REVIEW OF LITERATURE
REVIEW OF LITERATURE

Environmental pollution is one of the most serious issues in the present scenario due to increased industrial activities and human needs. Many pollutants such as heavy metals and hazardous substances exist in the environment when it comes to the contact with living organisms; it can be migrated from its origin and accumulates in the tissue. Accumulation of heavy metals in living tissue throughout the food chain is lethal. However, most of this heavy metal is toxic in nature at higher concentration. Many researchers have reported their research works of heavy metal pollution, its sources, toxicity and its solution to removal or reduction from the water, soil and air using different resources in the form of journals, books, book chapters, patents etc.

The literature has reviewed to study and design the present investigation and summarized in appropriate subheadings.

Heavy metal pollution in all over the world

Heavy metals come into the environment through natural such as weathering of rocks or anthropogenic activities of human like industrializations, burning of coal and petroleum products, mining etc. Therefore, heavy metal pollution observed in the different location of the world. Heavy metals such as cadmium, lead, mercury and arsenic pollution in the environment of U.K. was investigated by Hutton and Symon (1986). The main sources of this pollution were non-ferrous metal production, iron and steel production, fossil fuel combustion, petrol and coal combustion. Wadge and Hutton (1987) reported the potential mobility of As, Se, Pb and Cd through fly ash produced by coal combustion and refuse incineration.

High enrichment of Pb, Zn and Cd in soil samples of Mendip Hills North Somerset in England due to base metal mining and the natural process was investigated by Fuge et al. (1991). Pollution of heavy metals such as Fe, Mn, Ni, Co, Pb, Zn, Cu, Cr, Hg and Cd have studied by Sahu and Bhosale (1991) in Bombay city, India. The atmospheric pollution of lead was reported in an urban area of Brisbane, Australia by Simpson and Xu (1994). Pollution of Pb, Zn, Cu and Cd in urban areas of Britain due to industrial activity of Wolverhampton area was investigated by Kelly et al. (1996). Cadmium and lead pollution level were studied by Yilmaz and Sadikoglu (2011) in the seawater of Kepez harbour on the Dardanelles, Turkey. Street...
(2012) has discussed the heavy metal pollution in medicinal plants due to contaminated agricultural resources or poor quality of production. Higher concentration of Cu, Ni, and Zn and their distribution in sediment, snails, and grass roots was reported by Al-Musharafi et al. (2013) due to treated sewage effluent in Oman. Heavy metal pollution and its transportation in the agricultural ecosystem due to the Lead-acid battery factories in Baoding, China was investigated by Liu et al. (2014). They also studied the health risk to the consumption of wheat berries in rural population. Emission of heavy metals in sediments from an acid leaching site of e-waste in Guiyu, known for the largest e-waste recycling centre in China was investigated by Quan et al. (2014). Tiwari et al. (2015) has examined the higher concentration of heavy metal such as Mn, Cr, Cu, Fe, Pb and Zn in surface water resources in an industrial region of Chhattisgarh, India due to the leachate pollution caused by dumping and disposal of industrial solid waste from power plants and integrated iron and steel industries. Higher concentration of Cr, Cd, Cu, Pb, Ni, Zn and Fe in soils and sugarcane irrigated with the industrial effluent of a paper mill in Uttarakhand, India was investigated by Pandey et al. (2016). They also analyzed health risk in rural communities, which was mainly due to the consumption of contaminated sugarcane.

Assessment of water quality by physicochemical analysis

Rajmohan and Elango (2005) have stated that the rock water interaction and agricultural activities are the major sources for a high concentration of iron in groundwater in parts of Palar and Cheyyar river basin, Tamilnadu, India. Majagi and Vijaykumar (2008) studied on some heavy metals concentrations with other physicochemical parameters in Karanja reservoir, Bidar, India and result showed that Fe, Pb, and Ni concentration are higher than the standard. Rao (2008) has pointed out that higher amount of iron in the groundwater is due to the geogenic and anthropogenic sources. Igbinosa and Okoh (2009) have pointed out the impact of poorly treated effluents discharged from the wastewater treatment plant on the receiving watershed of typical rural community of the Eastern Cape Province of South Africa based on physicochemical characteristics study. Goyal et al. (2010) have examined the seasonal variations of $\text{Cl}^-$, $\text{F}^-$ and $\text{Fe}^{++}$ in the underground water of Unnao district in Uttar Pradesh, India and found the concentration of these ions were outside the permissible limits of WHO. Kaur et al. (2010) have focused their work on
the physicochemical analysis of effluents from sugar and textile industries and their harmful effects on the soil micro flora and aquatic ecosystems due to high BOD and COD values. Chatterjee *et al.* (2010) have carried out a physicochemical and bacteriological study on Damodar River, India and results stated that contamination of coliform counts, metals, and organic pollutants at a level above the permissible limits for domestic usage.

Rai (2010) studied on the seasonal variation of heavy metals and physicochemical characteristics in a lentic ecosystem of the subtropical industrial region, India in which all metals were above the permissible limit. Chinhanga (2010) has reported the effects of effluents from iron and steel manufacturing company on the river water quality on the basis of physicochemical and heavy metal concentration in bank soils, bed sediments and water of Kwekwe River, Zimbabwe. Priya and Arulraj (2011) used the correlation-regression model to study the physicochemical parameters of the groundwater in Coimbatore city, India and reported that quality of groundwater was worse due to exceeded limits of physicochemical parameters described by Indian drinking water standard. Thomas *et al.* (2011) conducted a study on seasonal variation in physicochemical and microbiological quality of drinking water at Mannuthy in Thrissur district of Kerala, India and found significant difference between seasonal observations of the parameters. Devi and Premkumar (2012) have studied the impacts of industrial activities on the ground water quality in and around SIPCOT Industrial complex in Cuddalore District, Tamilnadu, India. Hassan *et al.* (2013) have also worked on seasonal variation in physicochemical parameters in groundwater quality of the industrial area, Aurangabad, Maharashtra, India. Nirgude *et al.* (2013) reported that the physicochemical characteristics of industrial effluents were higher than the prescribed limit from Vapi industrial area, Gujrat, India. Banerjee and Gupta (2013) have reported that negative impact of the discharging high degree of metal (Fe > Mn > Pb > Cd) containing effluents from Durgapur industrial complex, West Bengal India on downstream of the Damodar river system. Shukla (2014) has reported high levels of iron followed by lead, Copper, Zinc, Chromium and Cadmium metals in drinking water samples collected from the northeastern coalfield region of Chhattisgarh. Kumari *et al.* (2014) have pointed out the groundwater quality in two industrial blocks of Ghaziabad district, India and reported that the presence of metal contamination in the groundwater makes it unfit.
for the drinking as per WHO/BIS guidelines. Olaniran et al. (2014) studied the seasonal variation in the physicochemical parameters and heavy metals concentrations of the Umgeni and Umdloti Rivers in Durban, South Africa and investigated that most parameters were exceeded the limits described by South African Guidelines and WHO of fresh water quality.

Affum et al. (2015) studied the total coliforms, arsenic and cadmium exposure on drinking water in the western region of Ghana and stated that several natural processes and anthropogenic activities significantly contributed to the groundwater salinization, hardness, toxic element and microbiological contamination. Yadav et al. (2016) observed that the discharged wastewater from 34 industries (i.e. iron, steel, power, paper and polymer) of Raipur area were acidic in nature.

**Heavy metal tolerance by some fungal species**

Gadd and Griffiths (1977) have discussed environmental and microbial factors that can influence heavy metal toxicity in microbes and mechanisms of metal tolerance by microbes. The ectomycorrhizal fungi including *Pisolithus tinctorius*, *Thelephora terrestris*, *Cenococcum geophilum*, *Hymenogaster* sp. and *Scleroderma* sp. have investigated by Tam (1995) for their heavy metal tolerance. All fungi have shown tolerance to Fe at high concentrations and sensitive to Ni, Cd and Cr at low concentration. Some ericoid mycorrhizal (ErM) and ectomycorrhizal (EcM) fungi have studied for Cd, Cu, Pb and Zn tolerance by Fomina et al. (2005). Marschner et al. (1999) have reported Al and Pb tolerance of different ectomycorrhizal fungi in divided Petri plate method to avoid complexation of metal by agar and precipitation of phosphate. Lopez Errasquin and Vazquez (2003) have studied *Trichoderma atroviride* strain isolated from sewage water treatment plant for its tolerance to copper, zinc and cadmium ions. Lead tolerance and sorption in a *Paecilomyces lilacinus* strain were studied by Zucconi et al. (2003).

Ray et al. (2005) have studied the uptake and growth of some ectomycorrhizal fungi in relation to metal tolerance on specially designed cocktail media of various heavy metal such as Al, As, Cd, Cr, Ni and Pb. Bellion et al. (2006) have discussed the extracellular and cellular mechanisms involved in the metal tolerance of ectomycorrhizal fungi. The fungal strain of *Aspergillus niger* RH17 and *Aspergillus niger* RH18 isolated from the contaminated soil and effluents of textile mills were
examined for their tolerance to different lead concentrations by Faryal et al. (2007). Siham (2007) have reported eighteen fungal species from the genera of Alternaria, Aspergillus, Cephalophora, Eurotium, Fusarium, Mucor and Penicillium were isolated from soil samples of the industrial city and tested for their growth in relation to lead and copper tolerance. Zafar et al. (2007) studied metal-resistant fungi belonging to the genera of Aspergillus, Penicillium, Alternaria, Geotrichum, Fusarium, Rhizopus, Monilia and Trichoderma. These fungal species were isolated from waste water-treated soil for determination of minimum inhibitory concentrations (MIC) for Cd, Ni, Cr, Cu, and Co.

Iram et al. (2009a) have reported the fungal strain such as Aspergillus niger, Aspergillus sp., Fusarium sp. and Penicillium sp. for their tolerance to Zn, Pb, Ni and Cd measured by MIC. Among all Aspergillus niger showed maximum tolerance against all heavy metals. The genera of Alternaria, Aspergillus, Fusarium, Geotrichum and Penicillium have been reported for their resistant to Pb, Cr, Cu and Zn metal by Ezzouhri et al. (2009) and resulted that the Aspergillus and Penicillium species have a higher tolerance to all metal. Purchase et al. (2009) studied the effect of temperature on Zn and Pb metal tolerance by Beauveria bassiana and Rhodotorula mucilaginosa isolated from wetlands receiving urban runoff.

Zeng et al. (2010) studied the MIC of Cd, Zn, Mn, Cu, Pb and Co metals for Paecilomyces lilacinus and result suggested that the fungus has marked tolerance to all metals, except cobalt exhibited toxicity to the fungus as compare to other heavy metals. Parameswari et al. (2010) have examined the MIC of Ni and Cr for Aspergillus niger, Phanerochaete chrysosporium and Trichoderma viride isolated from sewage contaminated soil. Anahid et al. (2011) studied on heavy metal (Ni, Co, Mo, V, Mn, Fe, W and Zn) tolerance of fungi strains Aspergillus niger, Aspergillus foetidus and Penicillium simplicissimum showed high growth at a higher concentration of some metals, thus it was high tolerant species. The MIC of cadmium and copper for ten entophytic fungal species namely, Rhizopus oryzae, Aspergillus luchuensis, Aspergillus tubingensis, Monacrosporium elegans, Penicillium duclauxi, Penicillium lilacinum, Curvularia lunata, Drechslera hawaiiensis, Verticillium Fungicola and Pestalotiopsis clavispora were investigated by El-gendy et al. (2011). The fungi Aspergillus niger and Penicillium chrysogenum have studied for its tolerance to copper, cadmium and lead by Al-Sohaibani (2011).
The yeast, *Candida tropicalis* was investigated for the MIC of Cd$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Hg$^{2+}$, Cu$^{2+}$, Cr$^{6+}$ and Pb$^{2+}$ by Rehman and Anjum (2011) and the tolerance of cadmium was high, therefore; this yeast also used for the biosorption of Cd$^{2+}$. Metal tolerance of some endophytic fungi isolated from dominant plant species of mine wasteland was tested against Pb$^{2+}$ and Zn$^{2+}$ by Li et al. (2012) and suggested that fungal endophyte colonization in Pb-Zn polluted plants have a potential to the removal of this metal from polluted sites through phytoremediation. The heavy metals (Cr and Pb) tolerance of different fungal strains namely *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus versicolor*, *Scopulariopsis* sp., *Curvularia* sp., *Helminthosporium* sp., *Humicola grisea* sp., *Nannizzia* sp. and *Fusarium* sp. isolated from contaminated agricultural soil were reported by Iram et al. (2012). The filamentous fungi belonging to the genera of *Aspergillus*, *Penicillium* and *Cladosporium* were reported to tolerance of metals such as Zn, Cu and Mn by Siokwu and Anyanwu (2012). The fungi belong to the genera of *Aspergillus*, *Curvularia* and *Pithym* were studied to their metal tolerance against Cu, Cd and Ni by Akhtar et al. (2013). The potential of *Trichoderma* spp. for Ni and Cd tolerance was investigated by Nongmaithem et al. (2016). *Neurospora* sp. (SG1) and *Penicillium* sp. (GK1) were reported for their resistance of heavy metals such as lead, nickel, cobalt, chromium, copper, manganese and zinc by Desai et al. (2016).

**Biosorption of iron with other heavy metals by microorganisms**

Metal recovery from industrial wastes and detoxification both by the potential use of fungi has received much attention in recent years. Removal of iron and other heavy metal ions from industrial effluents has been reported by some previous workers. Brady et al. (1994) have studied the yeast cells of *Saccharomyces cerevisiae* treated with hot alkali. They reported that these cells were capable of accumulating a variety of heavy metal cations (Fe$^{3+}$, Cu$^{2+}$, Cr$^{3+}$, Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ag$^+$, Ni$^{2+}$, and Fe$^{2+}$). Dry cells of *Rhizopus arrhizus* are a potential alternative to the removal of iron (III), lead (II) and cadmium (II) ions from industrial wastewater (Ozer et al., 1997). Sag et al. (1998) studied algal biomass *Chlorella vulgaris* and fungal biomass *Rhizopus arrhizus* in comparison for their ability to bind metals namely Cr(VI) and Fe(III).

Chandra Sekhar et al. (1998) studied on biosorption of Ca, Fe, Ni, Cr(III) and Cr(IV) using *Aspergillus niger* (industrial biomass) with some parameters like pH,
presence of co-ions in binary, ternary and quaternary combinations. Gomes et al. (1999) worked on cyano-metal complexes of gold, silver, copper, iron and zinc uptake by *Aspergillus niger*. In this investigation, they observed the combined effect of both metal ions on the biosorption of Cr(VI) and Fe(III) ions. Bag et al. (1999) worked on the determination of trace metals in geological samples by *Aspergillus niger* immobilized on sepiolite. Bag et al. (2001) reported a method for the determination of Fe(II) and Fe(III) in water using *Aspergillus niger* immobilized on sepiolite.

Aksu and Gulen (2002) suggested that many heavy metal bearing wastewaters also contain their metal-cyanid complex ions. In this study, individually and simultaneously examined the biosorption of iron (III) and iron-cyanid complex ions using *Rhizopus arrhizus* from aqueous solution. They observed that the presence of two or more species of metal ions in the solution showed synergistic or antagonistic interaction to each other them which might affect the individual uptake of the metal ion by the microorganism. Dias et al. (2002) successfully investigated the biosorption of chromium, nickel and iron from metallurgical effluents, using *Aspergillus terreus* immobilized in polyurethane foam. Goyal et al. (2003) described a process of competitive biosorption of Cr(VI) and Fe(III) ions on *Streptococcus equisimilis, Saccharomyces cerevisiae* and *Aspergillus niger* and also compared to single metal ion adsorption in solution. A bacterial biomass of *Streptomyces rimosus* treated with NaOH was studied for the biosorption of Fe$^{3+}$ from aqueous solution and up to 122 mg of Fe adsorbed by per gram of biomass (Selatnia et al., 2004).

Franco et al. (2004) worked on chitin and chitosan extracted from mycelial biomass of *Cunninghamella elegans* and performance for copper, lead and iron biosorption in aqueous solution was studied. In this study, they found that chitosan showed the highest affinity for copper and chitin for iron adsorption. Soylak et al. (2006) investigated the biosorption of Cu(II), Pb(II), Zn(II), Fe(III), Ni(II) and Co(II) ions on immobilized *Aspergillus fumigatus* on Diaion HP-2MG resin. Binupriya et al. (2006) were studied on removal of Fe(II), Cr(IV), Ni(II) and Hg(II) from aqueous solutions and electroplating industry using the fungal biomass of *Aspergillus japonicus*, thereafter; the toxicity of effluent was also tested for seed germination and seedling development of *Zea mays* plant. The results showed that effectiveness of fungal treatment to reduced phytotoxicity in the effluent. The biosorption of Cu(II), Pb(II), Fe(II) and Co(II) was investigated by Tuzen et al. (2007) using *Bacillus*
sphaericus biomass, immobilized in Diaion SP-850 resin. The fungus Polyporus squamosus was tested for Fe(III) adsorption from solutions with different types of the parameter and isotherm adsorption model studies were concluded that up to 31.2 mg of iron was fixed each gram of biomass (Razmovski and Sciban, 2008). Maruthi et al. (2010) were reported the removal of iron (II) and (III) was 96.94% and 99.82%, respectively by Thiobacillus ferrooxidans. Similarly, in the case of Aspergillus niger the removal of iron (II) and (III) was 99.62% and 80%, respectively. A seaweed biomass of Sargassum sp. was studied for mercury and iron biosorption process using kinetic and isotherms model (Saravanan et al., 2010). Mane and Kadam (2012) studied the potentiality of an algae Spirulina platensis for the removal of Cr, Fe, Mn and Se ions from aqueous solution in an immobilized form of biomass.

Kareem et al. (2014a) worked on a fungal biosorbent Aspergillus sp. TU-GM14, immobilized on Detarium microcarpum matrix was showed the high removal of Fe(II) and Mn(II) ions (>14 mg g⁻¹) from aqueous solution. Kareem et al. (2014c) examines the biosorption and bioaccumulation of Fe(II) by Aspergillus terreus and Trichoderma viride in a batch system and also studied the effects of important parameters, such as initial metal concentration, temperature and inoculum concentration on biosorption capacity. The effect of Al(III), Fe(II) and Mn(II) on growth, accumulation and sorption potential of some fungi including Aspergillus oryzae, A. fumigatus, A. niger, Trichoderma longibrachiatum, T. viride, Penicillium sp. and Rhizopus sp. was investigated by Osaizua et al. (2014). A fungal biomass Pleurotus mutilus collected from an antibiotic production plant was used to the removal of Mn²⁺ and Fe³⁺ from ground water by Madani et al. (2015) and maximum biosorption capacities of fungal biomass were 18.5 mg/g and 26.7 mg/g for Mn²⁺ and Fe³⁺, respectively.

**Biosorption of iron by other resources**

Ahamed and Balakrishnan (2010) worked on adsorption of a ferrous ion from aqueous solution using acid activated carbon prepared from Albizia lebbeck bark as low-cost carbon sources. Baskaran et al. (2011) were using Zea mays dust carbon (ZDC) as a low-cost adsorbent for the batch removal of ferrous ion. Prabakaran and Arivoli (2011) studied on Thespesia Populnea bark carbon (TPC) as an effective low-cost adsorbent for the removal of a ferrous ion from aqueous solution. Sheibani et al.
(2012) suggested that hazelnut hull was a suitable adsorbent for the removal of Fe(III) from aqueous solutions. It showed 83.5 % removal of Fe(III) under optimum conditions and the capacity of this adsorbent was 13.5 g mg/g. Rose et al. (2012) showed the efficiency of carbon obtained from wild jack and jambul as an adsorbent for the removal of iron(II) ions from aqueous solution. Mamatha et al. (2012) reported that *Pongamia pinnata* tree bark could be used as a biosorbent for the removal of iron from aqueous and industrial effluents. The maximum adsorption capacity was found to 146 mg/g of iron in wastewater. *Cucumis melo* rind was reported as a new biosorbent for the removal of Fe(II) and Mn(II) from synthetic wastewater and the maximum biosorption capacity of Fe(II) and Mn(II) were 4.98 mg/g and 1.37 mg/g, respectively (Othman and Asharuddin, 2013). Kamarudzaman et al. (2013) worked on spent mushroom compost of *Pleurotus ostreatus* for the biosorption of iron (III) under different parameters having 5.88 mg/g of maximum capacity for iron (III). Removal of Fe(II) using pomegranate peel carbon from aqueous solution reported by Moghadam et al. (2013) and they found maximum adsorption capacity of Fe(II) was 18.52 mg/g. The biomasses of oil palm such as empty fruit bunch (EFB), oil palm leaves (OPL), oil palm frond (OPF), and oil palm bark (OPB) were used as biosorbents to remove lead (II) and iron (III) by Khosravihaftkhany et al. (2013).

Zhang et al. (2014) were used an agricultural waste, rice husk ash (RHA) for the removal of Fe(II) and Mn(II) from aqueous solutions. Runtti et al. (2014) investigated that chemically activated carbon residue from biomass gasification process as a sorbent for iron (II), copper (II) and nickel (II) ions from an aqueous solution and maximum sorption uptake by activated carbon residue were 20.5, 23.1 and 18.2 mg/g, respectively. El-sayed et al. (2015) evaluated the ability of maize stalks to remove Fe(II) from aqueous solution as a cheap biosorbent and found 5.14 mg/g of maximum uptake capacity of iron. Abdel-ghani et al. (2015) worked on activated carbon prepared from rice hulls to remove aluminium (III) and iron (III) from synthetic and real wastewater in single and binary systems. A comparative study of the surface structure properties along with the Fe(II) and Mn(II) removal capability of rice husk ash (RHA), inactive *Saccharomyces cerevisiae* powder (ISP), and rice husk (RH) in aqueous solution was done by Jiang et al. (2016).
Biosorption of heavy metals using fungal biosorbent

Several researchers under several conditions have investigated different types of biomasses for their metal binding capability. Volesky and Holan (1995) have mentioned several microbes and their metal-binding capacities in their report. Kapoor and Viraraghavan (1998) studied the effect of pretreatment of *Aspergillus niger* biomass on biosorption of Pb, Cd, Cu and Ni. Kapoor *et al.* (1999) have studied the potential use of the fungus *Aspergillus niger* to the removal of lead, cadmium, copper and nickel ions. An attempt was done by Yan and Viraraghavan (2000) to use different chemicals in order to study the effect of pretreatment of *Mucor rouxii* biomass on biosorption of Pb$^{3+}$, Cd$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$. Their results showed that alkali pretreatment is an effective method to improve the biosorption capacity for metal ions by dead biomass.

Bai and Abraham (2001) studied the biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*. Say *et al.* (2001) studied the biosorption from artificial waste waters with heavy metals like Cd(II), Pb(II) and Cu(II) onto the dry fungal biomass of *Phanerochaete chrysoriparium*. A waste biomass of fermentation industry, *Aspergillus niger* was studied for adsorption of lead (II) from aqueous solution (Jianlong *et al.*, 2001). Heavy metal biosorption by entire mycelia and certain components of *Aspergillus niger*, *Rhizopus oryzae* and *Mucor rouxii* was accomplished by Baik *et al.* (2002). Say *et al.* (2003) studied the potential use of the fungus *Penicillium purpureogenum* for removal of Cd(II), Pb(II), Hg(II) and As(III) ions from aqueous solution and effect of pH on biosorption capacity was also studied.

Cabuk *et al.* (2005) investigated the effect of pretreatment of fungal biomass of *Aspergillus versicolor*, *Metarrhizium anisopliae* and *Penicillium verrucosum* on the Pb$^{2+}$ biosorption capacity. Ahmad *et al.* (2005) studied on biosorption potential of *Aspergillus* and *Rhizopus* species for removal of Cr(II) and Cd(II). Dursun (2006) observed the kinetics and thermodynamics of copper (II) and lead (II) biosorption on *Aspergillus niger* pretreated by NaOH with respect to pH, temperature and initial metal ion concentration in a batch system. Akar and Tunali (2006) have studied the biosorption characteristics of *Aspergillus flavus* for the removal of Pb(II) and Cu(II). Removal of Cr(VI) from solution and wastewater using live and pretreated biomass of *Aspergillus flavus* was investigated by Deepa *et al.* (2006). Mukhopadhyay *et al.*
have worked on the kinetic model for the biosorption of copper by treated biomass of *Aspergillus niger*. Das *et al.* (2007) have investigated the effects of pretreatment on Cd$^{2+}$ biosorption by *Pleurotus florida* biomass. Dead biomass of *Aspergillus niger, Aspergillus sydoni* and *Penicillium janthinellum* was reported for biosorption of Cr(VI) from aqueous solution as well as waste water by Kumar *et al.* (2008). Al-Garni *et al.* (2009) have examined the high tolerant fungi, *A. fumigatus* for the removal of cadmium from aqueous solution and living biomass was more efficient for biosorption rather than its dried biomass. The ability of *Aspergillus niger* resting cells entrapped in the poly vinyl alcohol (PVA) network to remove the Cu(II) and Cd(II) from single ion solutions (Tsekova *et al.*, 2010). Further, the biosorption of Pb$^{2+}$, Hg$^{2+}$ and Cd$^{2+}$ using free and immobilized *Aspergillus terreus* from aqueous solution were compared by Sun *et al.* (2010).

Hemambika *et al.* (2011) have worked on three fungal species namely *Aspergillus, Penicillium* and *Cephalosporium* species. They observed that immobilized fungal cells have a greater potential application for the removal of Cu, Cd and Pb from industrial wastewater rather than the dead fungal cells. Different morphologies of *Mucor indicus* biomass treated with NaOH performed for biosorption of Pb$^{2+}$ ions from aqueous solution and filamentous form of the grown biomass showed higher biosorption capacity (Javanbakht *et al.*, 2011). Rehman and Anjum (2011) have examined the ability of *Candida tropicalis* for cadmium tolerance and its biosrption from liquid medium as well as industrial wastewater. Shroff and Vaidya (2011) studied the physico-chemically treated fungal biomass of *Mucor hiemalis* for the removal of Ni(II). Peart *et al.* (2012) have worked on six fungi namely *Rhizopus oryzae* ATCC 11145, *Mucor plumbeus* ATCC 4740, *Cunninghamella echinulata* var. *elegans* ATCC 8688a, *Aspergillus niger* ATCC 9142, *Phanerochaete chrysosporium* ATCC 24725 and *Whetzelinia sclerotiorum* ATCC 18687 in order to develop a general technique for the immobilization of filamentous fungi. A fungus *Trichoderma longibrachiatum* was investigated for biosorption and bioaccumulation of lead (II) ions in aqueous solution (Adeogun *et al.* 2012). The fruiting body of jelly fungus *Auricularia polytricha* was investigated for Cd$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ biosorption from aqueous solution (Huang *et al.*, 2012). *Aspergillus versicolor* was studied for Pb$^{2+}$ and Cu$^{2+}$ removal from aqueous solution by Gazem and Nazareth (2012). Khani *et al.* (2012) have studied the experimental
parameters for the biosorption of strontium from aqueous solution using *Aspergillus terreus* biomass. The dead biomass of *Aspergillus tamari* was studied for its adsorption properties against heavy metals and effective for the removal of Pb$^{2+}$ ions in aqueous solution (Sahin et al., 2013). Ganguly (2013) has worked on As(III) resistant fungus *Aspergillus niger* X$_{300}$ to examine the changes in glucose concentration, pH and nitrogen content in the synthetic medium during fungal growth and biosorption of As(III). A response surface methodology was performed for optimization of Pb(II) and Ni(II) biosorption using *Penicillium* sp. biomass isolated from mine drainage (Aytar et al., 2014). Joshi and Sahu (2014) worked on lead, cadmium and nickel adsorption by live and NaOH pretreated biomass of *Mucor rouxii* (ATCC 24905) and found that live biomass was performed better than pretreated biomass at pH 4.0 and 5.0. The potential of *Rhizopus* sp. for the removal of Cu$^{2+}$ from aqueous solution using the different textile material to immobilization was investigated by Gomes et al. (2014). Gharieb et al. (2014) studied the effects of surrounding factors on the biosorption of Pb(II) and Co(II) using pretreated biomass of *Rhizopus oryzae*. An immobilized dead biomass of *Aspergillus awamori* for its ability for biosorption of Ni(II) was investigated by Shahverdi et al. (2014). Kordialik-Bogacka and Diowksz (2014) have investigated effects of modified biomass of *Saccharomyces pastorianus* using different pretreatment methods on biosorption of copper, lead and cadmium. Khalilnezhad et al. (2014) were studied the biosorption of manganese (II) using suspended and immobilized cells of fungal biomass and nano biomass of *Penicillium camemberti*. Sugasini et al. (2014) have studied the Cr(VI) tolerance and biosorption potential of four *Aspergillus* species including *A. terreus*, *A. tamarii*, *A. flavus* and *A. niger*. Rouhollahi et al. (2014) have examined the enzymatic and alkali pretreatments to enhance the biosorption capacity of *Rhizomucor pusillus* biomass.

The tolerance and biosorption potential of *Aspergillus awamori* to Cd(II) was investigated by El-Sayed (2015). Farhan and Khdom (2015) worked on the removal heavy metals including Pb, Zn, Cr, Co, Cd and Cu ions using raw and pretreated biomass of yeast *Saccharomyces cerevisiae*. Mohammadian Fazli et al. (2015) have examined the cadmium tolerance and removal capacity of some fungal species such as *Aspergillus versicolor*, *Aspergillus fumigatus*, *Paecilomyces* sp.9, *Paecilomyces* sp.G, *Trichoderma* sp, *Microsporum* sp., *Cladosporium* sp. isolated from cadmium polluted
sites. Biosorption of Cu(II) and Pb(II) was performed by Iram and Abrar (2015) using *Aspergillus flavus* and *Aspergillus niger* biomass. Sivakumar (2016) has studied the biosorption of Cr(VI) in a tannery industry wastewater using *Aspergillus niger*, *A. flavus*, *A. fumigates*, *A. nidulans*, *A. heteromorphus*, *A. foetidus* and *A. viridinutans*. Nwidi and Agunwamba (2016) have worked on *Saccharomyces cerevisiae* with other microorganisms for the removal of Zn, Cu and Mn ions.

**Analytical techniques used in identification of biosorption mechanism**

The instrumental analysis including infrared (IR) spectroscopy, electron microscope, X-ray dispersion and diffraction analysis revealed that the ion exchange mechanism is mainly involved in biosorption process (Kuyucak and Volesky, 1989). Figueira et al. (1999) was worked on brown macroalga *Sargassum fluitans* and revealed the mechanism of iron uptake by dry biomass of this seaweed at the molecular level using Transmission electron microscopy (TEM) and the elemental analysis by electron dispersive spectroscopy (EDS). The cell wall composition of two strains of *Cladosporium cladosporioides* was investigated by Pethkar et al. (2001) using XPS and FTIR analysis for comparative studies of metal biosorption. Selatnia et al. (2004) have reported that a bacterial cell wall of *Streptomyces rimosus* contains anionic groups such as -COO, -CO, -NH, -C=O, -OH by IR spectral analysis, whose ability to bind Fe$^{3+}$ ions was higher. The functional groups such as –COOH, –OH and –NH are involved in the biosorption process of Pb(II) on the surface of *Botrytis cinerea* and that cell-metal ion interaction was confirmed by SEM-EDAX analysis (Akar et al., 2005). Park et al. (2008) investigated X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) studies on Chromium-binding functional groups during Cr(IV) biosorption by *Ecklonia* sp. (brown seaweed). The FTIR analysis was suggested that the ionic exchange and complexation were involved in the biosorption of ammonium on sawdust (Wahab et al., 2010).

Simonescu and Ferdes (2012) worked on different fungal strain such as *Aspergillus oryzae*, *Aspergillus niger*, *Fusarium oxysporum* and *Polyporus squamosus* for the removal of Cu(II) from aqueous system and IR spectra (FTIR) revealed that interaction between fungal biomass and copper ions involves hydroxyl, amino, carboxyl and carbonyl groups of fungal biomass surface depending on types of fungal strain. Othman and Asharuddin (2013) have used FTIR, SEM-EDX and X-ray
fluorescence (XRF) analysis for the biosorption of Fe(II) and Mn(II) by *Cucumis melo* rind. The oil palm biomasses used as biosorbent for the removal of Pb(II) and Fe(III) and characterized by SEM and FTIR analysis (Khosravihaftkhany et al., 2013).

The biosorption of Fe(II) and Mn(II) using rice husk ash was characterized by the SEM and XRF analysis for structural, morphological and elemental composition study (Zhang et al., 2014). Adekola et al. (2014) reported biosorption of Fe(II) and Mn(II) using rice husk ash using XRF spectrometry for the characterization of the elemental composition of the adsorbent, FTIR spectrometry for functional groups analysis. The chemically modified *Lagenaria vulgaris* shell was characterized by FTIR, SEM-EDX analysis for the biosorption of Cu(II) (Kostic et al., 2015). The FTIR analysis was performed on a fungal biomass *Pleurotus mutilus* in order to obtain information about the presence of negatively charged functional groups such as carboxyl, amine, alcohol and hydroxyl and SEM analysis was also conducted to surface studies of the fungal cell wall by Madani et al. (2015). Huang and Lin (2015) was performed FTIR and SEM analysis for the determination of functional matrices and groups in Hg(II) and Cu(II) biosorption by algal biomass of *Sargassum fusiforme*. Amin et al. (2015) have investigated biosorption characteristics of fluoride ions using white rot fungus (*Pleurotus eryngii*) from aqueous solution and its surface and sorption characteristics were analyzed by SEM, EDX and FTIR spectrometry.

Shameer (2016) was isolated the Extracellular Polysaccharides (EPS) from *Bacillus* sp. and its chemical characteristics were documented using liquid FTIR spectra followed by an assessment of heavy metals (lead, copper and cadmium) biosorption using Atomic Absorption Spectroscopy (AAS). Several functional groups such as hydroxyl, carboxyl and amine on the surface of *Sargassum vulgare* (brown algae) biomass are involved in iron binding, which was confirmed by FTIR observations (Benaisa et al., 2016). Kumar et al. (2016) reported that after biosorption SEM analysis revealed the enhancement in weight percentage of Pb(II) and Cu(II) on the surface of *Plukenetia volubilis* L. shell biomass.