher metal-binding capacity and/or specificity and selectivity, which were expressed in bacteria and plants to improve their capacity to adsorb metals (Zhu et al., 1999; Kotrba et al., 1999a).

Metal uptake by plants and microorganisms occurs through a number of mechanisms. The understanding of these mechanisms is crucial for improvement of bioremediation processes. The implication of metal binding proteins and peptides in biosorption and bioaccumulation mechanisms is discussed in this review.

---

* Corresponding author at: School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Potchefstroom Campus, Potchefstroom, South Africa. Tel.: +27182991659; fax: +27182991535.
E-mail address: 24838616@nwu.ac.za (E. Fosso-Kankeu).

1474-7065/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.pce.2013.09.018

Please cite this article in press as: Fosso-Kankeu, E., Mulaba-Bafubiandi, A.F. Implication of plants and microbial metalloproteins in the bioremediation of polluted waters: A review. J. Phys. Chem. Earth (2013), http://dx.doi.org/10.1016/j.pce.2013.09.018

2. Use of plants in bioremediation of polluted effluents by heavy metals

2.1. Agricultural by-products as biosorbents

Limitations such as the high cost and production of by-product sludges have motivated the application of biological approach in the remediation of heavy metal pollution of water sources by industrial effluents. Agricultural by-products which are abundant, low cost and easily accessible biosorbents are recommended for such bioremediation processes. Adsorption potential of agricultural by-products is mainly attributable to the presence of proteins, polysaccharides and lignin which provide a large amount of surface functional groups responsible for metal ion adsorption (Wase and Forster, 1997; Bulut and Tez, 2007). Binding of heavy metals to agricultural by-products is mainly governed by columbic interactions which results from the electrostatic energy of sorption between the two particles (Volesky and Holan, 1995; Gang and Shi, 1998; Igwe and Abia, 2006). The efficiency of metal removal depends on a number of factors including the charge on the metal ion, the softness or hardness of the charges on the agricultural by-products and the sizes of these agricultural by-products. These factors may enhance the sorption capacity through interstitial diffusion (Igwe and Abia, 2006; Okoro et al., 2007).

A wide variety of agricultural by-products have been extensively studied for their capacity as biosorbents for metal removal from aqueous solutions.

Among the plant parts often solicited as biosorbents, are leaves of various plants. For example, tea is frequently used to remove metals from solutions. After removal of soluble and colored components, spent black and green tea leaves were assessed by Lavecchia et al. (in press) for their potential to remove lead from contaminated waters. They observed removal efficiencies that are higher than 95% from solutions containing 0.01 and 2 g/L of lead. The observed adsorption capacity was ascribed to the presence of charged and polar functional groups on the protein surface and phenolic compounds (Basso et al., 2002; Pagnanelli et al., 2003). In another study, Ahluwalia and Goyal (2005) used tea leaves for the removal of lead, iron, zinc and nickel from 20 mg/L metal solution and achieved removal efficiencies of 92.5%, 84% and 73.2% of lead, iron and zinc, respectively. They investigated the involvement of functional groups in metal removal experiment using Fourier transformed infrared (FTIR) spectroscopy and found that the carboxyl group was involved in the binding of lead and iron, whereas the amine group was involved in the binding of nickel and zinc.

Sharain-Liew et al. (2011) used dried leaves of the narrow leaf cattail plant, *Typha angustifolia* (an aquatic plant abundant in the tropics) for lead removal from synthetic wastewater. A maximum adsorption of 86.04% was achieved within 8 h of exposure of the leaves to a solution containing 25 mg/L of lead.

In another study, Bulut and Tez (2007) used dried and ground shells of hazelnut and almond for the adsorption of Ni(II), Cd(II) and Pb(II) from aqueous solutions. They found that adsorption of the metal ions to shells of hazelnut and almond was spontaneous and mainly governed by an ion exchange mechanism which entails the attachment of divalent metal ion to hydroxyl and oxyl groups that release two hydrogen ions into solution (Dorris et al., 2000). The authors suggested that lignin, tannins or other phenolic compounds were the active ion exchange compounds with the phenolic groups on those compounds being the active sites.

The peels of agricultural products have been widely used by researchers as biosorbent materials because of their low cost. Orange peel presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicelluloses and lignin. The use of orange waste as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment was previously reported (Li et al., 2007; Biswas et al., 2007; Perez et al., 2008; Liang et al., 2009). Tiny particles (less than 1.80 mm size) of oven-dried orange peels were used by Gonen and Serin (2012) for adsorption of nickel from aqueous solution. Carboxyl and hydroxyl groups of the orange peels were previously identified as the main functional groups involved in metal uptake (Perez-Marin et al., 2008).

A wide range of other agricultural by-products have been considered for the development of efficient, eco-friendly and cheap technology for removal of heavy metal ions from polluted effluents (Table 1). By-products of soybean processing, cotton seed hulls (Marshall and Champagne, 1995), barks of *Pinus pinaster* (Vazquez et al., 1994), hazelnut straw (Cimino et al., 2000), peanut hull (Johnson et al., 2002), barks from various sources (Seki et al., 1997), coconut husk (Babarinde, 2002), grape stalk (Villaescusa et al., 2004), papaya wood (Saeed et al., 2005), Ponkan mandarin peels (Pavan et al., 2006), corn cobs (Hawrhorne-Costa et al., 1995), apple waste (Maranon and Sastre, 1991), maize leaf (Babarinde et al., 2006), banana and orange peels (Annadurai et al., 2002) and sugarcane bagasse (Khan et al., 2001) are some of the agricultural by-products that have been investigated for their capacity to remove metal ions from solutions.

2.2. Phytoremediation

Phytoremediation is an age old technique that exploits the natural potentials of plants to preserve a clean environment and maintain the balance of the ecosystem. It consists of the use of plants to clean up water and soil sites contaminated with hazardous substances. Phytoremediation can be applied in various ways and for different reasons and is classified based on these parameters. For example, when plants are used to convert organic pollutants into non-toxic form, the phytoremediation process is classified as phytodegradation. Phytostabilization limits contaminants mobility and bioavailability in the soil or sludges, through sorption, precipitation, complexation, or transformation of metal to non-toxic species by changing the valence. The process is

Table 1
Sorption potential of selected agricultural by-product biosorbents (from Okoro and Okoro, 2011).

Type of biosorbents	Type of metal ions	Removal rate (%)
Yam peels	Pb^{2+}	98.76 ± 0.16
Yam peels	Cd^{2+}	99.71 ± 0.12
Cassava peels	Pb^{2+}	98.84 ± 0.30
Cassava peels	Cd^{2+}	99.70 ± 0.11
Sweet potato peels	Pb^{2+}	97.89 ± 0.32
Sweet potato peels	Cd^{2+}	97.27 ± 0.14
Irish potato peels	Pb^{2+}	99.50 ± 0.11
Irish potato peels	Cd^{2+}	97.00 ± 0.10
Banana peels	Pb^{2+}	97.71 ± 0.32
Banana peels	Cd^{2+}	97.71 ± 0.13
Orange peels	Pb^{2+}	95.78 ± 0.13
Orange peels	Cd^{2+}	97.78 ± 0.22
Maize cobs	Pb^{2+}	96.88 ± 0.22
Maize cobs	Cd^{2+}	93.23 ± 0.12
Native pear seeds (boiled)	Pb^{2+}	84.28 ± 0.11
Native pear seeds (boiled)	Cd^{2+}	–
Plantain peels	Pb^{2+}	99.93 ± 0.14
Plantain peels	Cd^{2+}	–
Fluted pumpkin stems	Pb^{2+}	97.61 ± 0.34
Fluted pumpkin stems	Cd^{2+}	–
Nypa frutican shoots	Pb^{2+}	55.60–92.20
Nypa frutican shoots	Cu^{2+}	55.60–92.40
Coca shells	Pb^{2+}	95.00 ± 0.15
Olive cake	Pb^{2+}	96.92 ± 0.13
Okra stem derived cellulose	Pb^{2+}	99.66 ± 0.12
Okra stem derived cellulose	Cd^{2+}	99.95 ± 0.14

Please cite this article in press as: Fosso-Kankeu, E., Mulaba-Bafubiandi, A.F. Implication of plants and microbial metalloproteins in the bioremediation of polluted waters: A review. J. Phys. Chem. Earth (2013), http://dx.doi.org/10.1016/j.pce.2013.09.018