

REVIEW ON ARSENIC INDUCED TOXICITY AND BIOSORPTION OF ARSENIC AS A MODE OF REMEDIATION

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ABSTRACT

Arsenic (As) is one of the most toxic pollutants, which is responsible for the contamination of water around the globe and it poses a major risk to human health which includes many types of cancer like lung cancer, breast cancer, skin cancer, etc. Bioremediation is a science that amplifies natural biological action to remediate polluted groundwater and contaminated soil. Instead of using expensive remediation equipment to remove untreated toxic materials and dispose of them elsewhere, the bioremediation technique uses biological microbes to do cleanup work. Hence, there is a growing need for the development of a novel, efficient, eco-friendly, and cost-effective approach for the remediation of As which is increasingly added into the biosphere through geogenic or anthropogenic sources. The objective of this review is to understand, analyze, and document the status of biosorption technology and critically review the obstacles to its commercial success, and provide insights into future research. In this regard, we analyze biosorption as a prospective alternative to the conventional techniques which uses self-renewable biological agents as the reactor material and thus can potentially avoid the use of harmful chemicals. Biosorption is a type of bioremediation process which gives prominent results and waste products can be utilized again for the As removal purpose and then it can be disposed of without any harm to the environment. For biosorption, not only living organisms but residuals or dead bodies of microorganisms can also be used as biosorbents. On the grounds of the literary reports many microbes, particularly bacteria, fungi, and algae have shown enough potential; and these can be employed for biosorption of Arsenic. The biosorbing fungi like *Penicillium chrysogenum*, *P. purpurogenum*, *Saccharomyces cerevisiae* can remove approximately 50% of arsenic at an average pH of 5 and an average temperature of 25°C. According to many researchers, bacteria like *Arthrobacter* sp, *Bacillus* sp.KL1, *Bacillus* KL4, *Bacillus* sp.KMO2 are very important for biosorption of arsenic at near-neutral pH 6, and temperature 35°C with 75% efficiency. Algae like *Spirogyra hyaline*, *Cyanobacteria*, *Microcystis*, *Chlorella*, *Oscillatoria*, *Scenedesmus*, and *Pandorina*, etc. give a result of nearly 30% removal at average pH 5, temperature 25°C. Objective of this review is mainly focus on the characteristic of biosorption and the operating conditions like the sample's alkalinity, required dose, initial concentration, temperature, sorption isotherms, and sorption kinetics, etc. In all, the review provides an overview of arsenic induced toxicity and practical significance of potential biosorbents and biosorption technologies.

Keywords: Biosorption, Contamination, Microorganism, Remediation, Resistance, Kinetics

Abbreviation: As, arsenic; As III, arsenite; As V, arsenate

INTRODUCTION

Arsenic is a well known element which is widely present in the earth crust. This element is generally considered as a metal but it possess the properties of non- metals also ,thus is generally referred to as a metalloid (Humans, 2012). This metalloid is of potentially hazardous nature owing to its molecular toxicity and bio-accumulative potential in biotic systems. Arsenic generally enters the environment through mining activities, industrial discharge, and even from household disposal into nearby water bodies (Bhattacharya *et al.*, 2010; Banerjee *et al.*, 2013; Chakraborty *et al.*, 2017; Gautam *et al.*, 2014; Mukhopadhyay *et al.*, 2002; Nickson *et al.*, 2000; Nordstrom 2002; Smith *et al.*, 2004). Arsenic (As)

belongs to group VA, period 4 and block p of the periodic table and can exist in four oxidation states - 3(arsine), 0(elemental arsenic), +3(arsenite), and +5(arsenate) (WHO 2001; IARC2004).

It exists in form of various organic or inorganic compounds with the inorganic forms dominating in the environment. Amongst the inorganic forms As (III) shows 70% more toxicity as compared to As (V) (Pepi *et al.*, 2007; Taran *et al.*, 2013) because it has an affinity to bind with functional groups, like SH group (sulphydryl and thiol group) and imidazolium nitrogen of different bio-molecules (Krumova *et al.*, 2008).

The toxicity of arsenic has been reported around the globe with significantly high contamination in countries like Bangladesh, Australia, Canada, India, Vietnam, Latin America, Taiwan, and many other countries including all southeast area (Mandal *et al.*, 2002; Podgorski *et al.*, 2017; Rodríguez-Lado *et al.*, 2013; Srivastava *et al.*, 2012; Tseng 2005). Arsenic contamination is stated as the, "largest poisoning of a population in history" (Vaughan 2006). The Agency for Toxic Substances and Disease Registry (ATSDR-2007) has included arsenic in the list of 20 most hazardous substances (Rensing and Rosen, 2009).

The International Agency for Research on Cancer classifies As in group 1, which includes known human cancer promoters (IARC 2004, 2012). The WHO/UNICEF Joint Monitoring Program for Water Supply, Sanitation, and Hygiene monitors progress towards global targets on drinking water. Under the new 2030 Agenda for Sustainable Development, the indicator of safely managed drinking water services calls for tracking the population accessing drinking water which is free of fecal contamination and priority chemical contaminants, including arsenic.

To protect the regular exposure of arsenic to the general population the development of arsenic removal technologies is of priority interest. The removal of arsenic can be achieved by chemical or biological methods. The biological method or bioremediation being more appropriate as these are comparatively eco-compatible and economically feasible option that works in very low concentration in comparison to other physiological removal methods which fail to operate in the same conditions (Riggle *et al.*, 2003).

Bioremediation includes methods of biological treatment like biosorption, oxidation, reduction, methylation, Demethylation and many more (Crini *et al.*, 2005; Costa *et al.*, 2008; Gouda *et al.*, 2018; Joo *et al.*, 2010; Karthik *et al.*, 2017; Kong and Glick 2017; Norton *et al.*, 2008; Olanrewaju *et al.*, 2017; Pagnanelli *et al.*, 2009; Rashid *et al.*, 2016; Siñeriz *et al.*, 2009; Satyapal *et al.*, 2016) have received considerable attention for the treatment of arsenic contamination from the environment.

In these methods, biological agents are used for the removal or detoxification of contaminants. These methods depend on the intrinsic arsenic reactive properties of the test organism (algae, fungi, bacteria) as many microorganisms use the contaminants as nutrients or energy sources (Tang *et al.*, 2007).

Various types of biological interaction of As with microorganisms generally form the basis of developing the remediation strategies. The bioremediation of arsenic can be achieved by either reducing its toxicity or removal. The reduction in toxicity can be achieved by biologically mediated enzymatic oxidation, reduction, sorption, or methylation process. The biological removal is achieved by absorption or adsorption of toxin through the cell surface.

The oxidation of arsenic is mediated by the enzyme As (III) oxidase which converts the more toxic As (III) to the less toxic As(V). This enzyme As (III) oxidase, which is classified as a member of the DMSO (dimethyl sulfoxide) reductase family has been identified and sequenced (Ellis *et al.*, 2005). Some chemolithotrophic bacteria even extract energy from oxidizing arsenite (Santini *et al.*, 2006). Arsenite oxidation is an exergonic process catalyzed by periplasmic arsenite oxidase (Oremland and Stolz 2003). This enzyme has been reported to occur in both heterotrophic and chemotrophic bacteria (Jackson *et al.*, 2003).

The methylated forms of arsenic are volatile and readily released into the environment where oxidation might convert them back to the oxidized form As(V). The primary mode of arsines and methyl arsenicals generation is As(V) reduction and subsequent oxidative addition of methyl groups (Dombrowski *et al.*, 2005). Methylation is catalyzed by homologs of As(III) S-adenosylmethionine (SAM) methyltransferases genes (Yang and Rosen 2016).

Biological removal of arsenic from environmental sources can be achieved by technique referred as biosorption. The technique involves the removal of arsenic using live or dead material which interacts with arsenic owing to their surface properties or functional groups. The sorption can be passive in case of dead material involving selective binding of metal on surface or an active process where in the metal is actively transported inside the biological material as in case of live biosorbents. In either case the level of sorption reaches to an equilibrium which can be estimated using Langmuir or Fredlich model. The present review drives the attention towards the various harmful repercussions on the health and well-being of general population due to arsenic exposure along with the promising strategies for its removal using biosorption technology.

Arsenic Induced toxicity

The exposure to high doses of arsenic to human population is mainly through the intake of arsenic contaminated food or water. The general population gets exposed to arsenic mainly through water and food. The main route of exposure to arsenic is ingestion. The regular exposure of arsenic in drinking water can predispose the vulnerable population to lung, kidney, skin and bladder cancer (Hong *et al.*, 2014; Smith *et al.*, 1992). The chronic exposure of human to arsenic is mainly by drinking untreated water derived from arsenic rich aquifers or by coming in direct contact with soil containing arsenic from anthropogenic or natural sources. Moreover, the plants and aquaculture products developing in the presence of arsenic also accumulate the same and ultimately reaches the human body through food (Hong *et al.*, 2014). The negative effects of arsenic exposure and accumulation in body tissues poses adverse impact on functioning of organ systems like respiratory, gastrointestinal, cardiovascular, nervous, hematopoietic, etc. (WHO, 1981) that leads to serious health effects like hyperkeratosis, restrictive lung disease, black foot disease, hypertension, cardio- and cerebro-vascular disease, diabetes mellitus, cancer of lung, bladder and kidney, reproductive toxicity, genotoxicity, etc. (Kitchin 2001; Wolz *et al.*, 2009) (Figure 1). The arsenic induced cancer can be due to the oxidative stress, DNA damage, co-carcinogenesis, tumour promotion and proliferation activity etc (Ghosh & Sil 2015).

The extent of damage due to arsenic exposure depends on its chemical species and forms. Inorganic forms of arsenic are more toxic than organic forms (Hopenhayn, 2006). The inorganic trivalent form of arsenic i.e arsenite (+3), is considered to be much more toxic than pentavalent form arsenate (+5), (Neff 1997; Al-Abed *et al.*, 2007; Taarakul *et al.*, 2007; Escalante *et al.*, 2009). The methylated forms of arsenic as MMA and DMA are observed in III form (Monomethylarsonous acid, Diethylarsenous acid) as well as V form (monomethylarsonic acid, Dimethylarsinic acid) forms, where in the III methylated species are comparatively more toxic. Usually the Monomethylarsenate (MMA), dimethylarsenate (DMA), trimethyl arsine oxide (TMAO) and tetramethyl arsomium (TETRA) cause moderate level of toxicity. In general it can be stated that the pentavalent forms of arsenic are less toxic than the trivalent forms (Ghosh & Sil 2015; Styblo *et al.*, 2000).

The arsenic induced oxidative stress is considered the main reason of arsenic induced toxicity which is a resultant of pro-oxidant and antioxidant imbalance in the stressed body (Samuel *et al.*, 2005; Sharma *et al.*, 2009).

The Arsenite (III) induced toxicity is due to its affinity for the sulfhydryl groups and binding with reduced cysteins in proteins, this binding results in its conformation change subsequent functional inactivity ((Lu *et al.*, 2007; Shen *et al.*, 2013) . Thus a number of cellular processes get disturbed under the arsenite stress as Krebs cycle, cellular glucose uptake, gluconeogenesis, fatty acid oxidation, etc. (Mittal & Mehta, 2008; Mittal and Flora, 2007; Szinicz & Forth, 1988) The arsenite cytotoxicity is witnessed in form of DNA fragmentation and apoptosis (Wang *et al.*, 2004).

The pentavalent form of inorganic arsenic i.e., arsenate possess molecular similarity with the phosphate as these are group VA elements and have similar configuration. Thus, this can mimic and replace phosphate in some of the biochemical reactions. In laboratory conditions arsenate readily reacts with glucose and gluconate to form glucose-6-arsenate and 6 arsenogluconate, both of these compounds are similar to the respective phosphate products (glucose-6-phosphate and 6-phosphogluconate). The glucose arsenate can also act as substrate of the enzyme for the phosphate analog i.e glucose 6

phosphate dehydrogenase and subsequently inhibits the hexokinase (Lagunas, 1980). Arsenate can also compete for the phosphate anion transporter and sodium pump and thus reduces its uptake (Kenney & Kaplan, 1988).

The toxic effects of As in humans depends on age, gender, and state of health as well as nutrition of the individual (Mathew & Beeregowda, 2014). Numerous studies have demonstrated negative impacts of arsenic exposure on cognitive development, intelligence, memory, adverse pregnancy outcomes, and infant mortality, with impacts on child health (Tolins *et al.*, 2014; Quanash *et al.*, 2015). Arsenic species get deposited in the skin, lungs, kidney, liver, etc. and cause severe diseases by oxidative stress, altered DNA methylation, altered DNA repair, mitochondrial damage, and proliferation of the cell, tumor promotion, and co-carcinogenesis (Sharma *et al.*, 2007; 2009; Ebele 2009; Butt *et al.*, 2011; Perpetuo *et al.*, 2011; Das *et al.*, 2013; Fazan *et al.*, 2013; Zhuang *et al.*, 2013; Abdul *et al.*, 2015) (Figure 1).

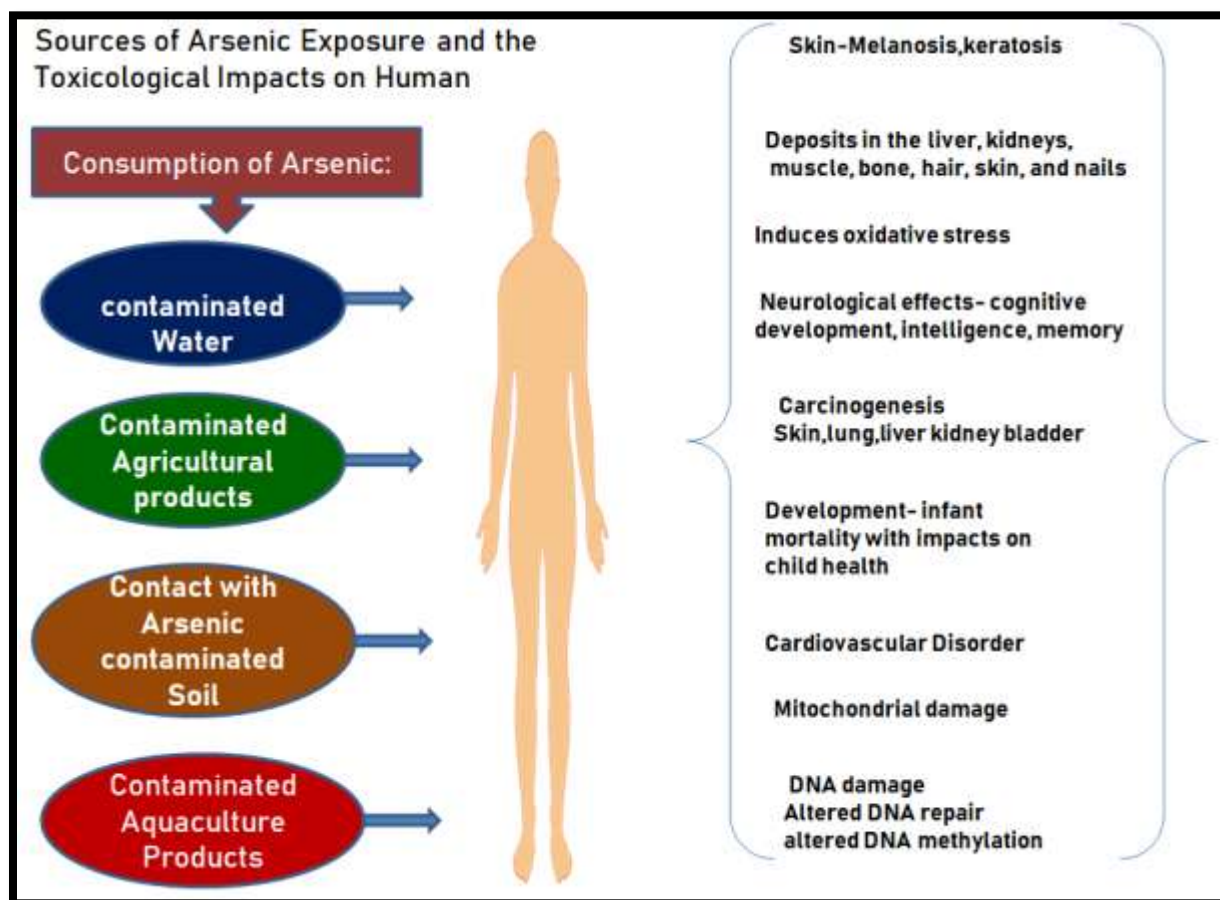


Figure 1: Pictorial depiction of various arsenic exposure sources to human body and the adverse outcomes

Biosorption

Biosorption is defined as the removal of toxic substances from a solution by biological material which provides the best option for the removal of toxicants like arsenic from polluted streams (Gadd 2009). It involves the use of natural materials as biosorbents such as agricultural residues (Kumar *et al.*, 1982), forestry waste products (Vazquez *et al.*, 1994), live or dead microorganisms (Brady *et al.*, 1994) sugar-beet pulp (Dronnet *et al.*, 1997), and casein (Mishra *et al.*, 1998). The natural materials offer high-capacity metal entrapment, which is attributed due to the presence of carboxylic, phosphate, sulfate, amino, amide, and hydroxyl groups, which are mostly found in the cell wall (Veglio *et al.*, 1997; Cox *et al.*, 1999).

The biosorption cycle includes a solid stage (biosorbent, biological material) and a fluid stage (normally water) containing a dissolved species to be sorbed (adsorbate, heavy metal) (Ahalya *et al.*, 2003). Because of the higher proclivity of the biomaterial (sorber) for the arsenic particle (sorbates), these are attracted and bound with various bioreactive molecules on biological material (Lizama *et al.*, 2011). The cycle proceeds till harmony or equilibrium is established between the measure of strongly bound and unbound arsenic species. Due to the attachment of the biomaterial (sorber) for the arsenic ion (sorbates), heavy metal (As) is attracted and bound with different mechanisms (Lizama *et al.*, 2011). So, this process continues till equilibrium is established between the sorber and sorbate. The biosorption process is also affected by several factors such as pH, temperature, kind of biosorbent material, contact time, presence of other metal, and many more. Metal ion uptake by biosorption depends upon the substrate and involves mechanisms like; complexation, coordination, chelation, ion exchange, adsorption and inorganic micro precipitation (Volesky, 1995).

Biosorption research centers work on utilizing cell items, organisms, agrarian items, just as non-living or living biomasses that can aggregate substantial metals (Mosbah *et al.*, 2013). The utilization of non-living biomass gives a bit of leeway in biosorption of metal particles since it doesn't have any prerequisite for development and digestion. The term sorption refers to a process that occurs between two substances and includes both the phenomenon of adsorption and absorption to remove contamination (Gadd, 2009). Adsorption consists of the binding of a molecule to a surface, while absorption, implies that the molecule is captured or internalized (Fomina & Gadd, 2014). The use of biosorption has received much momentum by the possible decontamination of not only arsenic but also other xenobiotic compounds like dyes, phenolic compounds, and pesticides, etc (Fomina and Gadd, 2014). Metals like K⁺, Mg⁺ are highly mobile and do not get accumulated with biomass during phytoremediation which can be easily removed through biosorption (Gadd, 2009).

Table 1: Popular biosorbents used for arsenic removal

| Biosorbents | Organism | References |
|--------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| Algae | <i>Chlorella</i> , <i>Oscillatoria</i> , <i>Spirogyra hyaline</i> | Hansen <i>et al.</i> , 2006; Vilar <i>et al.</i> , 2006 |
| Vascular plants | <i>Glycine max</i> | Hoffman <i>et al.</i> , 2004; Pandey <i>et al.</i> , 2009 |
| Fungi | <i>Penicillium purpurogenum</i> , <i>Saccharomyces cerevisiae</i> | Dambies <i>et al.</i> , 2002; Say <i>et al.</i> , 2003; Loukidou <i>et al.</i> , 2003; Mohan <i>et al.</i> , 2007 |
| Bacteria | <i>Bacillus sp.KL1</i> , <i>Bacillus sp. KL4</i> | Kuyucak and Volesky 1988 |
| Chemically treated seeds | Soya bean seeds | Kumari <i>et al.</i> , 2006; Koivula <i>et al.</i> , 2009; Gaur <i>et al.</i> , 2018 |
| Rice and orange waste | <i>Oryza sativa</i> | Ghimire <i>et al.</i> , 2003; Ranjan <i>et al.</i> , 2009 |
| Lignin, pectin | Milled wood lignin (MWL) and many other plants | Bailey <i>et al.</i> , 1999; Quek <i>et al.</i> , 1998; Senthil <i>et al.</i> , 2000 |
| Pyrolysed sludge | | Da-Costa <i>et al.</i> , 2003 |
| Fruit juice | Citrus X Sinensis | Senthil <i>et al.</i> , 2000 |

Potential biosorbents

The biological materials which possess the ability to accumulate contaminants from the contaminated site through metabolically mediated or physico-chemical pathways of uptake are called biosorbents (Fourest and Roux 1992). Biosorbents are a less expensive, more compelling option for the expulsion of metallic components like As (arsenic), Pb (lead), Cd (cadmium), Hg (mercury), etc. Bacteria, fungi, algae, industrial wastes, agricultural wastes, seaweeds, and other polysaccharide materials have proved as potential metal biosorbents (Volesky 1986; Ahluwalia & Goyal 2007; Shamin 2018). Not only living organisms but also dead organisms can also be used as biosorbents. Biosorbents can also be modified to

improve or redesign microorganisms for a higher intrinsic capability, greater resistance, binding site enhancement, and binding site modification like Immobilized biosorbents (Vegliò and Beolchini 1997), Genetically modified biosorbents (Bae *et al.*, 2000; Majareand *et al.*, 2001) and Chemically modified biosorbents (Selatnia *et al.*, 2004a; Göksungur *et al.*, 2005; Vijayaraghavanand 2007b). A few significant boundaries that influence the exhibition of living biosorbents should be viewed as like, the physiological condition of the life form, age of the biomaterial, accessible supplements for development, and ecological conditions provided during the bio sorption cycle.

Biosorption of Arsenic

In the present scenario, many biosorbents have been reported for removal of toxicants; but to select the most appropriate and encouraging sorting of promising biomass from an extremely large pool of readily available and inexpensive biomaterials is a big task. Biosorption by sorbents depends on its surface area and its polarity because sorption is a surface reaction. Various factors influencing biosorption like type and nature of biomass, starting solute fixation, physiological components like pH, temperature, ionic strength. Apart from this biomass can be used in many forms like living/dead biomass, free/immobilized, crude/pretreated, wild/freak cells, designed/non-engineered, lab culture/squander modern biomass and biomass from various industries (Park *et al.*, 2005). Many researchers found that Algae, Fungi, Bacteria are remarkable eco-friendly bio sorbents and give prominent results for the biosorption process.

Fungi as Arsenic Biosorbent

Fungi are one of the industrial fermentation waste biomasses which are an excellent metal sorbent. Fungi are eukaryotic living life form which incorporates yeasts, mushrooms, molds etc. The cell wall structure of organisms offers great metal-restricting properties. The cell mass of fungi is made essentially out of chitins, mannans, glucans, lipids, polysaccharides, pigments, melanin, etc. (Abbas *et al.*, 2013; Gadd 1980; Gadd 1985). The continuous cell wall can make up 30% or a greater amount of the dry load of the fungi.

Thus, fungi including yeasts have received increased attention because of the presence of a high level of cell wall materials. The importance of fungi as biosorbent include the following:

- In fungi, the cell wall structure showed excellent metal binding properties (Abbas *et al.*, 2014).
- It was reported that living and dead fungi can be used as biosorbent material (Wang *et al.*, 2006).

Table 2: Fungi as arsenic biosorbents along with conditions and efficiency of biosorption

| Fungi | Tem p. | pH | Agitatio n | Wt (g/ L) | % Remov al | Reference |
|-------------------------------------------------------------|-----------|----|---------------|-----------------|------------------|----------------------------------|
| <i>Penicillium chrysogenum</i> | 25°C | 3 | 3 h | 1 | 24.5% | Mamisahebei <i>et al.</i> , 2007 |
| <i>Paecilomyces sp.</i> | 30°C | 6 | 24 h | 1 | | Acosta <i>et al.</i> , 2013 |
| <i>Penicillium purpurogenum</i> | 25°C | 5 | 4h | 1 | 35.6% | Say <i>et al.</i> , 2007 |
| <i>Saccharomyces cerevisiae</i> | 27°C | 5 | - | 1 | 60% | Fomina and Gadd 2014 |
| <i>Aspergillus flavus</i> , IV, III, V, <i>Fumigatus</i> | 30°C | 6 | 24h | 1 | 85% | Cardenas <i>et al.</i> , 2017 |
| <i>Aspergillus nidulans</i> | 35°C | 4 | 11 Days | 1 | 84.35% | Maheswari <i>et al.</i> , 2009 |

The biosorption of arsenic with iron oxide coated fungi *Aspergillus fumigates I*, *Aspergillus flavus III*, IV,

V, *Paecilomyces* sp. are very efficient at eliminating 1mg/L of metal in the arrangement, utilizing nuclear retention spectroscopy (AAS), accomplishing rate evacuation about 83%, 92%, 97%, 90%, 89% respectively at pH6 and 30°C temperature after 24h of incubation of with 1 mg/L of fungal biomass (Cardenas *et al.*, 2017).

The table 2 summarizes various fungus based arsenic biosorbents along with the conditions and efficacy.

According to Maheswari *et al.*, 2009, As absorption potential of *Aspergillus nidulans* from contaminated soil was found to be 84.3% after 11 days at pH 4 at temperature of 35°C.

Arsenic (III) biosorption on iron-covered biomass of fungi *Paecilomyces* sp. was considered by Acosta *et al.*, 2013, in *Paecilomyces* sp. The highest adsorption was at pH 6.0, at 30°C after 24h of incubation using 1mg/L of altered fungal biomass with 64.5% removal efficiency.

The expected utilization of the parasite *Penicillium purpurogenum* to eliminate arsenic from fluid arrangements was evaluated by Say *et al.*, 2007, Biosorption of the metal particles came to equilibrium within 4h with 35.6mg/g for As(III) at pH 5. Substantial metal particle sorption by *Penicillium purpurogenum* was pH dependent. The metal stacking limit increased with expanding pH under acidic conditions. The growth *Penicillium purpurogenum* could be utilized for ten cycles for biosorption.

Bacteria as Arsenic Biosorbents

Bacteria are the most bountiful and adaptable microorganisms which establish a critical segment of whole living terrestrial biomass (Norberg *et al.*, 1984). Bacteria are classified based on their morphology as rod, cocci, or spirillum (Abbas *et al.*, 2014; Wang *et al.*, 2009). Various bacterial species as *Bacillus*, *Pseudomonas*, *E. coli*, and many more show biosorption property in view of their little size and capacity to survive in various natural conditions (Kinoshita *et al.*, 2013; Urrutia *et al.*, 1997; Vasudevan *et al.*, 2001). Gram-positive bacteria contain teichoic acid and teichuronic acid in their cell wall with anionic functional groups which promote metal-binding properties of bacteria. Similarly, peptidoglycan, phospholipids, and lipopolysaccharides in Gram-negative bacteria help in metal binding (Sherbert 1978). A few useful gatherings are available on the bacterial cell wall, many metal binding group such as carboxyl, phosphate, amine, and hydroxyl are present (Doyle *et al.*, 1980; Vanderwal 1997). These groups will bind to metals and then uptake occurs (Vijayaraghavan and Yun 2008).

The advantages of bacteria to be used as biosorbents are as following:

Bacteria have a little size, universality, and ability to develop under controlled conditions (Kinoshita *et al.*, 2003).

- Microscopic organisms have opposition against a wide scope of various environmental conditions (Urrutia 1997; Vasudevan *et al.*, 2001).
- It provides an eco-friendly environment.

The table 3 summarizes various bacteria based arsenic biosorbents along with the conditions and removal efficacy.

Table 3: Bacteria as arsenic biosorbents along with conditions and efficiency of biosorption

| Bacteria | Temp | pH | Contact time | Wt (g/L) | % Removal | References |
|-------------------------------------------------------------------|------|--------|--------------|----------|------------------|-------------------------------|
| <i>Arthrobacter</i> sp. | 28°C | 7 | 30min | 1 | 74.91% | Prasad <i>et al.</i> , 2013 |
| <i>Bacillus</i> sp. KL1, KL4, KL6 | 40°C | 5 | 24h | 1 | 80%, 91.66%, 88% | Taran <i>et al.</i> , 2019 |
| <i>Bacillus</i> sp. KMO2, <i>Aneurinibacillus aneurinilyticus</i> | 30°C | N D | 72h | 1 | 51.45%, 53.2% | Dey <i>et al.</i> , 2016 |
| <i>Rhodococcus</i> sp. WB-12 | 30°C | 7 | 30min | 1 | 77.3 % | Suranjit <i>et al.</i> , 2011 |
| <i>Exiguobacterium</i> sp. | 37°C | N D | 10days | 1 | 99% | Pandey <i>et al.</i> , 2015 |

A novel arsenic removal bacterial species *Exiguobacterium* sp. was isolated via enrichment culture technique from an arsenic-rich soil from Chhattisgarh, India which was observed for 99% arsenic removal under aerobic conditions from the aqueous environment in 10 days at 37°C temperature at 100 rpm (Pandey et al., 2015).

The role of arsenic-resistant bacteria *Arthrobacter* sp. biomass for removal of arsenite as well as arsenate from aqueous solution was reported by (Prasad et al., 2013). Trivalent Arsenic (As+3) and pentavalent arsenic (As+5) showed 74.91 mg/g (pH 7.0) and 81.63 mg/g (pH 3.0) biosorption limit of the biomass, respectively using 1 g/L biomass with a contact time of 30 min.

KL1, KL4 and KL6 are the arsenic-resistant strains of the genus *Bacillus*. These strains showed arsenic bioremediation activities. According to studies, that *Bacillus* sp. KL1 was involved in arsenic biosorption. It was obtained as 77% after 24 h incubation at 40°C, at pH 5 with 150 ppm of arsenic concentration. *Bacillus* KL4 achieved 91.66% arsenic removal after 24 h of incubation at 40°C, pH 5 with 60 ppm arsenic concentration while *Bacillus* KL6 achieved 88% at 35°C, 90 ppm concentration at pH 5 after 36 h of incubation period (Taran et al., 2019).

Rhodococcus sp. WB-12 cells have the potential of being used as biosorbent for the expulsion of arsenic from sullied water. The biosorption limit of the biomass for As(III) was found to be 77.3 % (pH 7.0) utilizing 1 g/L biomass with a contact time of 30 min at 30°C. Active assessment of trial information demonstrated biosorption of As (III) followed pseudo-second-order kinetics. Thus, biomass-derived from *Rhodococcus* sp. WB-12 cells have the potential for use as biosorbent for the removal of arsenic from contaminated water (Suranjit et al., 2011).

Two bacterial isolates namely *Bacillus* sp. KMO2 and *Aneurini bacillus aneurinilyticus* strain BS-1 were estimated to tolerate arsenate concentration up to 4500 ppm and arsenite concentration up to 550 ppm. These bacteria can remove 51.45% & 51.99% of arsenite and 53.29% & 50.37% of arsenate respectively from arsenic amended media in 72h (Day et al., 2016).

The table 4 summarizes various algae based arsenic biosorbents along with the conditions and efficacy

Table 4: Some Arsenic biosorbent algae along with conditions and efficiency of biosorption

| Algae | Temp | pH | Contact time | Wt (g/L) | %Removal | Reference |
|----------------------------------------------------------------------|------|----|--------------|----------|----------|-----------------------|
| <i>Spirogyra hyaline</i> | 25°C | 5 | 2h | 1 | 9.8% | Kumar et al., 2012 |
| <i>Cynobacteria microcystisnovacekii</i> | 15°C | - | 192h | 14.7 | 21.2% | Ferreira et al., 2018 |
| <i>Chlorella, Oscillatoria, Scenedesmus, Spirogyra and Pandorina</i> | 32°C | 4 | 5-10days | 0.8 | ND | Sibi, 2014 |
| <i>Maugeotiag enuflexa</i> | 20 | 6 | 60min | 4 | 57.48% | Sari, et al., 2011 |
| <i>Chlorella vulgaris</i> | 25°C | 5 | 2h | 24.4 | ND | Jahan, et al., 2004 |

Algae as Arsenic Biosorbent

Algae are viewed as perhaps the most encouraging kinds of biosorbents. They can fill in enormous biomass in any event, when less sustenance is given. Algae have a large size, high sorption limit, and no creation of harmful substances. Abbas et al., (2014) reported that algal cell wall contained polysaccharides (alginic corrosive, chitin, mannan) which provides some functional groups (sulfate,

hydroxyl, phosphate, imidazole, amino, amine). These functional groups referred as metal-restricting destinations (Oyedepo *et al.*, 2011). In biosorption measures, brown algae show higher take-up limit compared with red and green algae (Khani *et al.*, 2011; Flouty *et al.*, 2012; Trinelli *et al.*, 2013).

Algae as suitable biosorbents -These are considered good biosorbent material because of the following reasons. (Rincon *et al.*, 2005; Brinza *et al.*, 2007)

- Algae have high sorption limit and are promptly accessible in enormous amounts in oceans and seas.
- Algae have low supplement necessities, being autotrophic, they produce huge biomass.
- These generally do not create harmful substances.

Sibi (2014) investigated that the expulsion pace or pace of arsenic removal of Arsenic (III) was more than the Arsenic (V) by all out of five microalgae specifically *Chlorella*, *Oscillatoria*, *Scenedesmus*, *Spirogyra*, and *Pandorina* under the trial conditions and apart from this dried biomass demonstrated higher biosorption rate and quicker dynamics than the living ones. At pH 4.0, 32°C, and 0.8 g/l levels critical biosorption of arsenic was found.

In another study by Ferreira *et al.*, (1974) *Microcystis novacekii* exhibited normal growth in concentrations of As (V) similar to those found in natural environments also found that As(III) affected growth from 14.7 - 85.7 mg.L-1 from the culture medium. The absorption capacity remained constant with increasing As (III) concentrations in a dose-independent effect. This microorganism is recommended in As bioremoval studies due to its autotrophic-mixotrophic growth, low nutritional requirements, and high As (III) absorption capacity.

In aqueous medium, Arsenic (III) biosorption is mediated by dead green algae (*Maugeotia genuflexa*) biomass (Sari *et al.*, 2011). The maximum monolayer biosorption capacity of the biosorbent was discovered to be 57.48 mg/g at pH 6, biomass concentration 4 g/L, contact time 60 min, and temperature 20°C.

BIOSORPTION MECHANISMS

Metabolism dependent biosorption

The metabolism-dependent biosorption takes place only with viable cells and it requires energy from ATP. Factors that affect the metal uptake by living biomass include the nature of heavy metal ions, states of the medium, cell wall structure, and so forth (Joo *et al.*, 2010). The take-up cycle by living biomass involves adsorption to the cell wall and entering-into the cytoplasm (Galceran *et al.*, 2003; Wilkinson *et al.*, 2004; Gadd 2009; Hajdu *et al.*, 2010).

Various ligands such as phosphoryl, carboxyl, carbonyl, sulfa hydroxyl, and hydroxyl are present on the cell mass of biological material. These ligands tend to interact, cluster around the metal particles and immobilize the same (Volesky, 2003).

However, according to research in metabolism dependent processes this is not considered as actual biosorption, rather it is understood as bioaccumulation process, while metabolic-independent processes are actual biosorption process (Volesky, 2007; Chojnacka, 2010).

Bioaccumulation, also called as active biosorption, it involves two important mechanisms

(i) This mechanism is similar to biosorption as it involves attachment of potentially toxic elements to the surface.

(ii) In this, active transportation of metal ions into the cell take place (Chojnacka2010).

Bioaccumulation is a slow process. Metabolism dependent biosorption involves various mechanisms as following:

1. **Chelation:** In this mechanism, ions and molecules attaches to metal particles. In this process two or more separate coordinate bonds formed with a polydentate ligand and a single central atom (Farooq *et al.*, 2010).

2. **Physical adsorption:** It is a surface phenomenon, which involves adhesion of ions, particles, or atoms from a gas, fluid, or dissolved solid to a surface. In this process a film of the adsorbate was formed on the adsorbent. This method is considered as surface phenomenon. Broadly, this process is

classified as physisorption, with its characteristics of weak van der Waals forces, or chemisorption, and covalent bonding (Volesky, 2007).

3. **Precipitation:** Precipitation is the formation of a solid in a solution during a chemical reaction or by diffusion into a solid inside another solid. When this reaction happens in a liquid medium, the solid formed is known as the “precipitate” and the chemical that mediates this process is called the precipitant (Farooq *et al.*, 2010).

Metabolism independent biosorption

The metabolism independent process generally happens in biomass comprising of dead cells (Volesky 1994, Hajdu *et al.*, 2010). The adsorption process, ionic interactions, chemical sorption are the main key points behind such a physicochemical biosorption mechanism. This sort of biosorption, i.e., non-metabolism subordinate is generally fast and can be reversible (Kuyucak and Volesky 1988). In metabolism independent biosorption dead biomass has higher metal uptake capacity. In certain conditions the living natural mass is favored over dead mass since living cells have the ability for continuous metal uptake, and self-replenishment (Malik, 2004; Gadd 2009; Hajdu *et al.*, 2010).

Metabolism independent mechanism is the actual biosorption process. Biosorption is a passive process that occurs at a faster rate than bioaccumulation. Among many mechanisms, ion exchange is considered the principal mechanism of biosorption, which occurs through different functional groups present on the surface of biomass (Chojnacka, 2010, Vijayaraghavan *et al.*, 2015). The mechanism of biosorption usually depends upon the biomass that is used for the removal of potentially toxic elements. For instance, the composition of the cell wall is different in bacteria (peptidoglycan), fungi (chitin), and algae (alginate, sulfonated polysaccharides), therefore, variation in the presence of functional groups on the surface of the cell wall is responsible for the difference in mechanisms (Vijayaraghavan, 2008, Farooq 2010). Apart from the cell wall, extracellular polymer substances secreted by microorganisms are also found to play an important role in biosorption (Li *et al.*, 2014).

BIOSORPTION KINETICS

Biosorption isotherms are normally depicted by two models: (I) Freundlich Model and (ii) Langmuir Model. These two models are generally used to portray the balance state for the adsorption of metal ions experimental work (Abbas *et al.*, 2014).

Langmuir isotherm

Langmuir in 1918 distributed a model for portraying gas or fluid adsorbed on a solid material. Langmuir isotherm model assumes:

- A. Binding sites present over the adsorbent surface are generally homogeneously distributed.
- B. Binding sites bind to the single molecular layer with the same affinity.
- C. Curve gives a straight-line slope. Each molecule possesses constant enthalpies and sorption activation energy for estimate the equilibrium biosorption using biosorbents.

$$\frac{1}{q_e} = \left(\frac{1}{c_e} \times \frac{1}{k_a q_{max}} \right) + \frac{1}{q_{max}} \quad \dots\dots\dots (1)$$

In the linear formula of the Langmuir model, q_e is the equilibrium biosorption capacity of biomass in nmol /mg of biomass, C_e is the equilibrium concentration of an ion in nmol/L, q_{max} is the maximum amount of metal sorbed in nmol/mg of biomass, and K_a is the constant that is referred to the bonding energy of sorption in nmol/L. (Foo and Hameed, 2010)

Freundlich isotherm

Freundlich and Kuster in 1907 published the first mathematical equation to describe the isotherm. In Freundlich isotherm studies, the following are some important points:

1. The surface energies are distributed heterogeneously.

2. Gives the exponential distribution of active sites.

3 This empirical model can be multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface

$$\ln q_e = \ln K_f + \frac{1}{n} \quad \dots\dots\dots (2)$$

Where, K_f and n are Freundlich constants which demonstrate the adsorption capacity and adsorption intensity, respectively (Desta, 2013). Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of the monolayer (Foo and Hameed, 2010).

FACTORS AFFECTING BIOSORPTION

The biosorption potential depends on many factors which influence the overall extent of metal removal. These factors are described below.

Temperature: For the effective expulsion of metal particles from the climate using biosorbents, it is essential to determine the ideal temperature. It is for the most part expected that biosorption is completed somewhere in the range of 20 and 35°C. High temperatures above 45°C may result in harm to proteins which thus affect the metal uptake process (White *et al.*, 1997; Ahalya *et al.*, 2003; Goyal *et al.*, 2003; Abbas *et al.*, 2014).

pH: This affects the dissolvability of metal particles and restricting destinations of biomass. At lower and higher pH from neutral pH (7), the biosorption of metals is affected (Deng *et al.*, 2013). The general range of pH for metal uptake is 2.5–6 and increases by increasing the solution pH up to a certain limit.

Nature of biosorbents: Metal take-up is accounted for various structures like biofilms, uninhibitedly suspended, microbial cells, or immobilization of microbial cells. It very well may be changed by physical or substance treatments. Actual treatments include autoclaving, drying, bubbling and so on Synthetic treatment as the name demonstrates, synthetics like corrosive or soluble base to improve biosorption limit (Abbas *et al.*, 2014).

Surface area to volume ratio: The surface area property plays a significant role in the case of biofilms (Abbas *et al.*, 2014). The binding of metal particles with microbial cell wall is recently detailed (Gadd *et al.*, 1985; Deng *et al.*, 2014).

The concentration of biomass: The convergence of biomass is straight forwardly corresponding to the metal take-up (Abbas *et al.*, 2014, Gadd *et al.*, 1985, Modak *et al.*, 1995). It is accounted for that electrostatic connection between the cells which contributes a significant part in metal take-up. At a given harmony, the biomass adsorbs more metal particles at low cell fixation than at high concentration (Gourdon *et al.*, 1990).

Biosorption provides a cheap, environment-friendly, and potential biological source to recycle waste products as well as to adsorb and degrade arsenic from the contaminated system which is not possible from the chemical adsorbent. In the biosorption process waste products can be utilized again for the removal purpose and then can be disposed of without any harm to the environment. In biosorption technology, biosorbents must be natural and cheap with low cost and large availability with superior capability to detoxify contaminated arsenic. According to researches high surface to volume proportion of microorganisms should be found.

Now-a-days one of the major concern about the commercial interest of biosorption technology is that the current progress is still preserved at the laboratory level because these biosorbents have some problems like early saturation can occur if the binding sites are occupied immediately, the possibility to further increase the capacity of the biosorption is limited because cells are not metabolizing and have fixed metal valence state. The characteristics of the biosorbents cannot be controlled or modified as they are produced during the pre-growth (Ahluwalia and Goyal 2007). Nevertheless, at the same time it is also necessary to optimize the conditions for its use on a larger scale and explore other possibilities for implementation of this eco-friendly and cost-effective technique. Along with that, it is likewise essential to investigate the possible wellbeing and ecological effects of these biomaterials before their widespread

use. Apart from this many filters are available in the market based on this biosorption technology to observe effectiveness and social acceptability of As removal (Hanchett *et al.*, 2011). Although the suppliers and designs might differ in the market which is bound by same technologies: SONO filter (WIPO 2010), READ-F filter (Sanchez *et al.*, 2016), ALCON filter (Bhiuya *et al.*, 2005) and SIDKA filter (Matthews 2014). These filters have some limitations too like required maintenance costs, import export cost, household cost with higher storage capacity (Hanchett *et al.*, 2011, Bhiuya *et al.*, 2005).

CONCLUDING REMARKS AND FUTURE CONSIDERATION

Biosorption is the most efficient and eco-accommodating technique for the removal of heavy metals from domestic as well as industrial wastewater. Here we present some major conclusions of the study;

1. Waste biomasses from agricultural, fungal, bacterial, and algae origins can be developed as cost-effective and environment-friendly biosorbents for metal ions removal. Biological biomass can be regenerated easily and can be used again.
2. The biomass materials contain many effective functional groups that contribute positively to the metal ions biosorption process.
3. It has been generally found that the biosorption capacity increases as the initial metal ion concentration in the solution increases and on the other hand it is reduced when the biomass dosage increases continuously after a certain limit.
4. Living natural mass is favored over dead mass since living cells have the ability of continuous metal uptake, and self-replenishment. And somewhere contradictory this is also mentioned that dead biomasses can be used as better biosorbent for different toxic materials because dead cells are not affected by toxic wastes and do not require a continuous supply of nutrients. They can be regenerated and reused from many cycles. Dead cells may be stored or used for extended periods at room temperature without any occurrence of putrefaction.
5. Several experimental operating parameters have been found to influence the biosorption process including the solution pH, contact time, nature of biosorbents, and metal ion concentration.
6. The solution pH affects metal ion solubility as well as total charge on biosorbents. The removal of metal ions is almost negligible at highly acidic pH values and increases by increasing the solution pH up to a certain limit.
7. Several case studies said that biosorption offers a great opportunity for a clean, cheap, and high effective process for arsenic removal from a polluted environment. The new natural based innovations need not really supplement regular treatment methods however may complement them in near future. In this way, biosorption innovation turns out to be more valuable and alluring then the currently used technologies.
8. The pseudo-second-order reaction kinetics best described for metal ions biosorption with the intraparticle diffusion mechanism. The peculiarity of following the pseudo-second-request response energy of an adsorption cycle is that the instrument of evacuation is basically through substance holding or chemisorption. This finding demonstrates that most arsenic particles are adsorbed in monolayer structure.

Despite the modern expansion of the various types of bioremediation processes, numerous challenges still need to be addressed. For example, the emergence of new microbiological pollutants, potentially toxic elements dissemination profiles, eco-friendly detection, removal fate, and reliable and consistent monitoring are some research gaps that need to be addressed in future studies. In this context, proper management and strategies should be adapted to maintain environmental health and protection from further deterioration.

Furthermore, many other unsolved questions must be tackled. For example, insufficient detection methods, malpractices, and limitations within practice technologies greatly affect the detection of fate and removal behavior of potentially toxic elements. The role of low-risk contaminants in the emergence of new pollutants should also be addressed in future studies. It could be useful to involve

multidisciplinary scientists, policymakers, and stakeholders to strengthen the detection and removal/degradation of life-threatening pollutants at a global level.

ACKNOWLEDGMENT

Financial assistance provided by UGC in the form of Start Up Grant by letter no. F.30-91/2015 (BSR) dated 26.03.2015 to P.K. and in the form of Research Project by letter no. F.No. MS-97/304031/12-13/CRO dated 01.09.2014 to M.K.S. is highly acknowledged.

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