Review

Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions

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ABSTRACT

For the past few decades, biosorption has been widely investigated for the removal of different contaminants in aqueous media. A number of biomasses of different genre have been identified to possess good biosorption capacity. Insights into biosorption mechanisms have been provided by various researchers in order to develop a fundamental scientific understanding of the biosorption process. However, biosorption has not been employed widely for its large-scale commercial applications. The key factors that affect the growth and evolution of biosorption as a practical technology for decontamination of wastewaters include, (1) lack of investigations on multi-component solutions and wastewaters with complex matrix effects, (2) incomplete understanding of physico-chemical characteristics of biomasses of different types, (3) lack of studies to improve the performance of biosorbents through surface functionalization, and (4) non-integration of biosorption in wastewater/water treatment plants. This critical review aims to identify and discuss the practical limitations of biosorption and provide future research directions to make biosorption a technologically viable process with emphasis on selection and modification of biomasses to suit desired treatment applications, identify appropriate operation modes for large-scale applications of biosorption, and perform techno-economic evaluation of overall biosorption processes.

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1. Introduction

Metals play an important part in the life processes of living organisms. Several metals and metalloids, which are essential for biochemical and cellular processes, such as Zn, Cu, Fe, and Mg, are taken up by living organisms to different extents. They may be required for normal function, but excessive doses can become toxic (O’Connell et al., 2008; Smith et al., 2015). Other metallic elements with no biological role can enter the system and damage the performance of normal processes (Maestri et al., 2010). Toxicity essentially occurs due to displacement of vital metal ions from their native binding sites, or due to ligand interactions (Bruins et al., 2000).

Metals can enter the environment through different pathways, of which, anthropogenic sources play a significant role of increasing metal concentrations (Hermanson, 1991; Bhattacharya et al., 2015). In particular, modern industries are, to a large extent, responsible for pollution of the environment. The wastewaters emanating from various industries contain elevated concentrations of metals, and these are often disposed directly without any treatment into river or other water sources. This is a greater risk as these water sources are usually considered as the basis for drinking water. In most developing countries, treatment plants to decontaminate trace metals are generally not available (Malik, 2004). This, consequently, exposes every end-user to unknown quantities of pollutants in the water they consume.

Several remediation techniques to remove metal ions from aqueous solutions are available, which range from traditional physico-chemical methods to emerging bioremediation methods. The most commonly used physico-chemical processes include chemical precipitation, reverse osmosis, oxidation/reduction,
Electrochemical treatment and filtration (Kurniawan et al., 2006; Fu and Wang, 2011; Meng et al., 2012). Bioremediation methods include bioaccumulation, biosorption and phytoremediation. These methods are environmentally-benign, free of secondary pollution, and have low-costs, and have therefore gained significant attention to remediate industrial wastewaters. In particular, biosorption was identified as a potent bioremediation method which is comparable to the well-established ion-exchange resin-based treatment method for the removal of metal ions (Volesky, 2007).

Biosorption can be defined as the passive uptake of pollutants by dead or inactive biological materials through different physico-chemical mechanisms (Vijayaraghavan and Yun, 2008). Mechanisms of metal removal usually include physical adsorption, ion exchange, chelation, complexation, and micro-precipitation (Veglio and Beolchini, 1997; Abdolali et al., 2014). Since biosorption involves a variety of metabolism-independent processes taking place essentially in the cell wall, the mechanisms responsible for the metal binding differ according to the biomass type. Biosorbents that are commonly used for removal of metal ions include algae (fresh and marine), fungi, bacteria, industrial wastes, agricultural wastes and other polysaccharide materials. These biosorbents show good removal efficiency toward different metal ions. Several review articles discussed the performance of these biosorbents in metal biosorption (Kapoor and Viraraghavan, 1995; Crini, 2005; Davis et al., 2003; Vijayaraghavan and Yun, 2008; He and Chen, 2014; Kumar et al., 2015). It should be noted that most of the published studies in biosorption dealt with the removal capacity of a particular biosorbent toward a single metal ion in synthetic solution under laboratory conditions.

However, contaminated waste streams often comprise several metal ions with different concentrations. As a result, the performance of a biosorbent toward a metal ion of interest in a complex aqueous medium is highly compromised due to competition between metal ions (Vijayaraghavan and Yun, 2008). Consequently, the knowledge of how one adsorbate may influence the binding of another is necessary. Most of the past studies evaluated the performance of biosorbents with a synthetic solution containing a metal of interest based on which recommendations were made for treatment of real industrial effluents. However, the behavior of biosorbents tends to differ in a multi-component system (Saeed et al., 2005; Vijayaraghavan and Balasubramanian, 2010). For instance, industrial wastewaters often contain a large amount of light metal ions (high total dissolved solids (TDS)) in addition to metal ions of interest. In those cases, the biosorption of solutes of interest not only depends on the biomass surface properties and physico-chemical parameters of a solution such as temperature and pH, but also on the number of other contaminants and their relative concentrations (Vijayaraghavan et al., 2006). Thus, biosorption becomes highly competitive where one solute competes with others to get biosorbed.

The competitive biosorption of multiple chemical components is an important aspect to be considered for successful application of this remediation technique to industrial effluents with a complex matrix. However, only few application studies have been conducted in a systematic manner to evaluate the versatility of biosorption (Tsezos, 2001). Therefore, for development of the next generation biosorption technologies for practical applications, it is important to synthesize the current knowledge available in the field of biosorption. This review brings together the past and recent advances in the development and application of biosorption technologies, suggestions to synthesize a new breed of practical biosorbents and strategies to develop stand-alone or hybrid biosorption technology for practical wastewater treatment applications.

2. Current status of metal remediation technologies

Sources of surface water pollution can be broadly grouped into two categories: point and non-point source pollution (Young, 1981; Ongley et al., 2010). Pollution originating from a single source such as a discharge pipe from an industry or a sewage plant is point source pollution. On the other hand, pollution that originates from multiple sources is non-point source pollution. Non-point pollution occurs as water originates from natural processes (such as rainfall or snow melt), moves across the land or through the ground and picks up natural as well as anthropogenic pollutants, which can then be deposited in lakes, rivers and other water sources. Both point and non-point pollution are serious problems and should be addressed. Heavy metals represent one of the major contaminants in both sources of pollution. As these metals found many applications in industries and even in daily uses, their presence in water streams is of no surprise.

Industries such as electroplating, mining, tanning, metal-finishing, electronic-circuit, steel and aluminum, produce large quantities of wastewaters containing metals (O’Connell et al., 2008). Electroplating industries, which are one of the main causes of contamination of the natural environment with metal ions, are also one of the complicated wastewaters to handle (Islamoglu et al., 2006). This is due to the presence of a variety of metal ions along with counter anions, surfactants, brighteners and organic/inorganic addition agents. The concentration of metal ions also varies and depends upon the type of chemical operations, size and shape of the surfaces, and on the washing system applied (Bodzek et al., 1999). For example, Agarwal et al. (2006) reported that in chrome plating industries, the concentration of total chromium varied from 78 to 286 g/L in an electrolytic bath stream to 0.1–0.9 g/L in a diluted rinse discharge stream. Whereas, Dousouvi et al. (2005) identified that raw mining water from Kank locality found to consist of very high concentrations of 5.8 g Fe/L, 1.6 g Zn/L and 54 mg As/L along with 17.7 mg SO42−/L. For treatment, most of the metal-based industries prefer cheaper technology such as precipitation (Eccles, 1995). Precipitation of metals with lime, sulfide, and caustic soda is the most common method for metal removal (Kurniawan et al., 2006). However, precipitation is not selective and produces large quantities of solid sludge. Due to these constraints, other treatment processes such as ion-exchange (Jha et al., 2008), membrane (Cartwright, 1985; Cassano et al., 2001) and activated carbon adsorption (Kurniawan et al., 2006; Hadi et al., 2015) are getting popular in wastewater scheme. These techniques are firmly established, well understood and represent significant capital investments by industry. Several research reports demonstrated the potential of ion-exchange (Cavaco et al., 2007, 2009; Jha et al., 2008; Al Abdugalder et al., 2013), membrane (Cassano et al., 2007; Das et al., 2007; Feini et al., 2008; Carrera et al., 2009) and activated carbon (Suzuki et al., 1996; Mohan et al., 2008) techniques for the decontamination of metal-bearing industrial effluents.

Contaminated water originating from non-point source pollution usually comprises low concentrations of contaminants, but in high volume. One of the important sources of non-point pollution includes stormwater runoff, which has the potential to change the health of water bodies, impacts on aquatic habitats, recreation and aesthetics, or cause algae to grow uncontrollably (NSW-EPA, 1998). Pollutants found in stormwater runoff originate from a number of sources, which includes washings of road and roof surfaces, parking lots, motor vehicles, building materials, air pollutants, exhausts from industrial operations, and agricultural lands (Asaf et al., 2004). Stormwater runoff, because of the high contaminant level, is considered toxic and unacceptable for dispose into receiving surface waters without some treatment (USEPA, 1983). Typically, a
number of devices, collectively known as structural Best Management Practices (BMPs), are used to treat these contaminated runoffs. However, the majority of these structural BMPs (e.g., wet ponds) rely exclusively on physical separation processes such as sedimentation. Thus, only a majority of the suspended solids and associated pollutants are removed without any significant decrease in colloidal and truly dissolved pollutant fractions such as metal ions (Genc-Fuhrman et al., 2007). Hence, there is a need for secondary treatment of stormwater after passing through the BMPs. Since filtration of stormwater can efficiently remove colloidal and truly dissolved metal fractions, sorption technology can be a practical choice as a secondary treatment or hybrid technology along with BMPs. Some interesting reports highlighted the possibility of adsorption and ion-exchange techniques for the treatment of stormwater runoff (Pitcher et al., 2004; Genc-Fuhrman et al., 2007; Reddy et al., 2014).

3. Biosorption technology

With new discoveries of several biosorbents of different origins, biosorption is now a mature technology for removal of heavy metals. However, biosorption is mostly lab-restricted owing to lack of application studies. The diverse types of biomass which excelled in the removal of metals from aqueous solutions under controlled laboratory conditions did not show much potential in practical applications (Vijayaraghavan et al., 2006; Kumar et al., 2008; Vilar et al., 2009; El-Sayed and El-Sayed, 2014). To overcome this practical limitation of the biosorption technology, few researchers altered the characteristics of biosorbents and investigated their potential under real-world conditions by employing metal solutions, which were either simulated effluents or real wastewaters (Pethkar and Palnikar, 1998; Akhtar et al., 2004). Compared to other established treatment technologies, reports in the literature dealing with demonstration of the suitability of biosorption to industrial effluents are limited. Among very few biosorption studies using synthetic effluents, Muraleedharan et al. (1994) simulated a monazite processing wastewater consisting of anions (40 mg F⁻/L and 400 mg PO₄³⁻/L), traces of heavy metals (2 mg Zn/L and 2 mg Pb/L) along with rare earth elements (50 mg/L) and thorium (5 mg/L). With an aid of a column loaded with Ganoderma lucidum, the concentrations of both rare earth elements and thorium could be decreased to undetectable levels. Vijayaraghavan et al. (2010a) prepared a stormwater runoff by adding several metals at different concentrations in real rain water, which included the following metals in mg/L: 52.4 ± 1.63 (Na), 51.2 ± 0.99 (K), 48.2 ± 0.99 (Ca), 51.7 ± 1.77 (Mg), 20.6 ± 0.07 (Mn), 4.96 ± 0.12 (Co), 4.85 ± 0.03 (Ni), 5.14 ± 0.13 (Cu), 4.39 ± 0.38 (Zn), 3.22 ± 0.13 (Cd) and 1.01 ± 0.01 (Pb). This study employed a crab shell-loaded packed column for the treatment of stormwater runoff and was able to operate the column for 192 h by treating 115 L of runoff without exceeding the permissible limit for each of the metal ions.

Several studies on metal removal from real contaminated waters using biosorption technique evolved in recent years. Table 1 summarizes the important results of the studies associated with the application of biosorption for the treatment of real metal-bearing wastewaters. Even though some results were far from perfect, biosorption showed potential to remove metal ions from complex effluents. Akhtar et al. (2004) utilized loofa sponge-immobilized biomass of Chlorrella sorokiniana in a packed column to treat a complex bicycle industry nickel-plating effluent. The columns effluents were retained nickel(II) with an uptake capacity of 43.1 ± 1.6 mg/g. Vijayaraghavan et al. (2006) treated nickel-electroplating industrial effluent comprising significant quantities of Pb, Cu, Fe, Na, K, Cl and SO₄²⁻ in a Sargassum wightii-loaded packed column, which exhibited a removal efficiency of 99.7% for Ni. In general, most of the studies focused on plating industrial effluents with metal ions such as Cr, Cu, Pb and Ni as the main targets. Also, the results were basically obtained through the batch mode of operation and effluent conditions were adjusted to achieve maximum biosorption.

In-depth analysis of these research reports (Table 1) also revealed that most of the effluent studies were performed to investigate the possibility of a biosorbent to remove a metal ion of interest. High biosorption uptake was not considered as a main criterion in effluent studies, and some biosorbents were recommended for industrial applications based on low removal efficiency of metals. No significant effort was made to optimize the biosorption process so that improved efficiency or specificity can be obtained. Other important factors such as biosorbent physical characteristics, availability and treatment costs have always been overlooked. Atkinson et al. (1998) highlighted the questions to be considered concerning the feasibility of a potential biosorbent for metal removal from the industrial effluents. These include effluent characteristics such as volume, type of contaminant and competitive ions, solution chemistry, pH and temperature adjustment, etc.; biomass characteristics such as availability, mechanical stability, regeneration ability, contaminant specificity and reaction kinetics, etc.; and process characteristics such as capital and operating costs, batch/continuous and land space requirements. Thus, this article now discusses the aspects needed to develop biosorbent for commercial applications and the feasibility of the biosorption process to suit industrial applications.

4. Preparation of biosorbents for industrial applications

Biosorbents are available under different classes ranging from fragile microorganisms to highly stable particles. Even though the main purpose of using biosorbents is to immobilize metal ions, they should be rigid enough to withstand extreme operating conditions employed during the process. Other factors such as materials and treatment costs, availability and continuous supply play a major role in the selection of biosorbents. Thus, the requisite characteristics of a suitable biosorbent for its successful application to industrial scale can be generalized as:

➢ Operation over wide range of pH, temperature and other physico-chemical parameters
➢ No secondary pollutants released
➢ Good stability under acidic/alkaline environments
➢ Good uptake capacity towards different ions
➢ Cost effective
➢ No pretreatment necessity
➢ Sequential removal of metal ions
➢ Easy desorption and reuse ability
➢ No requirement of chemical modification or immobilization
➢ Easy adaptability to different system designs

Even though these characteristics are desirable, different classes of biosorbents are available and not all of them possess all the desired characteristics for real applications. In those cases, biosorbents can be technically tailored to suit the needs. There are numerous steps associated with preparation of biosorbents for a particular process, which are discussed in following sections.

4.1. Selection of biosorbents

The foremost important step in preparation of biosorbents is the selection of a suitable biosorbent itself. Cost effectiveness is the main requirement of the biosorption process, and this requirement should be an important criterion to be considered for the selection...
<table>
<thead>
<tr>
<th>Type of effluent</th>
<th>Characteristics of effluent</th>
<th>Metal ions focused (mg/L)</th>
<th>Other ions/impurities present (mg/L)</th>
<th>Biosorbent</th>
<th>Operating conditions</th>
<th>Efficiency of the process (as uptake (Q, mg/g) or removal efficiency (Re, %))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery effluent</td>
<td>pH – 0.5</td>
<td>Pb – 110</td>
<td>–</td>
<td>Bael leaves</td>
<td>Batch (pH – 2.2)</td>
<td>RE – 25</td>
<td>Chakravarty et al., 2010</td>
</tr>
<tr>
<td>Battery manufacturing industrial effluent</td>
<td>–</td>
<td>Pb – 102 ± 3.6</td>
<td>Mn – 0.32 ± 0.02 Ni – 0.28 ± 0.01 Fe – 0.28 ± 0.01 Zn – 0.09 ± 0.05 Cr – 0.07 ± 0.01</td>
<td>Saccharomyces cerevisiae</td>
<td>Batch</td>
<td>Q – 55.7</td>
<td>Parvathi et al., 2007</td>
</tr>
<tr>
<td>Chrome electroplating effluent</td>
<td>–</td>
<td>Cr – 204</td>
<td>Cu – 0.29 Ni – 0.05 Fe – 0.26 Zn – 0.10</td>
<td>Saccharomyces cerevisiae</td>
<td>Batch</td>
<td>Q – 6.6</td>
<td>Parvathi and Nagendran, 2008</td>
</tr>
<tr>
<td>Electroplating effluent</td>
<td>pH – 6.7</td>
<td>Ni – 5.25</td>
<td>Na – 115.39 Mg – 73.27 Ca – 46.52</td>
<td>Loofa sponge-immobilized Chlorella sorokiniana</td>
<td>Column (F – 5)</td>
<td>Q – 43.1</td>
<td>Akhtar et al., 2004</td>
</tr>
<tr>
<td>Electroplating industrial effluent</td>
<td>pH – 7.5</td>
<td>Ni – 109</td>
<td>Pb – 4.5 Cu – 1.3 Fe – 1.6 Cl – 289 SO4 – 558 Na – 101 K – 84</td>
<td>Saccharomyces cerevisiae NCYC 1364</td>
<td>Multi-batch</td>
<td>All heavy metal ions below USEPA limit for treated effluents</td>
<td>Machado et al., 2010</td>
</tr>
<tr>
<td>Electroplating effluent</td>
<td>pH – 7.9</td>
<td>Ni – 52</td>
<td>Pb &lt; 0.1 Cu &lt; 0.1 Fe &lt; 0.9 Cl – 230 SO4 – 300 Na – 76</td>
<td>Sargassum wightii</td>
<td>Column (pH – 7.9)</td>
<td>Q – 15.1</td>
<td>Vijayaraghavan et al., 2005b</td>
</tr>
<tr>
<td>Electroplating wastewater</td>
<td>pH – 2.2</td>
<td>Cr(VI) – 47</td>
<td>Cu – 0.9 Zn – 239 Fe – 8.6 Ni – 32 CN – 16.0 SO4 – 450 PO4 – 0.1</td>
<td>Aspergillus niger</td>
<td>Batch</td>
<td>RE – 71.2 ± 2.9</td>
<td>Kumar et al., 2008</td>
</tr>
<tr>
<td>Gold ore mining effluent</td>
<td>pH – 9.0</td>
<td>Cu – 5.4</td>
<td>CN – 73 Fe – 2.1 Hg – 0.035 Pb – 0.34</td>
<td>Chitosan</td>
<td>Batch (pH – 6)</td>
<td>RE (Cu) – 97.8 RE (Zn) – 71.3 RE (Hg) – 98.0 RE (Pb) – 94.1</td>
<td>Benavente et al., 2011</td>
</tr>
<tr>
<td>Source/Industry</td>
<td>pH</td>
<td>Conductivity (CDTY)</td>
<td>TDS</td>
<td>TSS</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
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</tr>
<tr>
<td>ICP-OES effluent</td>
<td>1.1</td>
<td>6.98</td>
<td>3.77</td>
<td></td>
<td>0.36</td>
<td>2.08</td>
<td>0.43</td>
</tr>
<tr>
<td>Industrial effluent</td>
<td>7.5</td>
<td>1420 ± 3</td>
<td>5956 ± 22</td>
<td>2765 ± 8</td>
<td>9.6</td>
<td>9.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Laboratory effluent</td>
<td>0-1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Laboratory effluent</td>
<td>2.9</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Metal plating industrial effluent</td>
<td>1.6</td>
<td>11.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Metal plating industrial effluent</td>
<td>6.3</td>
<td>1.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Metallurgical effluent</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Storage battery industry</td>
<td>1.5–1.6</td>
<td>42</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Tannery effluent</td>
<td>7.9</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Tanning industry effluent</td>
<td>4.0</td>
<td>1770</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Tanning industry wastewater</td>
<td>8.2</td>
<td>0.45</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Note: Q = uptake (mg/g); RE = removal efficiency (%); T = temperature (°C); A = agitation rate (rpm); F = flow rate (mL/min); CDTY = conductivity (mS/cm); TDS = total dissolved solid (mg/L); TSS = total suspended solid (mg/L).
of biosorbents. While choosing the biomass for metal biosorption, its origin is a major factor to be taken into account. Several bacteria, fungal and yeast biomasses were found to possess an excellent biosorption capacity (Kapoor and Viraraghavan, 1995; Vijayaraghavan and Yun, 2008) due to their cell wall composition. However, research reports revealed that most of these biomasses were cultivated and used to examine their biosorption potential (Wang and Chen, 2006; Vijayaraghavan and Yun, 2008). Apart from increasing the cost, the cultivation increases the uncertainty in maintaining a continuous supply of biomass for the process (Tsezos, 2001). Another alternative is to use microbial wastes generated by food/fermentation and pharmaceutical industries. These wastes often create disposal problems for many industries. The possible reuse of these wastes for another process (biosorption) might be environmentally benign and also generate revenue for the industries. Some studies explored the possibility of employing microbial wastes of several industries with good success in metal biosorption. This type of biomass includes Saccharomyces cerevisiae (Kapoor and Viraraghavan, 1995; Carmona et al., 2012), Corynebacterium glutamicum (Vijayaraghavan et al., 2008; Song et al., 2013), and Streptomyces rimosus (Selatnia et al., 2004a,b). Another important heavy metal biosorbent is marine algae, otherwise known as seaweeds. Seaweeds are biological resources, and are available in many parts of the world. They are plentiful and very fast growing. In some parts of the world oceans, they threaten the tourist industry by spoiling pristine environments and fouling beaches (Volesky, 2001). Thus utilizing seaweeds as biosorbents can be beneficial to local economies. Apart from being rigid, seaweeds are proved to be an excellent biosorbent for different metal ions (Volesky and Holan, 1995; Romera et al., 2006). In particular, brown seaweeds are established biosorbents due to their alginate content (Davis et al., 2003). Apart from this, their macroscopic structure offers a convenient basis for the production of biosorbent particles suitable for sorption process applications (Vieira and Volesky, 2000; Vijayaraghavan et al., 2005a). However, it should be noted that seaweeds are not regarded as wastes; in fact, seaweeds are the only source for the production of agar, alginate and carrageenan. Therefore, utmost care should be taken while selecting seaweeds for biosorption process. Several investigators used low-cost industrial and agricultural wastes for heavy metal biosorption (Crimi, 2005; Sud et al., 2008; Abdolali et al., 2014). Among these wastes, crab shell (Lee et al., 1997; Evans et al., 2002), activated sludge (Hammami et al., 2007; Sulaymon et al., 2014), and rice husk (Wong et al., 2003; Chuah et al., 2005) deserves particular attention. Apart from being cheap and available for sustainable biosorbent production, these wastes generated from various industrial and agricultural activities found to possess excellent biosorption capacity and reasonable rigidity. Thus, while screening the biosorbents care should be equally given for its uptake capacity, cost, availability and mechanical strength.

4.2. Influence of biosorption operational parameters

The performance of a biosorbent not only depends on the chemical composition of biosorbent and nature of solutes, but also strongly influenced by operational parameters such as pH, temperature, ionic strength, co-ion concentration, sorbent size, reaction time, sorbent dosage and initial solute concentration. Considering that several reviews (Wang and Chen, 2006; Arief et al., 2008; Vijayaraghavan and Yun, 2008) covered the influence of these factors on biosorption, the present article only focuses on important parameters which require better understanding for further reading. Among the different operational parameters, pH is the most important one which significantly influences the biosorbent characteristics and solution chemistry. The binding site/functional group of a biosorbent, which plays a vital role in biosorption, strongly depends on the solution pH. Most of biosorbents, irrespective of nature, were found to be influenced by solution pH. For instance, in the case of brown seaweeds, a maximum biosorption always occurs in the range of 3–5 for almost all metal cations (Davis et al., 2003). This is because of the negatively charged carboxyl groups (pKa = 3.5–5.5) which are responsible for binding metal cations through the ion-exchange mechanism (Kratovitch and Volesky, 1998; Davis et al., 2003). For metal anions, strong acidic pH is often required to protonate the functional groups to increase binding capacity (Niu and Volesky, 2003; Niu et al., 2007). The solution pH also affects the solution chemistry of metals. At a higher solution pH, the solubility of metal complexes decreases enough for the precipitation to occur and this may complicate the sorption process. At a lower solution pH, most of the cationic metals exist in a stable state and are easy to biosorb. Overall, to enhance the biosorption capacity of the particular biosorbent, it is preferable to perform experiments at optimum pH.

Next, the presence of co-ions strongly influences the removal capacity of the biosorbent towards a particular solute. Since biosorption is a passive process in which several chemical groups or functional groups of biosorbent particles interact with the solute. This is because of the negatively charged carboxyl groups (pKa ¼ 5.5) which are responsible for binding metal ions through the ion-exchange mechanism (Kratovitch and Volesky, 1998). Not all biomasses possess a good biosorption capacity. Important reasons for competition among species include the nature and number of binding components of biomass as well as the nature and concentration of metal ions. Each functional group has a particular preference towards metal ions, and this affinity toward metal ions generally depends on the electronegativity and atomic mass of metal ions (Matos and Arruda, 2003; Tarley and Arruda, 2004; Vijayaraghavan et al., 2010b). Important reasons for competition among species include the nature and number of binding components of biomass as well as the nature and concentration of metal ions. Each functional group has a particular preference towards metal ions, and this affinity toward metal ions generally depends on the electronegativity and atomic mass of metal ions (Chong and Volesky, 1995; Baig et al., 2009; Vijayaraghavan et al., 2010b). In two-metal systems (Cu + Zn or Cu + Cd or Cd + Zn), Chong and Volesky (1995) found out that the performance of Ascosphyllum nodosum toward a particular metal ion affected the presence of other ions. Owing to the presence of europium, cerium and ytterbium, the biosorption of lanthanum onto Turbinaria conoides decreased by 75.8% on comparison with single La biosorption data (Vijayaraghavan et al., 2010b). Important reasons for competition among species include the nature and number of binding components of biomass as well as the nature and concentration of metal ions. Each functional group has a particular preference toward metal ions, and this affinity toward metal ions generally depends on the electronegativity and atomic mass of metal ions (Matos and Arruda, 2003; Tarley and Arruda, 2004; Vijayaraghavan et al., 2010b). Tarley and Arruda (2004) proved that owing to high electronegativity and atomic mass, Pb(II) biosorption onto rice husk was superior compared to Cd(II). Furthermore, it should be noted that the initial concentration of metal ions usually plays a major role in the uptake capacity of the biomass in multi-component systems. Considering that most biosorbents possess only limited active binding sites, one can always expect a reduced biosorption capacity towards a particular ion in multi-component systems compared to single-component.

4.3. Treatment of biosorbents

Most of the biomass needs some form of chemical treatment to perform well in biosorption. The treatment may vary with biomass type, but generally falls under chemical modification and immobilization.

Chemical modification of biomass is usually aimed to improve the biosorption capacity and selected affinity towards a metal ion of interest. Not all biomasses possess a good biosorption capacity. S. cerevisiae, a well-known fermentation industry waste, is a
mediocre biosorbent for metal ions (Wang and Chen, 2006). These biomasses can be chemically modified to enhance the uptake capacity (Vijayaraghavan and Yun, 2008; Soares and Soares, 2012). Chemical modification can also be aimed to improve the affinity of a particular biosorbent toward a metal ion of interest. Effluents often comprise several metal ions, and it is always desirable that a biosorbent can specifically bind desired target ions out of the mixture. By suitable modification of binding groups or chemical composition of biosorbents, affinity toward specific groups of metal ions can be improved.

In general, chemical modification procedures include pretreatment, binding site enhancement, binding site modification and polymerization. Biomass pretreatment basically aims to clean up biomass to enhance biosorption capacity. In particular, acidic pre-treatment is one of the most frequent methods to clean up biomass, i.e. to leach out light metal ions, odor-causing substances and other impurities. Other common chemical pretreatments include alkaline (Kapoor and Viraraghavan, 1998; Zhang et al., 2010), ethanol (Gökşungur et al., 2005; Zhang et al., 2010) and acetone (Bai and Abraham, 2002; Rehman et al., 2013) treatments of the biomass. In many instances, chemical pretreatments proved successful and resulted in improved biosorption capacity. Several investigators also worked on enhancing/modifying a particular functional group of the biomass and thereby increasing its biosorption potential (Vijayaraghavan and Yun, 2008). In particular, groups such as carboxyl, amine, phosphonate, sulfonate and hydroxyl present in the biomass were specifically focused. These treatment processes resulted in significant success for different type of biomasses (Luo et al., 2006; Nadeem et al., 2008). Various procedures are available for the enhancement of these functional groups on the biomass. In general, futile/less important functional groups can be converted into active binding groups via several chemical treatment methods (Marshall et al., 1999; Klimmek et al., 2001; Li et al., 2007; Zhu et al., 2008). One more efficient way of improving the biosorption capacity is the introduction of functional groups onto the biomass surface by grafting long polymer chains onto the biomass surface via direct grafting or polymerization of a monomer. Polyethyleneimine (PEI) which is composed of a large number of primary and secondary amine groups in a molecule, improved biosorption capacity when cross-linked on the sorbent (Deng and Ting, 2005; Song et al., 2013; Won et al., 2014). Similarly, polyampholyte, when grafted on the biosorbent surface, exhibited 15- and 11-fold increases in the uptakes of cadmium and lead, respectively, compared to the pristine biomass (Yu et al., 2007).

All microbial biomasses require immobilization to be employed in continuous biosorption applications. Microbial biomasses are basically small particles, with low density, poor mechanical strength and little rigidity. Even though these biosorbents possess high biosorption capacity, rapid equilibrium attainment, good particle mass transfer, they often suffer from various drawbacks such as biomass swelling, solid—liquid separation problems, difficulty to regenerate/reuse and development of high pressure drop when used in the column mode (Vegliò and Beolchini, 1997; Vijayaraghavan and Yun, 2008). Several authors confirmed that immobilization solves most of these problems and assists in developing microbial biomass as a practical biosorbent for applications (Kapoor and Viraraghavan, 1995; Volesky, 2001). The important immobilization matrices used for biomass include sodium alginate (Aksu et al., 1998; Bai and Abraham, 2003; Batool et al., 2014), polysulfone (Blanco et al., 1999; Beolchini et al., 2003), polyacrylamide (Bai and Abraham, 2003) and polyurethane (Hu and Reeves, 1997; Blanco et al., 1999) showed that polysulfone-immobilized Phormidium laminosum can be reused for ten consecutive biosorption/desorption cycles without apparent loss of efficiency, Vijayaraghavan and Yun (2007) immobilized C. glutamicum to solve the issue of slurry formation and subsequent blockage of liquid flow when used as free cells in packed column. However, care must be taken to avoid the practical problems generated during immobilization, in particular mass transfer limitations and additional chemical costs. After immobilization, biomass will be usually retained in the interior of the immobilized matrix; hence mass transfer resistance plays a vital role in deciding the biosorption rate.

4.4. Desorption and regeneration of biosorbent

Reuse potential of spent biomass is an important criterion for selection of any biosorbent. The possibility of biomass regeneration decreases the overall process cost and the dependency of the process on the continuous supply of the biomass. The success of a desorption process depends on the mode of removal mechanisms and the mechanical stability of the biomass. Considering that most of the biosorbents exhibit an ion-exchange mechanism for cationic heavy metal ions, a mild to strong acidic condition is sufficient for desorption. Usage of acids for desorption is also beneficial in a way that acidic solutions are one of the common wastes in almost all industries, and if biosorbents are employed in industrial wastewater schemes, these acidic solutions can be used to regenerate biosorbents. However, care must be taken that the integrity of biomass should not be affected by the acidic environment. Kuyucak and Volesky (1989) identified that exposure of cobalt-loaded Ascochyta nodosum to acidic solutions provided a good desorption efficiency, but resulted in significant biomass weight loss which in turn affected the biomass performance in the next cycle. Hence, these authors tested other desorbents and identified that 0.05 M CaCl₂ (in HCl) as an efficient desorbent. Other mechanisms such as complexation, chelation, and microprecipitation require extensive screening for efficient desorbent. Few chemical agents proved effective and non-detrimental for different biomasses, including EDTA (Hammaini et al., 2007; Oyetibo et al., 2015) and CaCl₂ (Kuyucak and Volesky, 1989; Davis et al., 2000). Several biomasses of macrostructures were confirmed to be stable without immobilization under strong acidic or alkaline conditions, and this includes crab shell (Vijayaraghavan et al., 2004, 2010a), some macro-algae (Zhao et al., 1999; Davis et al., 2000; Vijayaraghavan et al., 2005a), industrial wastes (Hammaini et al., 2007; Kiç et al., 2008) and agricultural wastes (Saeed and Iqbal, 2003; Mata et al., 2009). Thus, the selection of a suitable biosorbent for removal of metal ions from contaminated waters is a challenging task, and this selection should be based on several criteria, which directly influence the performance of a biosorbent in complex matrices, usually found in wastewaters.

5. Scale-up of the biosorption process to industrial applications

With the fundamental knowledge gained through decades of research on the biosorption process, more efforts should now be taken to apply biosorption in real-world situations. For this, a complete understanding on the behavior of biosorbents in real water matrix, types of treatment schemes and process costs involved is also important.

5.1. Behavior of biosorbents in real wastewaters

As discussed earlier, biosorption potential strongly depends on various parameters. However, considering the huge volume and complexity of the real wastewaters, it will be difficult to control the process to suit specific biosorbents. For instance, many biosorbents require an optimum pH to achieve their maximum uptake.
Nevertheless, in reality, considering the huge volume of wastewater involved, it is impractical to alter the pH of the solution. Other important factors include the complexity of aqueous solutions. Previous results summarized in Table 1 indicated that biosorbents can be applied to real wastewaters, but in-depth analysis indicates that the sorption potential of a biosorbent toward a particular metal ion endured in the presence of competing ions. Schneider et al. (1999) conducted an exhaustive study on copper biosorption onto Potamalgonet lucens and identified that several ions, including cyanide and EDTA, strongly affected copper biosorption. Vijayaraghavan et al. (2006) compared the nickel biosorption potential of S. wightii in aqueous and electroplating solutions, and the results revealed that the complex nature of electroplating solutions affected the nickel biosorption potential of Sargassum biomass because of the competition from other ions. Thus, biosorption may be suited when removal of metal ions is non-specific, i.e. general improvement of water quality rather than the removal of a particular ion. Nevertheless, the ability of the biosorption process to improve the water quality with respect of removal of toxic metals is again a difficult concept that has not been sufficiently addressed by the research community.

A comprehensive study targeting the overall improvement of the quality of effluents generated by the associated operations is still lacking in the literature. It is well-known that parameters such as pH, conductivity, TDS, odor, and contaminant concentrations are important to consider while evaluating the overall quality of waters. Biosorption can cause deviations of the above parameters from their targeted values. For instance, many sorbents exhibit biosorption via an ion-exchange mechanism, which in turn release light metal ions for the uptake of heavy metal ions. This usually leads to undesirable changes in pH, as well as in enhancement in conductivity, TDS and co-ion concentrations. Since mostly waste biomaterials are utilized as biosorbents, the final treated effluents are likely to have a bad odor. For example, solutions treated by seaweed and crab shell generally yield effluents of fishy odor. Hence, an additional treatment step is required to neutralize the effluents produced by biosorption treatments. Some biosorbents such as seaweeds tend to swell and block the liquid flow, especially in flow-through columns (Schiewer and Wong, 2000; Vijayaraghavan and Joshi, 2013). Furthermore, it is well known that most of the biosorbents have no or less affinity toward anions such as nitrate and phosphate. These anions are more common in effluents, and if not removed may lead to eutrophication and other undesirable effects on the environment (Jickells, 2005). Not all biosorbents possess good affinity toward anions due to the predominant anionic sites.

The problems associated with excessive leaching and swelling can be tackled through proper engineering techniques; however, the processing costs and practicability are of concern. Vijayaraghavan et al. (2010a) pretreated crab shells with 0.1 M HCl to avoid extensive leaching of calcium and magnesium ions; nevertheless, the effluent emanated from the crab shell column still comprised 202 and 105 mg/L of Ca$^{2+}$ and Mg$^{2+}$ ions, respectively. This problem of leaching cannot be completely avoided as the mechanism behind the crab shell biosorption results in calcium and magnesium leaching. Owing to this leaching, the authors also reported a sudden rise in effluent pH. In order to control swelling in seaweed biomass, Chu and Hashim (2007) employed polyvinyl alcohol to immobilize Sargassum biomass; and the results revealed that the immobilized seaweed was successfully performed in packed columns. Again, the costs associated with biomass preparation and ultimate disposal of immobilized polymer waste should be considered. One simple way of tackling the swelling issue of seaweeds in a packed column is to mix seaweed with inert and stable materials such as sand. This will improve the porosity inside the column and thereby enhance the solute flow pattern. Other limitations of biosorption over effluent quality need extensive research.

5.2. Mode of biosorption

To decrease the initial capital expenditure for process development and setup, biosorption should integrate with a current industrial setup. Biosorption can be conducted via several modes, and the most important ones include batch and continuous modes of operation. The use of biosorption in a batch mode requires a similar setup as that of the established precipitation technique, including a contact vessel, some mode of agitation (mechanical stirrers with attached impellers), piping and other peripheral equipment such as pH probes and level controllers (Atkinson et al., 1998). Similarly, the use of biosorption in a continuous mode can be incorporated with any of the fixed columns in industries. The selection of proper mode of operation is critical for the successful application of biosorption. A direct comparison between two modes of operation is difficult as it is strongly dependent on the type of biomass, the mechanism of removal, rigidity of biomass, kinetics, swelling properties, etc. Microorganisms have been widely used in batch modes; whereas immobilization is required to use them in the continuous treatment scheme. Some other biosorbents which come in the form of powder (fermentation wastes and sludge), seaweeds (owing to their swelling properties), and some fragile plant biomasses can be preferably used in a batch mode of operation in their native form. The major drawback of batch operations is the separation of biomass from the effluent after treatment. Usually filter press is employed for separation, and the solid wastes can be desorbed for usage in further cycles. Other biosorbents such as the crab shell, some rigid seaweeds or plant materials and immobilized biomasses are best suited for a continuous mode of operation. Zhao et al. (1999) highlighted Azolla filiculoides as an efficient biosorbent for zinc ions in the column mode, and the biomass can be regenerated and reused for six cycles. Vijayaraghavan et al. (2005b) proved that highly rigid crab shell particles were very effective in nickel biosorption and can be used in multiple sorption—desorption cycles for seven times. In general, many biosorbents have been identified to perform efficiently in both batch and column modes of operation.

5.3. Process costs and overall scheme of biosorption

While estimating costs of biosorption treatment, collection, transportation, processing of biosorbents and maintaining optimum conditions along with regeneration/ultimate disposal of biosorbents are major aspects to be considered. Other costs such as capital expenditure and plant running costs are excluded from discussion as they depend on the plant type and nature of wastewaters to be treated. Many researchers employed the waste products generated from industries and natural wastes for the removal of metal ions from aqueous media. Most of these biomaterials were found to be good metal biosorbents, including crab shells from seafood industries (Lee et al., 1997; Niu and Volesky, 2003), bacterial wastes from fermentation industries (Vijayaraghavan and Yun, 2007), activated sludge from wastewater treatment plants (Hammaini et al., 2007; Kulig et al., 2008), fungal wastes from food industries (Kapoor and Viraraghavan, 1995) and plant wastes (Sud et al., 2008). Most of these wastes are considered to have low commercial importance, causing nuisance to the respective sectors because of disposal problems. For example, the annual world requirements for citric acid are estimated at ~400,000 tons, which results in ~80,000 tons of Aspergillus niger mycelium waste per annum (Wu et al., 2005). Hence, the waste of A. niger generated
after fermentation can be obtained from respective industries free or at low cost. Transportation costs can be minimized if the source for wastes is close to treatment facilities. Preparation of biosorbents is usually a major cost associated with the biosorption process. As discussed earlier (Section 4.3), some sort of biomass pretreatment is always necessary to attain high biosorption. Nevertheless, care should be taken that this process tends to increase the overall process costs due to chemical usage as well as produce chemical wastes to be disposed. Next, most biosorbents require optimum treatment conditions to perform well (Section 4.2), of which practically only pH can be controlled in real operating conditions to maximize the performance of biosorbents. However, considering the volume of wastewater to be treated, it will be expensive to alter pH. Once a biosorbent is completely utilized in repeated cycles, the ultimate disposal should be addressed. Landfilling or chemical or thermal destruction techniques seem practical for biosorbents. It should be noted that both these methods are not cost-effective and environmentally-benign. Due to high tax, landfills are expensive; whereas destructive techniques such as incineration or exposure to strong acids/bases may lead to sludge disposal costs. Some exhausted biosorbents can also be reused for other applications. For example, seaweeds are proven to be good for biogas production (Nkemka and Murto, 2010) and compost for soils (Eyras et al., 2008). Therefore, once heavy metal ions are completely removed from the exhausted seaweeds, they can be reused for these applications.

5.4. Developing practical biosorbents to suit real applications

Ideally, a good biosorbent should possess most if not all the characteristics discussed in Section 4. However, identifying a biosorbent which possesses all characteristics is a difficult task. Some of the characteristics such as operations over a wide range of physical parameters and sequential removal of metal ions are formidable tasks that even established treatment techniques lack. However, achieving these characteristics through continued research may open up several fascinating areas for applications of biosorption. It should be noted that biosorbents may have to be technically tailored to achieve most of the desirable characteristics. Now, we will see the steps required to convert lab proven biosorbents to practical biosorbents. Let us also assume that the developed biosorbent will be used for the treatment of electroplating effluent in a fixed column mode as discussed below.

Fig. 1 illustrates the schematic flowchart for the preparation of biosorbents for the treatment of electroplating effluent. Only biosorbents which performed well in their native form for several heavy metal ions and can be obtained free or at low cost from respective industries/activities were taken into account. Regarding

![Fig. 1. Schematic flowchart for the preparation of biosorbent for the treatment of electroplating industrial effluent.](image-url)
the procedures for biomass treatment, readers are encouraged to refer Section 4.3.

The prepared biosorbent can be loaded in a fixed column and metal-bearing electroplating effluent is allowed to enter the column from the top (Fig. 2). The parameters of column operation are deliberately avoided in the present discussion as it varies with the type of biosorbents used and effluent characteristics considered. Therefore, based on the preliminary studies on kinetics, the flow rate of the influent can be fixed. Once metal-bearing wastewater makes contact with the biosorbent inside the column, the binding sites are expected to sorb metal ions and metal-free solutions flow downwards out of the column to reach container C2 (Fig. 2). Either acid (C3) or alkali (C4) will be added to C2 to neutralize the effluent to meet discharge standards. This process continues until the column eventually becomes saturated, i.e. metal concentration in the effluent gradually increases to reach allowable limit. Once saturated, the column operation should be stopped and the flow should be diverted for desorption process. Mild acids in C5 should be allowed to flow through the column to unbind the bounded metal ions, and the concentrated metal solution will be collected in C6. After the effluent pH of utility water reaches the inlet, the rinsing process can be stopped and the biosorption column will be ready for next cycle.

6. Possible applications of biosorption in other research areas

For a successful demonstration of biosorption for its potential practical applications, it is very important to find an appropriate wastewater matrix. Previous sections highlighted the possibility of applying biosorption technology as a part of an industrial wastewater scheme. It will also be advantageous to explore other environmental fields where biosorption can be more practical. Volesky (2001) stressed the importance of exploring other areas where heavy metals need to be extracted from relatively dilute solutions. One such waste solution is laboratory waste effluent. Until now, not much attention has been focused on laboratory wastewaters owing to their complexity. This is because, unlike industries and other routine workplaces, laboratories often conduct various processes and store the waste liquids over extended periods for disposal, which lead to highly complex and varied effluent of relatively unknown chemical composition. This is an appropriate research domain for exploring the use of biosorption treatment technology for decontamination where there is no specific requirement for metal-ions removal. The wastewaters originating from chemical laboratories usually consist of metal ions in microgram to lower milligram levels. However, they are typically above the permissible level to be directly disposed into sewers. In those instances, biosorption can be a good tool for remediation and reduce the metal concentrations below the permissible limits. Vijayaraghavan and Joshi (2013) successfully employed hybrid Sargassum–sand sorbent to clean-up ICP-OES (inductively coupled plasma-optical emission spectrometer) wastewater comprising 14 metal ions. The authors reported that a biosorbent-loaded packed column cleaned 58 bed volume of wastewater before breakthrough occurred. In some cases, where laboratory wastes comprise metal ions in the concentration ranges of the upper milligrams to gram, biosorbents utilizing the ion-exchange mechanism alone may not provide a complete remedy. A common and cheap method to handle highly concentrated metal wastewater is precipitation. Few biosorbents, especially crustacean shells, employ a micro-precipitation mechanism for metal removal. Vijayaraghavan and Balasubramanian (2013) used crab shells to treat laboratory wastewater comprising high concentrations of 8 heavy metal ions. These shell particles in powder form was shown to perform better.
than even traditional precipitants for metal removal. However, additional research is needed in this area to prove the efficiency of biosorbent powders for highly concentrated metal solutions. Moreover, it should be noted that the application of biosorption should not be restricted to point sources of pollution only. With a strong fundamental understanding of biosorption science and continued engineering research, biosorption can also prove to be a technological solution to non-point sources of water pollution. One of the potential areas where biosorption can be effective is in BMPs. A variety of stormwater BMPs have been developed in recent years. Among these technologies, biofiltration (also known as bio-retention systems and rain gardens) operates by following diverted runoff through dense vegetation followed by vertical retention systems and rain gardens) operates by using low-cost cultivation techniques, thus decreasing the process cost as well making the process eco-friendly. However, most of the work done on biosorption so far has been confined to laboratory-based investigations from the fundamental research viewpoint without sufficiently addressing the major challenges involved in the treatment of wastewaters. Only limited investigations were attempted to examine the suitability of biosorption to industrial effluents. It is well-known that comprehensive fundamental understanding of the key concepts affecting the performance of biosorption, including mechanisms of biosorption involved with different types of biosorbents, the relative influence of different experimental parameters affecting biosorption, modes of operation and biosorption capacity and other related phenomena has already been established. With this knowledge, further advances are needed to transform this highly effective technique into practical applications. In particular, scale-up of biosorption processes to various types of wastewaters in a continuous large-scale operation is on the horizon. Biosorption can find potential applications in areas where heavy metals need to be extracted from relatively concentrated solutions such as laboratory effluents, mining effluents or from dilute solutions such as urban runoffs and green roof runoff. Thus, more research should be focused on commercialization of biosorption in various fields. Specifically, cross-disciplinary inputs from biosorption researchers, wastewater treatment professionals, materials engineers and industrial communities will enhance the scope of ongoing research efforts on biosorption and will lead to development of the next generation biosorption-based treatment technologies in a cost-effective manner toward commercialization.

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References


Bai, R.S., Abraham, T.E., 2003. Studies on chromium(VI) adsorption-desorption using
Benavente, M., Moreno, L., Martinez, J., 2011. Sorption of heavy metals from gold mining wastewater by Bacillus sp. TIBTECH 16, 291.


Parvathi, K., Nagendran, R., Nareshkumar, R., 2007. Lead biosorption onto waste


Saeed, A., Iqbal, M., Akhtar, M.W., 2005. Removal and recovery of lead(II) from


