Biosorption: current perspectives on concept, definition and application

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HIGHLIGHTS

- Up-to-date critical review.
- Covers concept, definition and application.
- Provides directions for future research.

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ABSTRACT

Biosorption is a physico-chemical and metabolically-independent process based on a variety of mechanisms including absorption, adsorption, ion exchange, surface complexation and precipitation. Biosorption processes are highly important in the environment and conventional biotreatment processes. As a branch of biotechnology, biosorption has been aimed at the removal or recovery of organic and inorganic substances from solution by biological material which can include living or dead microorganisms and their components, seaweeds, plant materials, industrial and agricultural wastes and natural residues. For decades biosorption has been heralded as a promising cost-effective clean-up biotechnology. Despite significant progress in our understanding of this complex phenomenon and a dramatic increase in publications in this research area, commercialization of biosorption technologies has been limited so far. This article summarizes existing knowledge on various aspects of the fundamentals and applications of biosorption and critically reviews the obstacles to commercial success and future perspectives.

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1. Introduction

Anthropogenic activity and industrialization has put increasing pressure on the environment by generating large quantities of toxic aqueous effluents containing toxic metals, metalloids, radionuclides as well as various organic pollutants. Detrimental effects on ecosystems and the health hazards associated with organic and inorganic pollutants have been established beyond any doubt, making it absolutely necessary to apply ever increasing standards of pollutant detection and treatment. Industrial treatment methods aimed at preventing or limiting toxic discharges demand increasing expenditure.

Various physico-chemical and biological processes are usually employed to remove pollutants from industrial wastewaters before discharge into the environment (Gadd, 2009). Biological processes such as standard sewage and water purification treatments as well as auxiliary reed bed and wetlands approaches have been used for many years because of the remarkable capabilities of microorganisms to detoxify organic and inorganic pollutants (Gadd, 1986,

2000, 2007). Biosorption is one of the significant properties of both living and dead microorganisms (and their components) relevant for treatment of pollutants (Tsezos and Volesky, 1981; Gadd and White, 1993; Texier et al., 1999). However, practically all biological material including macroalgae (seaweeds) as well as plant and animal biomass and derived products (e.g. chitosan) is capable of biosorption. For a number of years, biosorption has been claimed as a promising biotechnology for pollutant removal and/or recovery from solution, due to its simplicity, analogous operation to conventional ion exchange technology, apparent efficiency and availability of biomass and waste bio-products (Gadd, 1986; Volesky, 1990, 2001, 2007; Gadd and White, 1993; Veglio and Beolchini, 1997; Tsezos, 2001; Wang and Chen, 2006; Mack et al., 2007).

Since the first reports on biosorption, great efforts have been made to prepare efficient, effective, and economic biomaterials and apply them for wastewater treatment. Initially being focussed on metals and related substances, biosorption research has expanded into additional areas of potential use by application to particulates and all kinds of organic substances including pharmaceuticals. However, despite the fact that biosorption phenomena have been discussed in the literature for a long time (over 13,000 scientific papers have been published to date in peer-reviewed

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journals) there has been little or no obvious successful exploitation in an industrial context. This article gives a critical overview of the area of biosorption research, its fundamentals, applications and problems, and attempts to clarify future perspectives and commercial feasibility.

2. Defining biosorption

The conception of "biosorption" is multidimensional and has been evolving over the past few decades. The difficulties with a sound definition of the term "biosorption" are related to the existence of many mechanisms, the biosorbent used, environmental factors and the presence or absence of metabolic processes in the case of living organisms. It is also affected by expanding areas of suggested potential applications (Volesky, 2007; Gadd, 2009; Michalak et al., 2013). The term "biosorption" has been used by different authors for a diverse range of processes including bioadsorption, bioabsorption, and biosorption by living or dead biomass, bioaccumulation, and a diverse array of substances, e.g. metals, radionuclides, and organics. However, the quality and productivity of specialist communication depends to a large extent on the quality of the terminology employed.

Sorption is a physico-chemical process by which one substance becomes attached to another. Despite the 'bio' prefix that denotes the involvement of a biological entity, biosorption is a physico-chemical process that can be simply defined as the removal of substances from solution by biological material (Gadd, 2009). However "sorption" to biological material may not be as simple as might be perceived. One of the dimensions here is bioadsorption versus bioabsorption (Gadd, 2009). Sorption is a term that has been used for both absorption and adsorption. Absorption is the incorporation of a substance in one state into another of a different state (e.g. liquids being absorbed by a solid or gases being absorbed by water), i.e. into a three-dimensional matrix. Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule, i.e. onto a two-dimensional surface. Many researchers consider biosorption as a subcategory of adsorption, where the sorbent is a biological matrix (Michalak et al., 2013). Adsorption is the most common form of sorption involved in 'traditional' clean-up technologies but unless it is clear which process (absorption or adsorption) is operative, sorption is the preferred term, and can be used to describe any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a sorbent (i.e. a solid surface) resulting in an accumulation at the sorbate–sorbent interface (Borda and Sparks, 2008). If adsorption occurs and continues through the formation of a new three-dimensional surface species, this new species can be defined as a surface precipitate. A number of different systems clearly exist in the continuum from adsorption to precipitation (Gadd, 2009).

Another dimension of the term "biosorption" is related to the traditional and expanding areas of its application, primarily to the target substances to be sorbed. Traditionally, the term referred specifically to metals as biosorbates and, often, or microbial material as biosorbents. Most biosorption research still concentrates on metals and related elements and several authors have emphasized this in their definition of biosorption (Gadd, 2009). However, biosorption research and applications have been extended to removal of organics, e.g. dyes, to the recovery of high-value proteins, steroids, pharmaceuticals and drugs, and to enrichment with microelements biological feed supplements and fertilizers (Volesky, 2007; Kaushik and Malik, 2009; Michalak et al., 2013). Thus, the term biosorption can apparently describe any system where a solid surface of a biological matrix interacts with a sorbate resulting in the reduction in the solution sorbate concentration (Gadd, 2009).

A different dimension of the term "biosorption" relates to passive versus active processes. Three overlapping levels of definitions in this dimension can be recognised: (i) a narrow definition when biosorption is defined as a passive, metabolically-independent process; (ii) a wider definition including both passive and active processes in case of living biomass and often referred to as bioaccumulation and, finally, (iii) biosorption as a fundamental generalization covering all aspects of interactions of any sorbate with a biological matrix.

Biosorption has been defined by most researchers as a passive and metabolically-independent process, e.g. the passive uptake of metals by microbial biomass (Volesky, 1990; Malik, 2004; Gadd, 2009). It can be performed either by dead biomass or fragments of cells and tissues which may have some advantages for both the ease and safety of handling and preparation of the biological substrate. However, it can also be performed by live cells as passive uptake or metabolically-independent adsorption of a sorbate via surface complexation onto cell walls and/or other outer layers being the first, fast and reversible adsorption step operating within a much slower and complex overall bioaccumulation mechanism (Volesky, 1990; Malik, 2004). Both mechanisms can overlap bringing additional confusion in the use of terminology. Bioaccumulation is a function of living organisms dependent on a variety of physical, chemical and biological mechanisms including both intra- and extracellular processes where passive uptake plays only a limited and not very well-defined role (Gadd, 1993, 2010; Dhankhar and Hooda, 2011; Gadd and Fomina, 2011; Gadd et al., 2012). It should be noted that passive biosorption processes occurring in living biomass are subject to effects of changing physico-chemical conditions resulting from changes in pH, available ligands and other metabolites as a result of metabolic activity and possible stress responses caused by the toxic sorbate. This complicates adequate descriptions of the process and predictive modelling for practical use. Therefore, in this account, bioaccumulation is used to describe the process involving living cells, whereas biosorption mechanisms refer to the use of dead biomass.

The overall generality of biosorption processes as a property of living and dead biomass to bind and concentrate inorganic and organic compounds should also be noted (Kotrba, 2011). Biosorption is an important part of many processes occurring in nature including, e.g. sorption in soil, antigen–antibody immune reactions and adsorption to host cells as a first stage in virus replication, which are all subjects of different scientific disciplines. Many methodological approaches used in life sciences, biotechnology and medicine are, in fact, based on biosorption processes, e.g. staining microbial cells for electron microscopy and targeted therapies in cancer treatment. In one sense, all life phenomena are somehow related to interactions between biological surfaces and a sorbate.

3. Fundamentals of biosorption

As mentioned previously, biosorption is a physico-chemical metabolism-independent process resulting in the removal of substances from solution by biological material (Gadd, 2009). The biosorption process therefore involves a solid phase (biosorbent) and a liquid phase (solvent: normally water) containing the dissolved or suspended species to be sorbed (sorbate).

3.1. Biosorbates

A wide range of target sorbates can be removed from aqueous solution using biosorbents. As well as metals, particulates and colloids have been studied as well as organometal(loid) inorganic and organic compounds including dyes, fluoride, phthalates, and pharmaceuticals (Volesky, 2007; Gadd, 2009; Michalak et al., 2013). A

variety of mechanisms are involved in the removal of such diverse substances from solution and, as discussed above, such diverse approaches in using biosorbents would benefit from clear terminology. However, most biosorption research has been carried out with metals and related elements, including actinides, lanthanides, metalloids, and various radioisotopes of these substances (Gadd, 2009; Dhankhar and Hooda, 2011). 75% of elements in the Periodic Table are classified as metals and almost all of them have received attention regarding biosorption. The only exceptions, perhaps, are highly mobile elements of low toxicity, e.g. K^+, Mg^{2+}. Metal toxicity and importance as a pollutant, whether it is radioactive, or valuable are the main reasons that determine the metals of interest for biosorption. This also defines the important goals of the research, e.g. environmental clean-up, health protection, recycling and/or recovery, as well as differences in scale and approach, and potential economic consequences. Some of the most widespread metals studied are key environmental pollutants, e.g. lead, copper, mercury, cadmium, chromium and arsenic as well as radionuclides of cobalt, strontium, uranium, thorium, etc. (Gadd, 2009, 2010; Gadd and Fomina, 2011). Even in such a short list of elements, exists a wide range of chemical properties. Among these elements, predominant chemical species may be cationic or anionic, exist as complexes, and exhibit a range of oxidation states. In many systems, even such common metals as Cu, Cd, and Zn, are hydroxylated, or complexed (e.g. to Cl) depending on the pH and medium composition. However, metal speciation is ignored in many studies and it is often assumed that metals are entirely present as divalent cations which will not be true in many cases (Gadd, 1992; Stumm and Morgan, 1996).

While a large portion of current research has been carried out on removal of metal cations, anion removal using biosorption has been a growing concern in fields of mining, metallurgy, and surface finishing industries with a number of toxic metal(oid)s occurring in anionic forms, such as arsenic, selenium, chromium, molybdenum, and vanadium (Michalak et al., 2013). Conventionally, most of these anionic species are removed using activated carbon, ion exchange, solvent extraction, or precipitation. However, biosorption has been proposed as an effective alternative treatment for anionic pollutants (Michalak et al., 2013).

Unlike metals, many organic compounds released into the environment are degraded by natural microbial populations, and such biodegradation potential is the basis of many established and emerging treatment processes. Nevertheless, in many cases, the products of biodegradation may be hazardous, while some xenobiotics are extremely resistant to biodegradation. Biosorption has been promoted as a potential biotechnology for removal of these and related organic substances from waste streams and effluents. Some substances that have received attention include dyes, phenolic compounds, and pesticides (Aksu, 2005). Wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules (particularly azo dyes), resistant to aerobic digestion, stable to oxidizing agents, and may be present in low concentrations. Common methods for removing dyes may be economically unfavorable and/or technically complicated. Because of the high costs, many of the physico-chemical methods for treating dyes in wastewater have not been widely used, with a combination of different processes often being used to achieve the desired water quality. Biosorption has therefore been proposed as an effective de-colorization method for dye-contaminated effluents (Crini and Badot, 2008).

3.2. Biosorbents

Any kind of biological material has an affinity for inorganic and organic pollutants meaning there is enormous biosorption potential within countless types of biomaterials (Gadd, 2009; Dhankhar and Hooda, 2011). In the search for highly-efficient and cheap biosorbents and new opportunities for pollution control, element recovery and recycling, all kinds of microbial, plant and animal biomass, and derived products, have received investigation in a variety of forms, and in relation to a variety of substances (Volesky, 1990, 2003a).

The kinds of substrates of biological origin that have been investigated for biosorbent preparation include microbial biomass (bacteria, archaea, cyanobacteria, filamentous fungi and yeasts, microalgae), seaweeds (macroalgae), industrial wastes (fermentation and food wastes, activated and anaerobic sludges, etc.), agricultural wastes (fruit/vegetable wastes, rice straw, wheat bran, sugar beet pulp, soybean hulls, etc.), natural residues (plant residues, sawdust, tree barks, weeds, sphagnum peat moss) and other materials (chitosan, cellulose, etc.) (Park et al., 2010; Dhankhar and Hooda, 2011).

The biosorptive capacities of various biomass types have been reported in thousands of research papers and quantitatively compared in many reviews (Ahluwalia and Goyal, 2007; Vijayaraghavan and Yun, 2008; Park et al., 2010). In some cases, uptake of toxic metals by biomass has reached as high as 50% of the dry weight (Park et al., 2010). Biosorption capacity may vary considerably within biomass of the same microbial species. For example, lead biosorption capacity varied from 2 to 93 mg g dry wt^{-1} for the filamentous fungus *Aspergillus niger* and from 79 to 270 mg g dry wt^{-1} for yeast *Saccharomyces cerevisiae* (Dhankhar and Hooda, 2011). However, biosorptive capacity of a biosorbent largely depends on experimental conditions and its prehistory and pretreatment. When comparing biosorptive capacities of biosorbents for a target pollutant, the experimental data of each researcher should be carefully considered in the light of these factors.

A major challenge has been to select the most promising types of biomass from an extremely large pool of readily available and inexpensive biomaterials. In theory, for large-scale industrial uses the biosorbent should be readily available and cost-effective and could come from: (i) industrial wastes, which could be available free or at low charge; (ii) organisms easily obtainable in large amounts in nature; and (iii) organisms that can be grown easily for biosorption purposes (Park et al., 2010). There seems little justification in examining yet more different bacterial, fungal and algal species for remarkable new properties because so many representative organisms have already been studied. There also seems little justification for examining systems which could never be applied in an industrial context, e.g. pathogenic bacteria and fungi, nutritionally-fastidious extremophiles, rare or endangered plants, macroalgae, macrofungi and lichens, examples of which are found widely in the literature. Perhaps research should employ those biomass types that are efficient, cheap, easy to grow or harvest and concentration be given to biomass modifications and/or alteration of bioreactor configuration and physico-chemical conditions to enhance biosorption. Basically, a low cost biosorbent requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Bailey et al., 1999).

A common rationale is that 'waste' biomass will provide an economic advantage. This has motivated studies of the biosorptive capacity of macroalgae (seaweeds), plant materials (leaves, bark, sawdust), and animal materials (hair, crustaceans) (Zhang and Banks, 2006; Ahluwalia and Goyal, 2007;) as well as sludges from sewage treatment and other waste processing applications (Hawari and Mulligan, 2006; Barros et al., 2007; Pamukoglu and Kargi, 2007). Their metal sorbing properties, however, may sometimes be low (Volesky, 2001). A variety of bacterial and fungal biomass types arise from several industrial fermentations and these also receive continued study (Brierley, 1990; Fourest and Roux, 1992; Ringot et al., 2007). However, 'waste' will still incur treatment and transport costs while, if a commercial biosorption

process was developed using a 'waste', it would soon be found that 'waste' costs would rapidly rise, i.e. it would cease to be a waste! If biomass is to be grown specifically for biosorption applications, then cheap substrates would be preferable, just as in other industrial fermentations. Renewable biomass harvested from the environment, or cultured in 'farms', is another rationale and the harvesting and use of natural seaweeds, which may lend themselves to aquaculture, has also received support (Volesky, 2001).

Even though there are virtually no limits to exploration of new biomass types, one of the problems is that native biomass composition may not vary significantly between different species of the same genus or order. For example, cell wall structure and composition (the main site of metal/radionuclide biosorption) is similar throughout Gram-positive bacteria (Kim and Gadd, 2008). Similarly, all Gram-negative bacteria have the same basic cell structure (Kim and Gadd, 2008). Main fungal orders are similarly uniform in wall structure and composition, with some variations due to varying content of chitin, glucans, etc. (Gow and Gadd, 1995). Plant and algal material similarly shows considerable uniformity, albeit with some differences between major genera (Davis et al., 2003).

Peptidoglycan carboxyl groups are the main binding site for metal cations in Gram-positive bacterial cell walls with phosphate groups contributing significantly in Gram-negative species (Gadd, 2009). Other bacterial metal-binding components include proteinaceous S-layers, and sheaths largely composed of polymeric materials including proteins and polysaccharides. Cyanobacteria (formerly known as blue-green algae) have cell walls similar to Gram-negative bacteria. Thus, a major cyanobacterial cell wall biosorptive component is peptidoglycan, with some species also producing sheaths as well as copious mucilaginous polysaccharide (extracellular polymeric substances, EPS). Archaeal cell walls are of diverse composition and, depending on the genus, may include pseudomurein (which resembles peptidoglycan), sulfonated polysaccharide and glycoprotein as major components providing anionic sites such as carboxyl and sulphate groups. There is some variation in the composition of algal cell walls, the only common component across algal divisions being cellulose (Davis et al., 2003). Other algal components include other polysaccharides like mannan, alginic acid, xylans, as well as proteins. These provide binding sites such as amino, amine, hydroxyl, imidiazole, phosphate and sulfate groups (Gadd, 2009).

Fungal cell walls are complex macromolecular structures consisting of chitins, glucans, mannans and proteins, but also containing other polysaccharides, lipids and pigments, e.g. melanin (Gadd, 1993). This variety of structural components ensures many different functional groups are able to bind metal ions to varying degrees (Bailey et al., 1999). Chitin is a very important structural component of fungal cell walls and is an effective biosorbent for metals and radionuclides, as are chitosan and other chitin derivatives. In *Rhizopus arrhizus*, U biosorption involves coordination to the amine N of chitin, adsorption in the cell wall chitin structure and further precipitation of hydroxylated derivatives (Tsezos and Volesky, 1982). Fungal phenolic polymers and melanins possess many potential metal-binding sites with oxygen-containing groups including carboxyl, phenolic and alcoholic hydroxyl, carbonyl and methoxyl groups being particularly important (Gadd, 1993, 2009). Fungal biomass has also received attention as biosorbent materials for metal-contaminated aqueous solutions, because of the ease with which they are grown and the availability of fungal biomass as an industrial waste product, e.g. *A. niger* (citric acid production) and *S. cerevisiae* (brewing) (Gadd, 2009).

Chitosan is of low cost compared with commercial activated carbon (chitosan is derived by deacetylation of chitin, the most abundant amino-polysaccharide in nature) and strongly complexes pollutants, especially metals. However, industrial production of chitosan generates large quantities of concentrated effluent containing polluting bases and degradation products while conversion to chitosan at high temperature with strong alkali can cause variability of product properties and increase the processing costs which appears to limit industrial acceptance. Since chitin is a dominant component of fungal cell walls, a fermentation approach to cultivate fungi for chitosan preparation has been proposed (Crini and Badot, 2008) although the economics of this do not appear favourable and extraction procedures would still result in production of noxious wastes. Chitosan and its grafted and cross-linked derivatives have also been assessed for dye removal from aqueous solutions (Crini and Badot, 2008; Guibal, 2004).

Microorganisms can excrete many kinds of metal-binding metabolites (Gadd, 2009). Many organisms from all the major groups can produce extracellular polymeric substances (EPS), largely composed of polysaccharide, and such capsules, slimes and sheaths can be an important biosorptive component in living cell systems, especially biofilms, depending on the nature of the polysaccharide and associated components (Comte et al., 2008; Flemming, 1995). Extracellular polymers are intimately involved in Cd biosorption by activated sludges (Comte et al., 2008). EPS can also adsorb or entrap particulate matter such as precipitated metal sulfides and oxides (Flemming, 1995; Gadd, 2009). Biofilms are capable of binding significant quantities of metals under natural conditions, and serve as matrices for precipitation of insoluble mineral phases.

Another aspect of the nature of biosorbents that should be highlighted here is that biomass used for biosorption may be living or dead. While the use of dead biomass or derived products may be easier by reducing complexity, the influence of metabolic processes on sorption is often unappreciated, particularly where there is scant biological input to the problem. The use of dead biomass seems to be a preferred alternative for the majority of metal-removal studies reported with advantages summarized as: (1) absence of toxicity limitations; (2) absence of requirements for growth media and nutrients in the feed solution; (3) easy absorbance and recovery of biosorbed metals; (4) easy regeneration and reuse of biomass; (5) possibility of easy immobilization of dead cells; (6) easier mathematical modelling of metal uptake (Dhankhar and Hooda, 2011).

Despite obvious advantages of using of dead biomass over living microorganisms, many attributes of living microorganisms remain unexploited in an industrial context (Gadd and White, 1990; Malik, 2004). Living microorganisms degrade organic pollutants and can sorb, transport, complex and transform metals, metalloids and radionuclides and many different processes may contribute to the overall removal process. They can be used for specific applications when pure biosorptive metal removal is not feasible and may be of value in systems where additional benefits will result from metabolic activity, e.g. biodegradation of organic substances (Malik, 2004; Gadd, 2009). For example, application of a consortium of metal-resistant cells can ensure better removal through a combination of bioprecipitation, biosorption, and continuous uptake of metals after physical adsorption which may lead to simultaneous removal of toxic metals, organic pollutants, and other inorganic impurities (Malik, 2004).

Metabolic processes are highly important in pollution treatments such as sewage treatment, biofilm reactors for pollutants, anaerobic digestion, soil and water bioremediation processes, phytoremediation, reed bed and wetlands biotechnologies, etc. Many of these living organism-based processes are of established commercial use and biosorption is a component of the overall removal process in such systems (Gadd, 2009).

3.3. Mechanisms of biosorption

Decades of biosorption research have provided an understanding of the mechanisms underlying microbial biosorption of toxic metals and related elements (Gadd, 2009; Kotrba, 2011). For a narrow definition of biosorption as a physico-chemical passive process, mechanisms include: adsorption, ion exchange and complexation/coordination with biosorption being rapid and reversible with biosorbent properties analogous to conventional ion exchange resins (Gadd, 2009). However, biological material is complex and the variety of structural components present in biomass means that many functional groups are able to interact with metal species, e.g. carboxyl, phosphate, hydroxyl, amino, thiol, etc., to varying degrees and influenced by physico-chemical factors. In reality, depending on the system and given conditions biosorption can be a mechanistically highly complex process (Gadd, 2009; Stumm and Morgan, 1996). Precipitation and crystallization are other possible mechanisms that may occur and complicate sorption and/or desorption. It can lead to very high uptake capacities but this may inhibit desorption. A good example is the extensive precipitation of actinides such as uranium and thorium on non-living fungal biomass (Gadd and White, 1992). The various mechanisms involved in biosorption are likely to operate simultaneously to varying degrees.

Ligand preferences in metal complex formation are highly relevant for understanding biosorption. The different ways of classifying metals according to their chemical properties include the hard-soft-acid-base principle (HSAB) with the Irving-Williams series of stability of metal complexes as its earliest evidence (Gadd, 1992). Type A (hard acids) preferentially bind to oxygen-containing ligands (hard), while type B (soft acids) preferentially bind to S and N-containing ligands (soft) (Table 1). However, such a principle is more descriptive than explanatory and definitions are not absolute. Some behaviour will be affected by metal concentration, as well as the relative metal concentrations in mixtures where competitive effects may occur (Avery et al., 1993). The hard/soft scheme predicts that bonds formed between hard acids and hard ligands will be predominantly ionic whereas soft acid–ligand complexes are more covalent in character. However, this varies depending on the nature of the biomass and availability of surface ligands. For example, Sr^{2+} binding to denatured yeast biomass was ionic, probably due to involvement of phosphate and carboxylate groups, but interactions with cell walls of living yeast exhibited increased covalent binding which could indicate the involvement of amine and sulphydryl groups (Avery et al., 1993; Gadd, 2009).

Many biosorption researchers do not restrict themselves to dead biomass or purified products which brings a further mechanistic complication because metabolic activities (respiration, nutrient uptake, EPS, metabolite release and oxido-reductive transformations) will alter the microenvironment around the cells which, in turn, may affect adsorption, ion exchange, complexation and precipitation, and change the speciation of target metals/radionuclides (Gadd and White, 1993; Gadd, 2000, 2009; Gadd and Fomina, 2011; Hockin and Gadd, 2007). The analysis and modelling of such multiple mechanisms may be difficult. However, if the prime research goal is to identify an efficient biosorbent system, from a pragmatic point of view it may not be necessary to have a complete understanding of what mechanism(s) are operative.

Surface complex formation of cations like Cu^{2+} may involve coordination of metal ions with oxygen donor atoms and proton release and formation of bidentate surface complexes (Gadd, 2009). A cation can associate with a surface of biosorbent as an inner-sphere or outer-sphere complex depending whether a chemical (i.e. largely covalent) bond is formed between the metal and the electron donating oxygen ion in this case (inner-sphere complex) or if a cation approaches the surface negative groups to a critical distance but the cation and base are separated by at least one water molecule.

Mechanisms of anion biosorption have been little studied. This can be apparently affected by chemical conditions such as the pH. For example, anionic species like TcO_4^-, $PtCl_4^{3-}$, CrO_4^{2-}, SeO_4^{2-} and $Au(CN)_2^-$ exhibit increased biosorption at low pH value (Garnham, 1997; Gadd, 2009).

The chemical structure of organic pollutants is very diverse which means that biosorption will be affected by molecular size, charge, solubility, hydrophobicity, and reactivity, as well as the type of biosorbent and wastewater composition. Hydrophobic sorption clearly occurs when hydrophobic compounds encounter biomass in biosorption systems (Stumm and Morgan, 1996). The lipophilic nature of hydrophobic compounds lets them pass through membranes and be absorbed into the organic matrix. Absorption may be a significant component of biosorption of organic pollutants. In dye biosorption onto chitosan, the various mechanisms include surface adsorption, chemisorption, diffusion and adsorption-complexation, with the most important steps

Table 1
Classification of metal ions (adapted from Gadd, 1992; Stumm and Morgan, 1996; Szefer, 2002).

| Type-A, transition, and type-B metal cations according to Ahrland, Chatt and Davies		
Type-A	Transition	Type B
Electron configuration:		
Inert gas type (d^0)	1–9 outer shell electrons	10 or 12 outer shell electrons
(H^+), Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	Cu^+, Ag^+, Au^+, Ga^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}
HSAB according to Pearson		
Hard acids	Borderline	Soft Acids
All type-A metals plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+}	All divalent transition metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}, SO_2, NO^+, $B(CH_3)_3$	All type-B metal cations minus Zn^{2+}, Pb^{2+}, Bi^{3+}
Preference for ligand atom:		
N » P O » S F » Cl		P » N S » O I » F
Qualitative generalization on complex stability sequence:		
Cations – charge/radius stability	Cations – Irving–Williams series: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$	
Ligands:		*Ligands:*
F > O > N = Cl > Br > I > S		S > I > Br > Cl = N > O > F
$OH^- > RO^- > RCO_2^-$		
CO_3^{2-} » NO_3^-		
PO_4^{3-} » SO_4^{2-} » ClO_4^-		

being film diffusion, pore diffusion and chemical reactions like ion exchange and complexation (Crini and Badot, 2008). Intermolecular interactions of the dye molecules are most probable in chitosan–dye systems with amine sites being the main reactive groups followed by a possible contribution from hydroxyl groups (Crini and Badot, 2008).

3.4. Factors affecting biosorption

Apart from the type and chemical form of the sorbate, a number of physico-chemical factors determine overall biosorption performance (Gadd, 2009; Park et al., 2010). Important factors include:

(1) Solution pH which is the most important regulator of biosorption affecting the solution chemistry of the pollutants themselves, the activity of functional groups in the biosorbents, and competition with coexisting ions in solution (Vijayaraghavan and Yun, 2008). Increasing pH enhances removal of cationic metals or basic dyes, but reduces that of anionic metals or acidic dyes.

(2) Ionic strength of solution which when increased, reduces biosorptive removal of adsorptive pollutants by competing with the adsorbate for binding sites on the biosorbent.

(3) Initial pollutant concentration which when increased, increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases removal efficiency.

(4) Other pollutant effects including competition for binding sites or other interferences. Increasing concentration of competing pollutants will usually reduce biosorptive removal of the target pollutant. However, cation loading of biomass may enhance biosorption of another cation because of pH buffering effects. Calcium-saturated fungal biomass showed enhanced Zn biosorption, for example (Fourest et al., 1994). In some cases, cations may increase biosorption of anionic species by enhancing binding of negatively-charged anions (Gadd, 2009). Anionic effects on metal biosorption capacity depend on metal speciation, co-existing metal(s) and the nature of the biosorbent. For example, inhibitory orders for the biosorption of Cr(VI) and Cr(III) ions were, respectively: $NO_3^- > Cl^- > SO_4^{2-}$ and $SO_4^{2-} > Cl^- \approx NO_3^-$ (Michalak et al., 2013). Anions like CO_3^{2-} and PO_4^{2-} may clearly affect biosorption through the formation of insoluble metal precipitates while chloride may influence biosorption through the formation of complexes, e.g. $CdCl_3$ (Gadd, 2009).
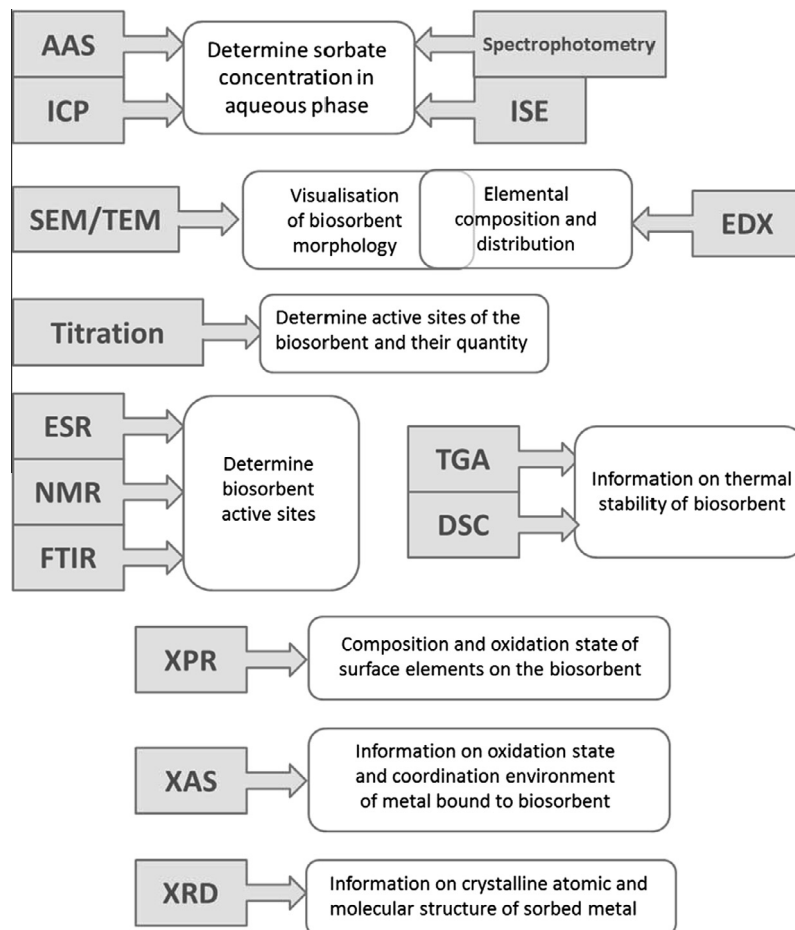
Fig. 1. Analytical techniques in biosorption research. These include atomic absorption spectrophotometry (AAS), ion selective electrodes (ISE), spectrophotometry. Scanning or transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/TEM–EDX), Fourier-transform infrared spectroscopy (FTIR), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), titration, electron spin resonance spectroscopy (ESR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

(5) Biosorbent nature and the availability of binding sites, prehistory of growth and treatment, physical or chemical modification, dosage and size are of major importance for performance (Gadd, 2009; Park et al., 2010; Kotrba, 2011; Li and Tao, 2013).

(6) Temperature, which usually enhances biosorptive removal of adsorptive pollutants when increased by increasing surface activity and kinetic energy of the adsorbate, but which may also damage the physical structure of the biosorbent (Park et al., 2010).

(7) Increasing agitation speed in appropriate aqueous systems enhances the biosorptive removal rate of adsorptive pollutants by minimizing mass transfer resistance, but may damage the physical structure of the biosorbent (Park et al., 2010).

3.5. Analytical techniques in studies of biosorption

A number of analytical techniques that have been used to study the biosorption process include atomic absorption spectrophotometry (AAS), ion selective electrodes (ISE), UV–Vis spectrophotometry, potentiometric titration, scanning or transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/TEM–EDX), infrared spectroscopy or Fourier-transform infrared spectroscopy (IR or FTIR), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) analysis, electron spin resonance spectroscopy (ESR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) (Fomina and Gadd, 2002; Wang and Chen, 2006; Ngwenya, 2007; Park et al., 2010; Michalak et al., 2013) (Fig. 1). These techniques may complement each other in giving insights into the mechanisms of biosorption (Park et al., 2010).

3.6. Desorption

One of the important steps in the development of biosorption-based technologies is desorption of the loaded biosorbent which enables re-use of the biomass, and recovery and/or containment of sorbates. It is desirable that the desorbing agent does not significantly damage or degrade the biomass and in some cases there may be a loss of efficiency of the biomass. However, in other cases desorption treatments may even improve further sorption capacities (Gadd and White, 1992). Bioreactors in parallel arrangement may allow sorption and desorption processes to occur in continuous flow systems without significant interruption. A variety of substances that have been used as metal/radionuclide desorbents include acids, alkalis, and complexing agents depending on the substance sorbed, process requirements and economic considerations. There may also be a means of selective desorption for certain target sorbates. So-called "destructive recovery" that includes combustion and subsequent recovery of metal/radionuclides from ash may also be a possibility. Organic solvents such as methanol, ethanol, surfactants and NaOH can be used for elution and regeneration of dye-laden biomass (Aksu, 2005). For desorption of phenolic compounds and pesticides distilled and deionized water and $CaCl_2$, and NaOH have been used (Aksu, 2005).

3.7. Modelling and simulation tools in biosorption

Biosorption modelling and simulation are aimed at experimental data analyses, understanding process mechanisms, predicting answers to operational condition changes, and optimizing processes. Various models for predicting and describing batch equilibria kinetics and of flow-through or continuous reactor operational data have been developed (Volesky, 2003b; Aksu, 2005; Crini and Badot, 2008; Liu and Liu, 2008; Vijayaraghavan and

Yun, 2008). To be able to compare pollutant uptake capacities of different types of biosorbents and the affinities of different substances for the same biosorbents, the adsorption process can be expressed as a batch equilibrium isotherm curve. It can be modelled by either mechanistic equations which can explain, represent, and predict experimental behaviour or empirical equations which can reflect the experimental curves but do not reflect the mechanism (Vijayaraghavan and Yun, 2008). In equilibrium sorption models providing some basic information on a given system, the sorbent accumulates the sorbate to equilibrium: the equilibrium value of sorbate uptake (q_e) by the biosorbent is plotted against the equilibrium (final) sorbate concentration (C) (Gadd, 2009). These range from simple single component models, of which the Langmuir and Freundlich versions are probably the most widely used with a high rate of success (Fig. 2), to complex multi-component models (Gadd, 2009; Pagnanelli et al., 2002). These models were originally derived for adsorption of gases in monolayers to activated carbon and are based on assumptions that are quite simplistic for biological systems. The Langmuir isotherm assumes a finite number of uniform adsorption sites and the absence of lateral interactions between adsorbed species. These assumptions are clearly invalid for most complex systems (Gadd, 2009). Some models reflect multilayer adsorption (de Rome and Gadd, 1987) although these are also usually derived from simple non-biological systems. The most commonly-used is the Brunauer–Emmett–Teller (BET) isotherm representing multilayer adsorption assuming that a Langmuir equation applies to each layer (Fig. 2) (Gadd, 2009). The simplest adsorption isotherm equation is linear adsorption where the distribution coefficient may only be effective over a narrow sorbate concentration range (Goldberg and Criscenti, 2008).
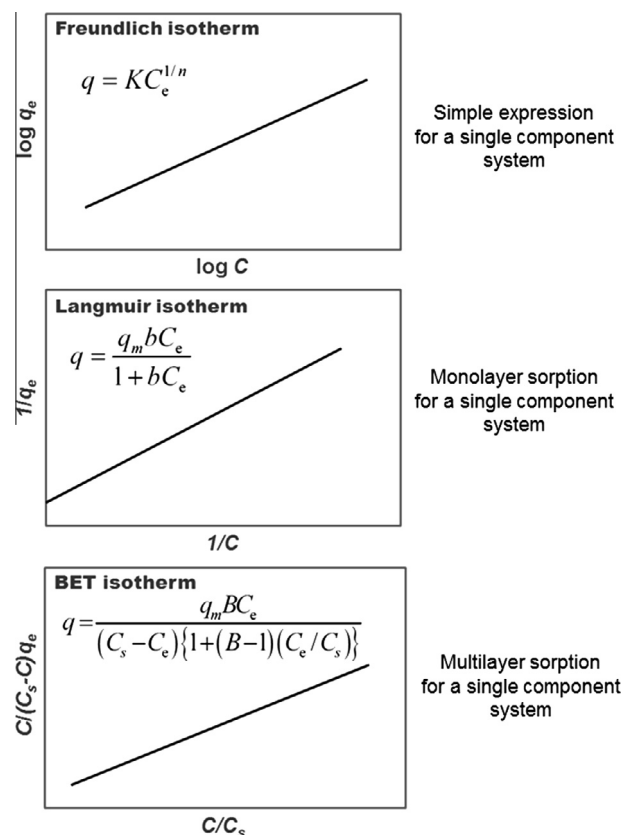
Freundlich isotherm

$$q = KC_e^{1/n}$$

Simple expression for a single component system

(x-axis: log C; y-axis: log q_e)

Langmuir isotherm

$$q = \frac{q_m b C_e}{1 + b C_e}$$

Monolayer sorption for a single component system

(x-axis: $1/C$; y-axis: $1/q_e$)

BET isotherm

$$q = \frac{q_m B C_e}{(C_s - C_e)\{1 + (B-1)(C_e/C_s)\}}$$

Multilayer sorption for a single component system

(x-axis: C/C_s; y-axis: $C/(C_s - C)q_e$)

Fig. 2. Equations and graphical representation of three of the most common adsorption isotherms used in biosorption studies: Freundlich, Langmuir and Brunauer–Emmett–Teller (BET) isotherms (adapted from Gadd, 2009; Park et al., 2010).

However fitting biosorption data to adsorption isotherm equations provides no information about the mechanisms, and should be considered simply as numerical relationships used to fit data. Use of these equations for prediction of metal adsorption behaviour under changing pH, ionic strength, and solution metal concentration is impossible (Goldberg and Criscenti, 2008). Application of adsorption isotherms may also be inadequate when precipitation of metals occurs although the Langmuir isotherm has sometimes been applied to such cases despite being theoretically invalid (Gadd, 2009).

The description of the kinetics of biosorption demonstrating the rate of solute bonding to the surface of biosorbents is complex due to the many facets of the process (Park et al., 2010). Intraparticle diffusion has often been shown to be an important factor in determining the attainment of equilibrium in immobilized biosorbents (Vijayaraghavan and Yun, 2008). The widely used Weber–Morris intraparticle diffusion model describes well the kinetics of biosorption for the first 10 min of the process (Michalak et al., 2013).

The common use of the volumetric concentration of adsorbate in the Langmuir isotherm equation without any theoretical consideration has eventually led to misapplication of the Langmuir isotherm equation in calculating ΔG in thermodynamic studies (Park et al., 2010). The use of molar terms in any comparative
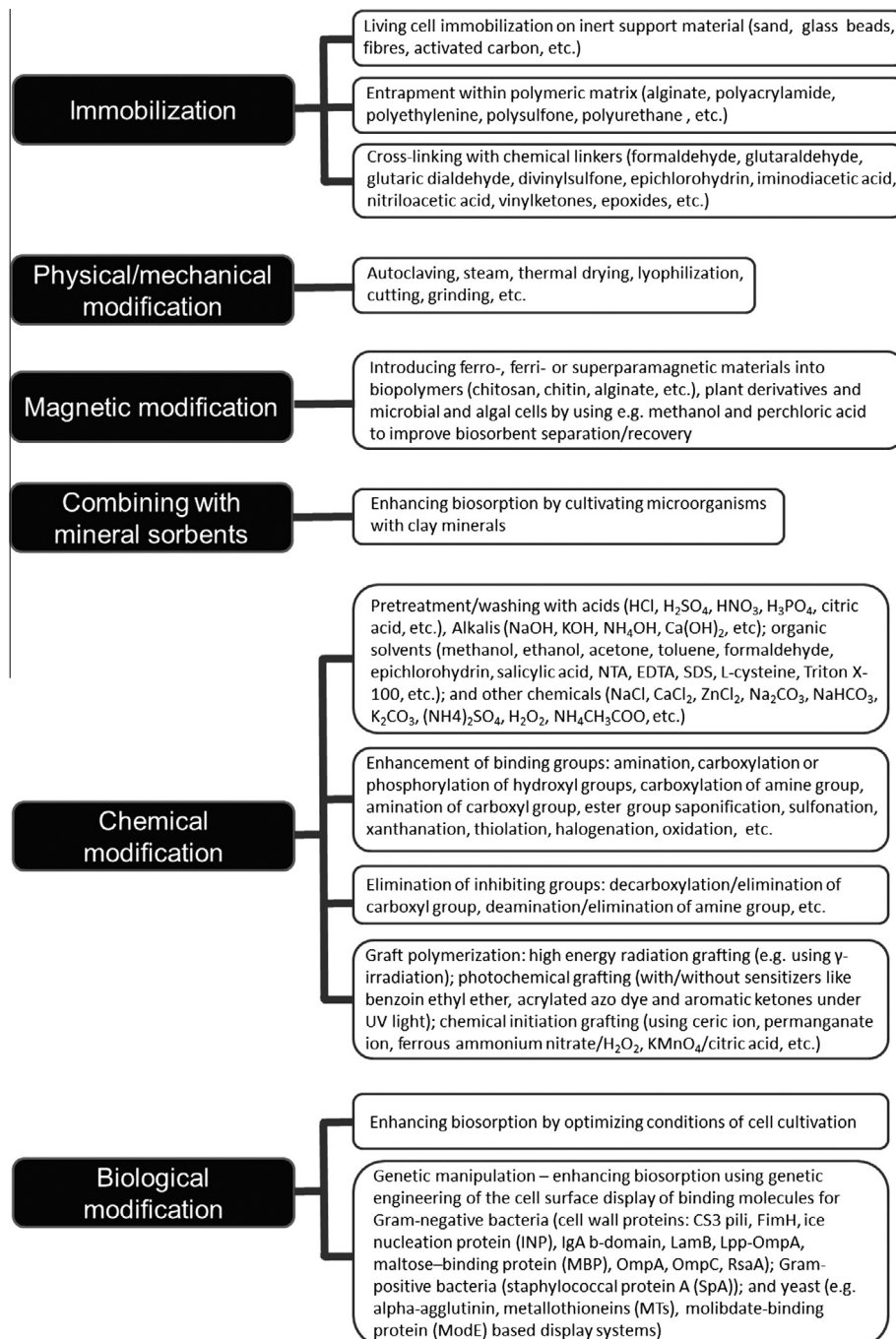
Fig. 3. Manipulations of biomass to improve biosorptive capacity and separation/recovery (after Fomina and Gadd, 2002; O'Connell et al., 2008; Vijayaraghavan and Yun, 2008; Wan Ngah and Hanafiah, 2008; Gadd, 2009; Park et al., 2010; Safarik et al., 2011; Kuroda and Ueda, 2011; Li and Tao, 2013).

and mechanistic studies should therefore be favoured in biosorption modelling.

Other problems with many isotherm and kinetic studies of biosorption include the use of unrealistic high sorbate concentrations compared with an industrial or environmental context, unattained equilibrium uptake values, complete removal of sorbate from solution which may occur over a wide concentration range for a given biomass concentration, possible changes in solution chemistry, and nucleation, deposition and precipitation phenomena (Gadd, 2009). Probably, due to their relatively simple nature, a great many batch biosorption studies are published in the literature for all kinds of biomass, metals and other substances. Most of them, unfortunately, contain little novelty or contribution to the field. Furthermore, much needed mathematical expression of biosorption models with strong theoretical characteristics is complicated by the complexity of the biosorption process and uncertainties about mechanisms and the application of biosorption isotherms may remain questionable in many studies (Liu and Liu, 2008).

Surface complexation models have an advantage in giving the process predictions and insight into biosorption mechanisms by providing information on stoichiometry and the reactivity of adsorbed species and an equilibrium approach that defines surface species, chemical reactions, mass and charge balances (Goldberg and Criscenti, 2008). They may require independent experimental determination of adsorption mechanisms using sophisticated techniques e,g, FTIR, NMR, XAS which have been used only in a small number of biosorption studies (Gadd, 2009).

Batch studies often precede continuous dynamic studies where the most effective approach is usually considered to be a flow-through fixed-bed bioreactor, with efficacy being characterized by means of break-through points that occur when column contents become saturated with the sorbate (Volesky, 1990, 2001, 2003a, 2003b). Various models are used to describe fixed-bed columns, including the Bohart-Adams, Thomas, Wolborska, Yoon-Nelson, Modified dose–response, and Clark models (Park et al., 2010). Bohart-Adams and Thomas models have been widely applied to determine the characteristic parameters during the biosorption of a target pollutant (Volesky, 2007; Vijayaraghavan and Yun, 2008). These models have primarily originated from research on activated carbon sorption, ion exchange, or chromatographic applications (Volesky, 2007; Vijayaraghavan and Yun, 2008). A column model predicting breakthrough curves of each element in a multicomponent system has been developed by Volesky (2003b, 2007). Nevertheless, in the industrial context, much more modelling and simulation work is still required to scale up biosorption applications and to reach the necessary level of technology readiness.

4. Manipulation of biosorbents

The different ways to manipulate biomass to improve various aspects of biosorption have been described by many authors and are summarized in Fig. 3. In terms of scaling up the biosorption process, the use of freely-suspended microbial biosorbents has some disadvantages including small particle size, low density, poor mechanical strength, and little rigidity. These cause problems in column processes such as difficulties in solid–liquid separation, biomass swelling, clogging, poor regeneration/reuse: the use of immobilized biomass particles in packed- or fluidized-bed reactors may minimize these disadvantages (Vijayaraghavan and Yun, 2008; Gadd, 2009; Park et al., 2010). Alternative means of immobilization, when applicable, could be the use of exceptionally rigid biomass (e.g. seaweeds) or separation of sorbate-loaded biomass via flotation (Park et al., 2010). Another approach simplifying biosorbent separation from aqueous solution or suspension is the

preparation of magnetically-responsive biocomposite materials (Safarik et al., 2011). Because the biosorption process primarily occurs on the surface of the biomass, surface modification can greatly alter biosorption efficiency (Vijayaraghavan and Yun, 2008; Wan Ngah and Hanafiah, 2008). Physical/mechanical methods of modification are usually simple and inexpensive, but are generally less effective than chemical modification. Vast improvements in the biosorptive capacity of a biosorbent can be obtained through chemical enhancement or modification of functional groups (Vijayaraghavan and Yun, 2008; Wan Ngah and Hanafiah, 2008). An efficient way to introduce binding groups onto the surface of a biosorbent is the grafting of long polymer chains onto the surface of raw biomass (O'Connell et al., 2008). Improvement of biosorptive capacity, rigidity and pellet formation was also observed for microbial biomass grown with certain clay minerals (Fig. 4) (Fomina and Gadd, 2002). Biological manipulations such as simple optimization of culture growth conditions or by using genetic engineering techniques could also enhance biosorptive capacity (Fomina and Gadd, 2002; Kuroda and Ueda, 2011; Li and Tao, 2013).

Despite apparent great potential of manipulation and surface modification techniques for biosorption, these increase the commercial cost of the biosorbents closer to the price range of man-made ion-exchange resins compromising the biosorbents' low-cost as their major advantage. Additionally, most manipulations raise a number of environmental and health and safety issues such as the use of: (i) aggressive and hazardous chemicals in physical and chemical manipulations and modifications; (ii) high energy electro-magnetic radiation in graft polymerization; (iii) potentially harmful microorganisms and controversial genetically-modified organisms in biological manipulations.

5. Critical assessment of biosorption application and perspectives

Biosorption as an interdisciplinary branch of science and technology emerged to provide a low cost treatment method with a "low tech" and environmental approach. Because of the apparent promising potential of biosorption including low operating costs, high efficiency and minimization of the volume of chemical and/ or biological sludge to be handled. a number of proposed processes have been patented for commercial application (Table 2). Pilot installations and a few commercial scale units have also been constructed (Tsezos, 2001). However, despite unquestionable progress made over decades of research, most biosorption processes are still at the laboratory scale.
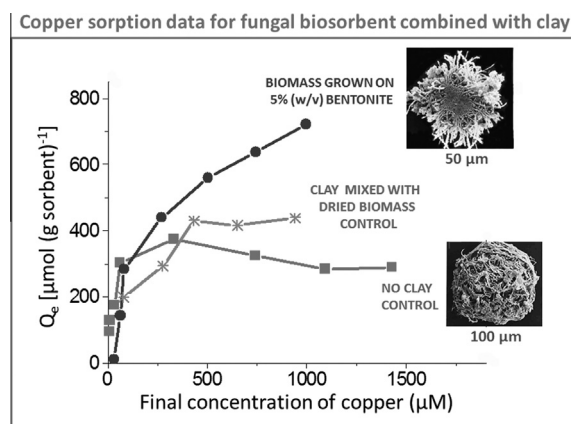

Fig. 4. Improved copper biosorptive capacity for biomass of the melanin-forming fungus *Cladosporium cladosporioides* grown on bentonite. Insets: scanning electron micrographs of fungal pellets (adapted from Fomina and Gadd, 2002).

Biosorbents that have been developed as commercial products for removing/sequestering metals from aqueous solutions include: AlgaSORB™ manufactured from a fresh water microalga, *Chlorella vulgaris*, immobilized on silica; B.V. Sorbex Biosorbent manufactured from a variety of sources including macroalgae; AMT-Bioclaim™ manufactured from a *Bacillus sp.* immobilized with polyethyleneimine and glutaraldehyde; Bio-Fix Biosorbent manufactured from a variety of sources including algae immobilized in porous polypropylene beads; and RAHCO Bio-Beads prepared from a variety of sources including peat moss immobilized within an organic polymer. However, these products have not been commercially successful in a sustained context (Vijayaraghavan and Yun, 2008; Park et al., 2010). It is important to analyse the possible reasons underlying lack of commercial success.

One reason is, generally, the low technology readiness level, including a poor understanding of the mechanisms, kinetics and thermodynamics of the process. This, for example, hindered the adequate assessment of process performance and limitations for AlgaSORB™ and AMT-Bioclaim™ processes commercialized in the early 1990s (Kotrba, 2011). Even the most technologically mature B.V. Sorbex Biosorbent is not yet a commercially-proven technology (http://www.bvsorbex.net/sx.htm). Another reason is obviously related to the existence of established and successful competing technologies of physical and chemical treatments of metal pollutants such as ion exchange, activated carbon and metal phosphonate hybrid mesostructure adsorption, chemical precipitation, oxidation/reduction methods, electrocoagulation, electrodialysis, ultrafiltration, reverse osmosis and solvent extraction (Arief et al., 2008; Gadd, 2009; Li and Tao, 2013; Lin and Ding, 2013). Some disadvantages including high costs, incomplete metal removal, high reagent and energy requirements, and generation of toxic waste products have often been used as the basis for

Table 2
A list of patents related to biosorption.

Year	Title of the invention	Number
1973	Apparatus for the biological treatment of waste water by the biosorption process	GB1324358
1973	Sorbent and method of manufacturing same	US3725291
1977	Process of treating mycelia of fungi for retention of metals	US4021368
1978	Method of treating a biomass	US4067821
1981	Microbiological recovery of metals	US4293333
1981	Process for recovering precious metals	US4289531
1982	Separation of uranium by biosorption	US4320093
1987	Process for the separation of metals from aqueous media	US4701261
1987	Treatment of microorganisms with alkaline solution to enhance metal uptake properties	US4690894
1987	Process for the separation of metals from aqueous media	US4701261
1988	Removal of contaminants	US4732681
1988	Biosorbent for gold	US4769223
1989	A process for the removal of thorium from raffinate	GB2228612A
1990	Metal recovery	US4898827
1990	Recovery of heavy and precious metals from aqueous solutions	WO9007468
1991	Removal of metal ions with immobilized metal ion-binding microorganisms	US5055402
1992	Process and apparatus for removing heavy metals from aqueous media by means of a bioadsorber	EP0475542
1992	Processes to recover and reconcentrate gold from its ores	US5152969
1992	Bioadsorption composition and process for production thereof	US5084389
1994	Ionic binding of microbial biomass	WO9413782
1994	Polymer beads containing an immobilized extractant for sorbing metals from solution	US5279745
1995	Method for adsorbing and separating heavy metal elements by using a tannin adsorbent and method of regenerating the adsorbent	US5460791
1996	Process for the removal of species containing metallic ions from effluents	US5538645
1996	Bead for removing dissolved metal contaminants	US5578547
1997	Polyaminosaccharide phosphate biosorbent	GB2306493
1997	Method for production of adsorption material	US5648313
1998	Biosorption system	WO9826851
1998	Biosorbent for heavy metals prepared from biomass	US5789204
1998	Bacteria expressing metallothionein gene into the periplasmic space, and method of using such bacteria in environment cleanup	US5824512
1998	Biosorption agents for metal ions and method for the production thereof	WO9848933
1998	Adsorption of PCBs using biosorbents	US5750065
1999	Hydrophilic urethane binder immobilizing organisms having active sites for binding noxious materials	US5976847
2000	Precipitating metals or degrading xenobiotic organic compounds with membrane immobilized microorganisms	US6013511
2000	Method for removing a heavy metal from sludge	US6027543
2001	Process for producing chitosan–glucan complexes, compounds producible therefrom and their use	US6333399
2002	Bioadsorption process for the removal of colour from textile effluent	WO0242228
2002	Biosorption system	US6395143
2002	Adsorption means for radionuclides	US6402953
2003	Biosorbents and process for producing the same	US6579977
2003	Biocomposite (Biocer) for biosorption of heavy metals comprises an inorganic gel containing immobilized dry-stable cellular products	DE10146375 A1
2004	Composite biosorbent for treatment of waste aqueous system(s) containing heavy metals	US6786336
2004	Heavy metal adsorbent composition	WO04022728
2006	A novel process for decolorization of colored effluents	WO06059348
2006	Process and plant for the removal of metals by biosorption from mining or industrial effluents	US20060070949
2007	Biosorption agents for metal ions and method for the production thereof	CA2282432 C
2007	Petroleum biosorbent based on strains of bacteria and yeast	US20070202588
2008	Process for the removal of metals by biosorption from mining or industrial effluents	US7326344
2008	Biosorption system produced from biofilms supported in faujasite (FAU) Zeolite, process obtaining it and its usage for removal of hexavalent chromium (Cr(VI))	US20080169238
2010	Use of *Rhizopus stolonifer* (Ehrenberg) Vuillemin in methods for treating industrial wastewaters containing dyes	US7658849
2010	Use of *Cunninghamella elegans* Lendner in methods for treating industrial wastewaters containing dyes	US7790031
2011	Use of *Rhizomucor pusillus* (Lindt) Schipper in methods for treating industrial wastewaters containing dyes	US7935257
2011	*Pseudomonas alcaliphila* MBR and its application in bioreduction and biosorption	US0110269169
2011	Bacterial strain for a metal biosorption process	US7951578

arguments supporting a cost-effective biological approach (Gadd, 1986; Eccles, 1999; Volesky, 1990). However, the market for the closest similarity to a biosorbent product, i.e. ion exchangers, is very strong and increasing reaching $16.5 billion/y world-wide while costs are around 800–1500 USD/ton ion exchange resins (Li and Tao, 2013). Ion-exchange resins can be made to have only one type of specific metal binding functional group of high affinity and are much more predictable for a given metal ion and suitable for selective recovery of target substances. The commercial success of ion exchange technology was achieved largely due its proven fidelity and predictability. However, because of the diversity of functional groups and their availability on biosorbents, the stability and predictability of the biosorption process remain problematic.

Important attributes to be considered for commercial biosorbents are capacity, selectivity, regenerability, mass transfer kinetics, and cost. Sorption capacity as the amount of sorbate taken up by the sorbent per unit mass or volume of the adsorbent is paramount for capital costs. Despite some selectivity limitations, modern inorganic or hybrid adsorbents like Ti- and Zr-phosphates have hundreds of times higher specific surface area and can provide a much higher capacity than microbial biomass (Lin and Ding, 2013). The lack of specificity and lower robustness of biomass-based systems compared with competing technologies are often cited as major reasons limiting biosorption commercialization (Eccles, 1999). Suspended biomass is not effective and durable in repeated long-term application (Gadd, 2009).

Two major arguments have been recently highlighted supporting commercialization of biosorption as a clean-up technology: low cost of the biosorbent and increasingly stricter environmental regulations (Volesky, 2007; http://www.bvsorbex.net/plan/all.pdf). However, the paradox is that any attempt to overcome the various problems associated with biosorbents contradicts these arguments. As previously discussed, manipulation of biosorbents to improve sorbent separation and durability, e.g. immobilization, or chemical and biological modification of biomass to improve sorption capacity and specificity not only significantly increase price but also raise serious environmental questions about the generation of toxic wastes and biological hazards. Needless to say, there have been always questions regarding the safe disposal of loaded biosorbent, sorbate recovery, and regeneration or replacement of the biosorbent.

All these issues create a need for other commercially-sound applications of biosorption process technology. It has resulted in suggestions for the use of biosorption for recovery of precious metals and, more recently, of pharmaceuticals (proteins, antibodies, and peptides) (Volesky, 2007; Kaushik and Malik, 2009; Park et al., 2010). However, heat resistance of the biosorbents and the release of impurities during autoclaving and purification must be considered for pharmaceutical applications. A rapidly growing research area of biosorption application is in the treatment of organic pollutants, e.g. dyes. There are still no systematic or comparative studies taking into account the physico-chemical properties of the different pollutant dyes and the effects of their chemical structures on biosorption capacity (Crini and Badot, 2008). Another new niche application of the passive biosorption process is its use for the enrichment of microelements, biological feed supplements and fertilizers, which appears straightforward: supplements obtained this way have already demonstrated good results on animals (Michalak et al., 2013; Saeid et al., 2013). Future directions may also include addressing problems with real industrial effluents containing multiple pollutants and the applications of hybrid technologies.

As mentioned previously, there has been poor communication and loose terminology in use in the field of biosorption, which together with the great complexity of this phenomenon has complicated the process of prioritising fundamental scientific and commercial tasks and creating clear messages for industry. Unfortunately, it is doubtful whether the dramatic rise in published output on biosorption has significantly improved knowledge of the process, or aided any commercial exploitation (Gadd, 2009). It would be probably beneficial to use mutually agreeable specific and clear terms and definitions in new emerging technologies based on biosorption, e.g. immune-adsorption in the case of monoclonal antibodies.

Biosorptive processes may contribute to any form of primary or secondary biological treatment process for aqueous waters and process streams including domestic, municipal and industrial wastes, and in some circumstances, solid wastes. Some examples have been described where organic and inorganic transformations are closely linked to biosorptive removal, e.g. rotating biological contactors to treat dilute metal-containing mine waste streams (Gadd and White, 1993). Despite the apparent advantages of biosorption, it is ironic that many established and novel biotreatment methods for pollutants rely on living cell systems (Gadd and White, 1993; Malik, 2004). It is the unique biogeochemical properties of certain living micro- and macro-organisms (e.g. plants) (Gadd, 2007, 2009, 2010; Gadd and Fomina, 2011) that can provide commercially unique selling points to compete with physico-chemical and engineering competitors in the clean-up market. Biosorption as a technology is still developing and commercial success will depend on better understanding of this process governed by a pragmatic rationale of its commercial development and potential applications.

6. Conclusions

Decades of biosorption research have revealed the complexity of the process, its dependence on physico-chemical and biological factors, and uncertainty about the mechanisms involved. Biosorption has not been commercially successful and its traditional direction as a low-cost and environmentally-friendly pollutant treatment method should be re-considered. Attempts to improve biosorption (capacity, selectivity, kinetics, re-use) by physico-chemical and biotic manipulations increase cost and may raise environmental issues. Pragmatic market and cost rationale should be considered in directing further research into alternative applications such as organics removal, recovery of pharmaceuticals, valuable metals and elements, and the manufacture of enriched feed supplements and fertilizers.

Acknowledgements

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