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Biotechnological remedies for the estuarine environment polluted with heavy metals and persistent organic pollutants



Ganiyu Oladunjoye Oyetibo ^{a, b, *, 1}, Keisuke Miyauchi ^b, Yi Huang ^{b, c}, Mei-Fang Chien ^c,
Matthew Olusoji Ilori ^a, Olukayode Oladipo Amund ^a, Ginro Endo ^b

^a Department of Microbiology, Faculty of Science, University of Lagos, Akoka, Lagos, Nigeria

^b Biotechnology Research Common, Faculty of Engineering, Tohoku Gakuin University, Tagajo, Miyagi, 985-8537, Japan

^c Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi, 980-8579, Japan

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ABSTRACT

Estuaries in the areas prone to anthropogenic activities are exposed to multifarious pollutants. Toxic concentrations of heavy metals do exist with persistent organic compounds in such estuaries prolonging the recalcitrance and ecotoxicological consequences of the chemicals, which impact on the health of the brackish water and by extension, the oceans. The quest for high aesthetic quality of the estuarine environment is gaining attention from global campaign, which requires effective remedial strategies to replace the physical and chemical methods in use that are costly and often leave behind toxic residues in the environment. Contrary to physico-chemical remedial processes, bioremediation strategies are projected as a promising green technology to remove pollutants from the estuarine environment. The concept of bioremediation involves the use of competent biological elements such as microorganisms and plants, along with or without the biomolecules they produced, to ameliorate pollution. Therefore, this paper reviews the various bioremediation technologies that would be applicable to decommissioning estuarine environments polluted with toxic metals and persistent organic compounds.

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1. Introduction

An estuary is a partially enclosed body of water along coastlines where freshwater and saltwater meet and mix. It is a transition zone between ocean and continent that freely connects with the open sea, whereby the sea water is diluted with fresh water derived from land drainage. It is generally referred to as “nurseries of the sea” because it is a vital habitat to several marine species. It serves as buffering zone between terrestrial and marine ecosystems in urban and industrial areas by removing pollutants and filtering sediments through biochemical activities in the environment before it empties into the ocean, thereby, contributing to the health of the ocean. Anthropogenic activities frequently introduce elevated concentrations of heavy metals (HMs) and metalloids

along with organic pollutants into estuary water in urbanized areas (Oyetibo et al., 2010, 2013a). Some specific examples of estuaries where HMs and organic pollutants have been reportedly co-exists due to anthropogenic activities include Lagos Lagoon in Nigeria (Oyetibo et al., 2015a; Obi et al., 2016); Victoria Harbor in Hong Kong (Zhang et al., 2008), Ancona Harbor of Adriatic Sea in Italy (Barbato et al., 2016), Gujarat coastline of the Arabian Sea in India (Patel et al., 2015), Santos-Sao Vicente estuary in Brazil (Pinto et al., 2015), and Tinto, Odiel and Piedras rivers' estuaries in Spain (Mesa et al., 2015a, 2015b) among others across the globe.

The toxicity of HMs to microbial community in polluted environments had been reported to inhibit biodegradation of organic pollutants in co-contaminated sites (Said and Lewis, 1991; Sandrin et al., 2000; Bamforth and Singleton, 2005), prolonging the recalcitrance of organic pollutants in the environments (Bamforth and Singleton, 2005). The continual outflow of effluents laden with HMs and organic pollutants alters the ecological status of the affected estuary with the evolution of (i) competent microorganisms that can simultaneously reduce and detoxify HMs while metabolising the organic pollutants, (ii) HM-resistant microorganisms that perform their metabolic activity in the presence of the

* Corresponding author. Department of Microbiology, Faculty of Science, University of Lagos, Akoka, Lagos, Nigeria.

E-mail addresses: goyetibo@unilag.edu.ng, goyetibo@mail.tohoku-gakuin.ac.jp (G.O. Oyetibo).

¹ Visiting Postdoctoral Research Scientist at Biotechnology Research Common, Faculty of Engineering, Tohoku Gakuin University, Tagajo, Miyagi, 985-8537, Japan.

metals, and (iii) microorganisms, which are inactive in the presence of HMs in the affected estuarine environment, and only perform their metabolic activities once the metals have been reduced via extracellular processes (Nakatsu et al., 2005; Oyetibo et al., 2013a). The evolved traits in microorganisms, widely borne in transposons and plasmids (mercury resistance [*mer*] operon, for example, have been extensively described as transposon-borne: Huang et al., 1999, 2002; Endo et al., 2002; Narita et al., 2002, 2004; Matsui et al., 2005, 2016; Chen et al., 2008; Chien et al., 2008, 2010), are often reported as resistance/tolerance mechanisms that are exploited in environmental biotechnological decommissioning strategies of polluted estuarine environment (modelled in Fig. 1).

2. Toxic metals and organic pollutants of importance in estuarine environment

HMs are usually those elements with a molecular weight greater than 53, a density greater than 6 g cm^{-3} , and an atomic number greater than 20 (AMAP/UNEP, 2013). In the context of this definition, arsenic (As) and selenium (Se) are not metals but regarded as metalloids and are generally lumped with toxic metals whenever ecotoxicology of metals is discussed. They belong to the group of elements described geochemically as ‘trace elements’ that occur naturally in the earth’s crust. All trace elements are toxic to living organisms at excessive concentrations, but some including iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), molybdenum (Mo) and so on, at low but critical concentrations are micronutrients used in the redox processes, regulation of osmotic pressure, and also enzyme components that are essential for the normal healthy growth and reproduction by living organisms (Perales-Vela et al., 2006). The classic metal(loid)s about which there is most concern in the estuarine environment are cadmium (Cd), cobalt (Co), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), As, Cu, Mo, Se, and Zn (ATSDR, 2008; Oyetibo et al., 2010). While some of the metals provide metabolic functions in the estuarine ecosystem, others including Hg, Pb, Cr and Cd are with no known metabolic and physiological merit to life and, therefore, tagged “bad/toxic metals” (Todorova et al., 2007). Toxic metals do not only impact the estuarine ecological balance as notable environmental stressors, they also arouse or exacerbate environmental-induced diseases including cancer, chronic lung disease, diabetes and neurodegeneration (Hansen et al., 2006; Franco et al., 2009). In unrecognised or inappropriately treated cases, HM toxicity can result in significant deformation, morbidity and mortality as reported for ‘Minamata’ and ‘Itai-itai’ diseases caused by Hg and Cd poisoning,

respectively (AMAP/UNEP, 2013). The bioavailable toxic metal(loid) ion inside the cell interacts with cellular proteins producing their toxicity by forming complexes that make biological molecules lose their ability to function properly via induced alterations in redox homeostasis (Hansen et al., 2006; Franco et al., 2009), and result in malfunctioning or death of the affected cells (Franco et al., 2009). Children are more susceptible to the toxic effects of HMs and are more prone to accidental exposures (ATSDR, 2008), just as dozens of children were reportedly killed in Northern Nigeria due to Pb poisoning from illegal artisanal mining of gold.

Persistent organic pollutants (POPs) are extremely stable (being resistant to environmental degradation processes) toxic organic compounds released into the estuary through various anthropogenic activities, affecting the health of estuarine ecosystems and humans (Lasserre et al., 2009; Kanissery and Sims, 2011; Sanchez-Sanchez et al., 2013). POPs are also of global concerns and remained banned in many countries because they persist in the environment, have capability of long-range transport, bioaccumulate in human and animal tissues, and biomagnify in food chains (Tchounwon et al., 2003; Sanchez-Sanchez et al., 2013). In 2004, the Stockholm Convention committed more than 90 signatory countries to phasing out or eliminating large stocks or other sources of POPs (Jepson and Law, 2016). Yet, POPs still continue to threaten the health of the estuarine environment via lithospheric run-off pollution or accidental spillage as they are currently or were in the past used as pesticides, industrial chemicals or by-products. The 12 POPs, otherwise called “dirty dozen” POPs, that the United Nations Environment Program (UNEP) classified as the most hazardous to human health and the environment are presented in Table 1. POPs exposure through diet, environmental exposure, or accidents can cause death and illnesses including disruption of the endocrine, reproductive, and immune systems; neurobehavioral disorders; and cancers possibly including breast cancer (Goff et al., 2005; ATSDR, 2008).

3. Heavy metal and persistent organic pollutants remediation techniques

The primary management goal during the remediation of a contaminated environmental-component is to obtain closure, i.e., to achieve a set of conditions that are considered environmentally acceptable and which will ensure that no future action will be required at the site (Sebai et al., 2011; Sagarkar et al., 2013). Generally, remediation technologies are classified into four categories based on the process acting on the contaminants. These include removal, separation, and destruction as processes that reduce or remove the contaminants (Oyetibo et al., 2013b, 2014, 2015a, 2015b); and containment technologies that control the migration of a contaminant to sensitive receptors without reducing or removing the contaminant. The only approaches available for remediating heavy metal-polluted estuary are to remove the metals or to convert the metals into less bioavailable forms. In case of POP pollution, degradation or process leading to structural transformation to non-toxic compound is aimed (Sagarkar et al., 2013). The conventional procedures for removing pollutants (HM ions in particular) from aqueous system include chemical precipitation, ion exchange, reverse osmosis, ultrafiltration, electrodialysis, solvent extraction (Salt et al., 1998; Singh et al., 2003).

According to Khan et al. (2004), the various pitfalls of the common pollutant removing mechanisms include:

- i) Very expensive with respect to cost of procuring chemicals and energy requirements in reverse osmosis, ion exchange
- ii) Formation of metal hydroxides that clog membranes in electrodialysis

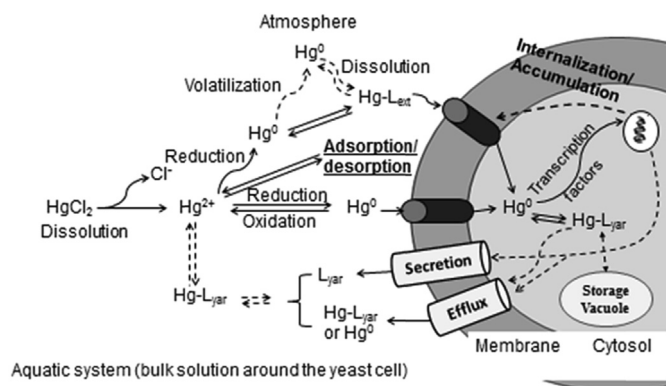


Fig. 1. Conceptual model of the biogeochemical activities of *Yarrowia* sp. on naturally-occurring and/or anthropogenically-derived mercury, as HgCl_2 , in lagoon environment. L_{yar} intracellular ligands; L_{ext} extracellular ligands; Hg-L_{yar} and Hg-L_{ext} are complexation of Hg by ligands (Oyetibo et al., 2015b).

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