ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Screening of Macrofungi for the Removal of Ag (I) and Zn (II) Ions from Aqueous Environment.

Devlina Das, Vimala R, and Nilanjana Das*.

Environmental Biotechnology Division, School of Bio Sciences and Technology, VIT University, Vellore-632014, Tamil Nadu, India.

ABSTRACT

Reports are available on Ag(I) and Zn (II) binding capacity of some microorganisms and other adsorbents. However, reports are scanty on biosorption of silver and zinc by macrofungi. The present study was conducted using dried biomass of macrofungi viz. oyster mushroom (*Pleurotus platypus*), milky mushroom (*Calocybe indica*) and paddy straw mushroom (*Volvariella volvacea*) for the removal of Ag(I) and Zn(II) ions from aqueous medium. The influence of various factors viz. pH, biomass dosage , initial metal concentration, contact time and temperature on removal of Ag(I) and Zn(II) ions were investigated under batch mode. Under optimized condition, maximum removal of Ag(I) was Zn(II) was noted by *Pleurotus platypus* followed by *Calocybe indica* and *Volvariella volvacea*. Among the three macrofungi, maximum uptake of Ag(I) and Zn(II) were noted onto *P.platypus* which were found to be 46.7 mg /g and 135.1 mg/g respectively under optimized conditions. Therefore, *P.platypus* may serve as a potential biosorbent for the removal of Ag(I) and Zn(II) ions from industrial waste water.

Key words: Ag(I); Biosorption; Macrofungi; *P.platypus*; Removal ; Zn(II)

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Silver as one of the precious metals is in high demand since it plays an important role in many aspects of human life. It is widely employed in the photographic and imaging industry for many years. Silver and its compounds are used as disinfectants in wastewater treatment, food/beverages/drugs processing, and drugs, etc. [1]. But the monovalent ionic silver i.e. Ag(I), is of particular environmental concern, due to its potential impact on human health and ecosystems. It is known to be released to the environment through its various industrial applications, leading to the possible exposure of aquatic organisms [2]. The accumulation of silver ions in organisms (including humans) through the food chain causes numerous diseases and disorders [3]. Mild allergic responses have been attributed to dermal contact with silver [1]. When silver is ingested by humans, it is metabolized and deposited in the subcutaneous fat causing cosmetic disorder of argyria, in which the affected person's skin is discolored [4] The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) classified soluble silver ions as hazardous substances in water systems and limited the level of silver in drinking water to be 100µg /L [5]. Therefore, with the increasing concerns on the toxicity of soluble silver ions in water, it is necessary to remove and recover silver from wastewater.

Zinc is an essential element required for growth and metabolism of living organisms, but it may be toxic when its concentration exceeds that required for correct biological functioning causing muscular stiffness, loss of appetite, nausea and irritation [6,7] . Zinc is often found in high concentrations in the effluents discharged from industries such as manufacture of alloys, sheet metal galvanization, TV picture tubes etc. Discharging these effluents into natural systems adjoining landmasses and sewer systems is a normal practice in small and medium scale industries. This poses serious problems to the environment and ecosystems. Environmental quality standards for Zn (II) according to the European Union are 40 mg/ L for estuaries and marine waters and 45–500 mg/L for freshwater based on its hardness [8]. Zinc is phytotoxic, and the recommended level of zinc for disposal on agricultural land is 2.5 mg/g of dried sludge solids. The permissible limit of Zn (II) in drinking water as set by the World Health Organization (WHO) is 4.0 mg/L [9]. Therefore, there is a significant need for the removal of zinc from wastewater [10].

The conventional technologies used for silver removal from wastewaters include chemical reduction, membrane filtration, ion exchange, adsorption and electrochemical methods [11-15]. There are reports on zinc removal using traditional technologies viz. chemical precipitation, reverse osmosis, ion exchange technology, electrocoagulation, ultrafiltration, electrodialysis and adsorption [16- 21]. Although the conventional methods can remove silver and zinc ions from the effluents, they are practically not economical. It urgently needs a new technology. Biosorption has emerged as promising eco-friendly technology for the removal and recovery of metal ions from aqueous solutions in water pollution control [22]. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery [23].

The use of microorganisms including algae, microfungi, yeast and bacteria on silver biosorption has been reported [24-27]. Recent reports on biosorption of Zn(II) include bacteria, fungi, yeast and algae [28-30]. But reports are scanty on the application of macrofungi as potential biosorbent for the removal of silver and zinc. Macrofungi are considered to be ideal for the purpose of evaluation as biosorbent of metals [31] . They are macro in size, tough in texture and have other physical characteristics conducive for their development as biosorbents [32].

In the present study, macrofungi were used as biosorbents and screened for the removal of Ag(I) and Zn(II) from aqueous solution. The effects of various factors viz. solution pH, biosorbent dosage, initial metal concentration, contact time and temperature on Ag(I) and Zn(II) removal have been investigated in batch mode.

MATERIALS AND METHODS

Preparation of biosorbents

Three types of macrofungi *viz.* oyster mushroom (*Pleurotus platypus*), milky mushroom (*Calocybe indica*) and paddy straw mushroom *(Volvariella volvacea)* were used for batch adsorption experiments. Fruit bodies were washed thoroughly with deionized water and dried at 50^{o}C for 24 h. The dried fruit bodies were

pulverized in a mortar and pestle and kept in air tight plastic bottles. Particles with 425-600 µm size were used for the experiment

Preparation of Ag(I) and Zn(II) solution

Batch experiments were conducted in a continuously stirred (120 rpm) conical flasks containing 100 ml of Ag(I) and Zn(II) solution separately. In the present study, five parameters viz., pH, biosorbent dosage (g/L), initial metal concentration (mg/L), contact time (h) and temperature (°C) were varied. Samples were collected at regular time intervals, filtered and analysed for the residual metal concentrations by Atomic absorption Spectrophotometer (Varian AA-240, Australia). Absorbance was measured at 338.3 nm for Ag(I) and at 213.9 nm for Zn(II) ions.

The metal uptake capacities were calculated using the mass balance equation as shown below:

$$q = \frac{C_0 - C_f}{M} \times V \qquad (1)$$

Where q is the sorption capacity i.e. the amount of metal ion biosorbed onto unit amount of biomass (mg /g) ; C_0 and C_f are the concentrations (mg/ L) of the metal ion in the initial solution and after biosorption respectively; V is the volume of the aqueous phase (l) ; and M is the amount of the biomass.

The efficiency or removal (%) of metal ions was calculated using the formula :

$$\text{Removal (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

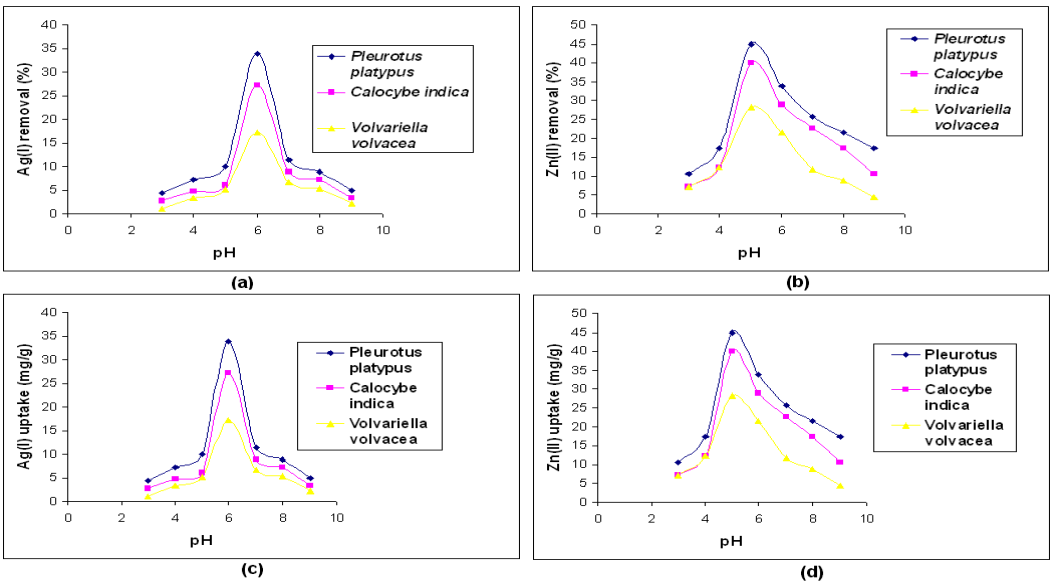
Effect of pH

The removal of silver (I) and zinc(II) by the biosorbents viz. *Pleurotus platypus*, *Calocybe indica* and *Vovariella vovacea* at various pH values are presented in Fig 1. Percent removal of silver was noted to be maximum at pH 6.0 for all the biosorbents (Fig. 1a). Silver removal was maximum (33.95%) in case of *P.platypus* followed by *C.indica* (27.3%) and *V. volvacea* (17.25 %) (Fig.1a). Maximum silver uptake was noted in case of *P.platypus* (Fig.1c)

Maximum removal percentage of zinc was found to be 44.9 %, 39.9 % and 28.3 % for *P.platypus* , *Calocybe indica* and *Vovariella vovacea* at pH 5.0 (Fig.1b). There was a decrease in removal beyond the optimum pH values. Zinc uptake was found to be maximum at pH 5.0 for all the three macrofungi *P.platypus* , *Calocybe indica* and *Vovariella vovacea* at pH 5.0 (Fig. 1d). So, it could be seen that for all the three macrofungi, silver and zinc removal increased along with the increase of pH of the adsorbate solution and decreased beyond optimum values. At pH values more than optimum, metal precipitation was noted.

This pH dependency of biosorption efficiency could be explained by the functional groups involved in metal uptake and metal chemistry [33]. According to Malkoc and Nuhoglu [34], H^+ ions would compete with metal cations for exchange site at pH values lower than the optimum value which would result in a decrease in metal uptake values. A decrease in metal biosorption was noted at pH values greater than the optimum value which could be possibly due to the formation of metal hydroxides. Previous researchers reported that the functional groups such as carboxyl, amine group and phosphate were responsible for biosorption of heavy metals [35,36]. Thus, higher pH value may affect the number of negatively charged sites, which is highly dependent on the dissociation of functional groups [37] .

ISSN: 0975-8585



(Initial metal concentration: 100 mg/L; Time: 2h; Biomass dosage: 1g/L; Temperature: 30°C)

Figure 1: Effect of pH on biosorption of Ag(I) and Zn(II) ions using macrofungi

Effect of biomass dosage

The number of available sites and exchanging ions for adsorption depends upon the amount of biosorbent in the biosorption process. The effect of adsorbent dosage on the silver and zinc removal is presented in Fig 2. The silver and zinc removal was found to be maximum in case of *P.platypus* which increased rapidly with an increasing concentration of biosorbents (Fig. 2a, 2b). In case of *P.platypus*, at an optimum biosorbent dosage (2.5 g/L) , the maximum Ag(I) uptake values were found to be 39.9 and Zn(II) uptake was 44.9 mg/g at dosage of 1.5 g/L respectively (Fig. 2c,2d). Requirement of low dosage in case of Zn(II) ions compared to Ag(I) ions could possibly account for the increased potential of Zn(II) biosorption. At dosage values beyond the optimum value, metal uptakes were found to decrease. This could be probably due to the clumping of the macrofungi particles thereby decreasing the surface area [38,39]. The uptake potential of the biosorbents was found to be higher in case of zinc as compared to silver. The increase in uptake can be attributed to the increased number of sites and exchangeable ions available for adsorption [40-42].

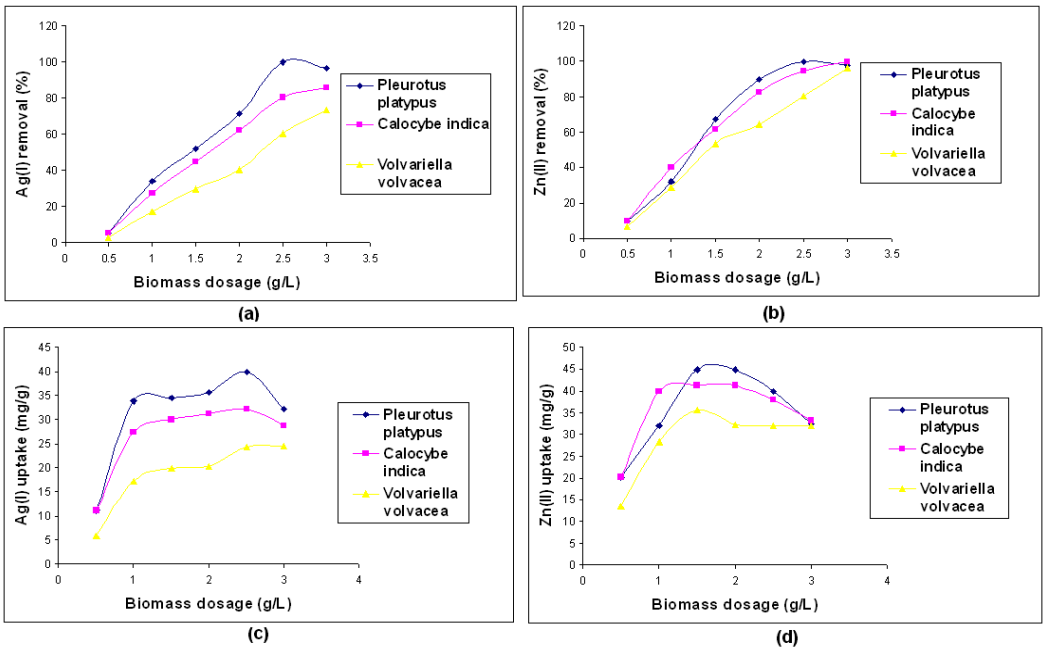


Figure 2: Effect of biomass dosage on biosorption of Ag(I) and Zn(II) using macrofungi

ISSN: 0975-8585

Effect of initial metal concentration

The initial metal concentration provides an important driving force to overcome all mass transfer resistance of heavy metal ions between the aqueous and solid phases. The effect of initial metal concentration in the range 50 mg/L - 300 mg/L on the biosorption of Ag(I) and Zn(II) by macrofungi was evaluated in a batch system. Maximum Ag(I) and Zn(II) removal was shown by *P.platypus* at an optimum concentration of 100 mg/L as shown in Fig. 3a and Fig. 3b. Maximum Ag(I) uptake was found to be 43.5 mg/g of biomass in presence of silver concentration of 200 mg/L (Fig. 3c) whereas Zn(II) ions exhibited a higher uptake value of 89.9 mg/g at an initial zinc concentration of 250 mg/L respectively (Fig.3d) onto *P.platypus*. Beyond the optimum concentration, a decrease in uptake was noted due to the insufficient availability of surface functional groups.

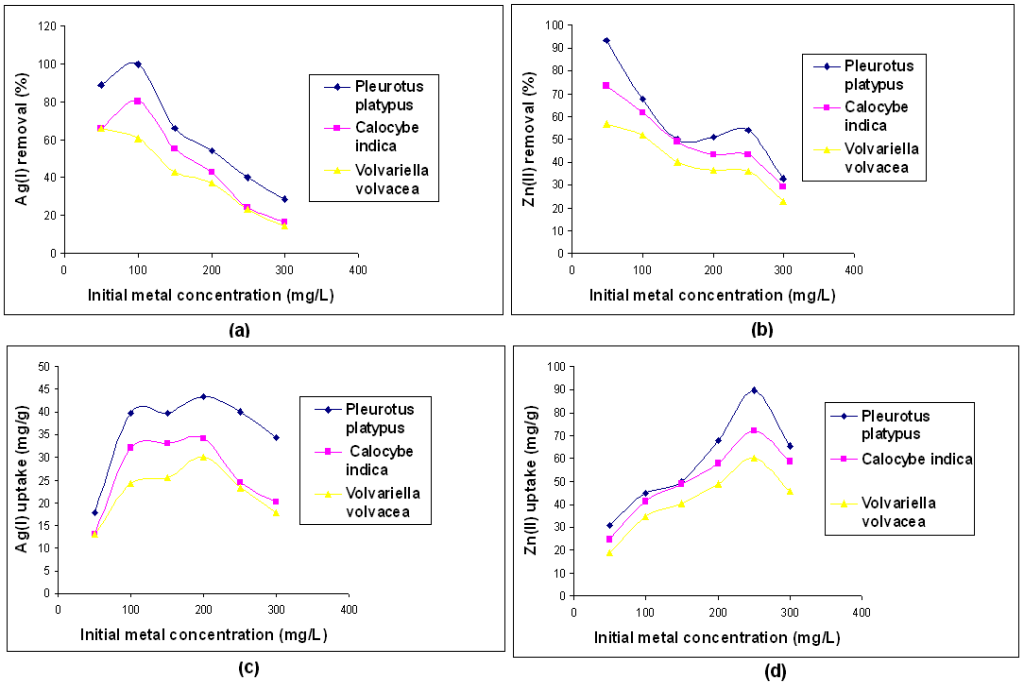


Figure 3: Effect of initial metal concentration on biosorption of Ag(I) and Zn(II) using macrofungi

Effect of contact time

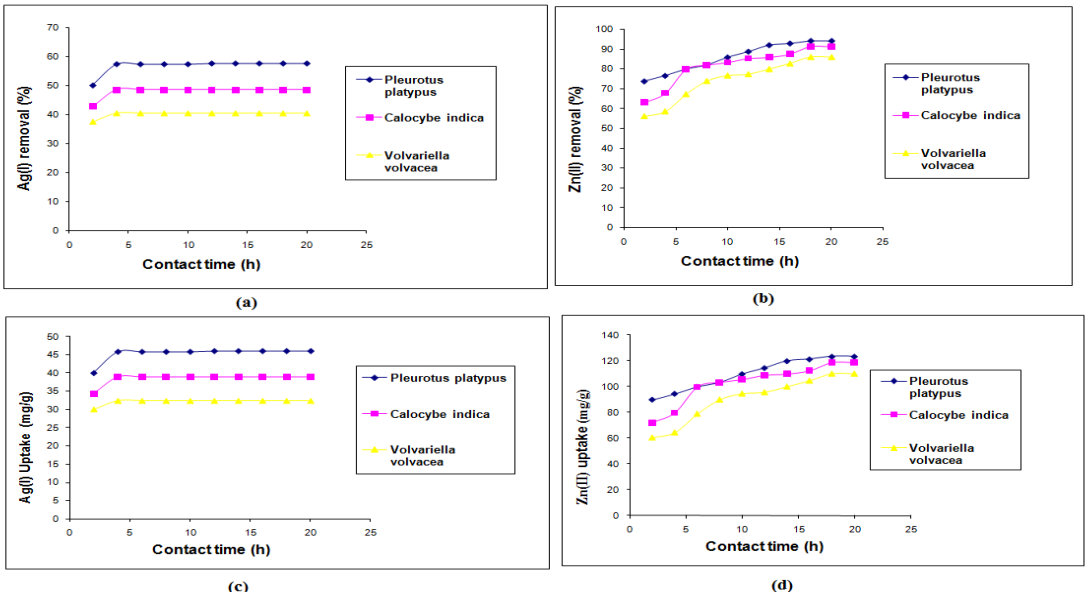


Figure 4: Effect of contact time on biosorption of Ag(I) and Zn(II) using macrofungi

ISSN: 0975-8585

The effect of contact time on the biosorption of Ag(I) and Zn(II) ions is depicted in Fig.4. The maximum removal was noted in case of *P.platypus* which was found to be 57.3 % at the end of 4 h in case of Ag(I) shown in Fig.4a whereas 94.0 % removal was noted in case of Zn(II) at the end of 18 h (Fig. 4b). The uptake efficiency reached equilibrium after 3 h and 19 h in case of Ag(I) and Zn(II) respectively (Fig 4c, d). Zn(II) biosorption was found to be considerably higher than Ag(I) at all stages.

A two-stage kinetic pattern was observed in case of Zn(II) ions where a rapid increase in uptake was noted till a time period of 16 h followed by a gradual increase till 19 h. Beyond this time period, a plateau effect was noted. Similar results were reported in case of Pb(II) and Ni(II) biosorption onto olive tree pruning waste [43]. In case of Ag(I) biosrption, The extremely rapid adsorption rate in the first few minutes, decelerated abruptly, apparently due to the saturation of the more accessible adsorption sites. In the initial stages, the removal efficiencies of the metal by the adsorbent increased rapidly due to abundant availability of active sites on the biomass, and with the gradual occupancy of these sites, the sorption became less efficient in the later stages [44,45]. The above results were obtained possibly due to the electrostatic attraction, cellular affinity and active transport. Among them, electrostatic attraction and cellular affinity were based upon physicochemical interactions between the heavy metal ions and functional groups of cell wall. Because this process was independent of metabolism, the binding of heavy metals was very quick [46- 49].

Effect of temperature

Temperature is an important parameter to be studied in order to determine the thermodynamic parameters (enthalpy, entropy and gibbs free energy of the system). The removal of Ag(I) and Zn(II) ions by macrofungus *Pleurotus platypus* at different temperatures ranging from 10-50°C was evaluated in a batch system (Fig 5a,b). The biosorption of Ag(I) was found to prefer a low temperature of 20°C for *P.platypus* [50].

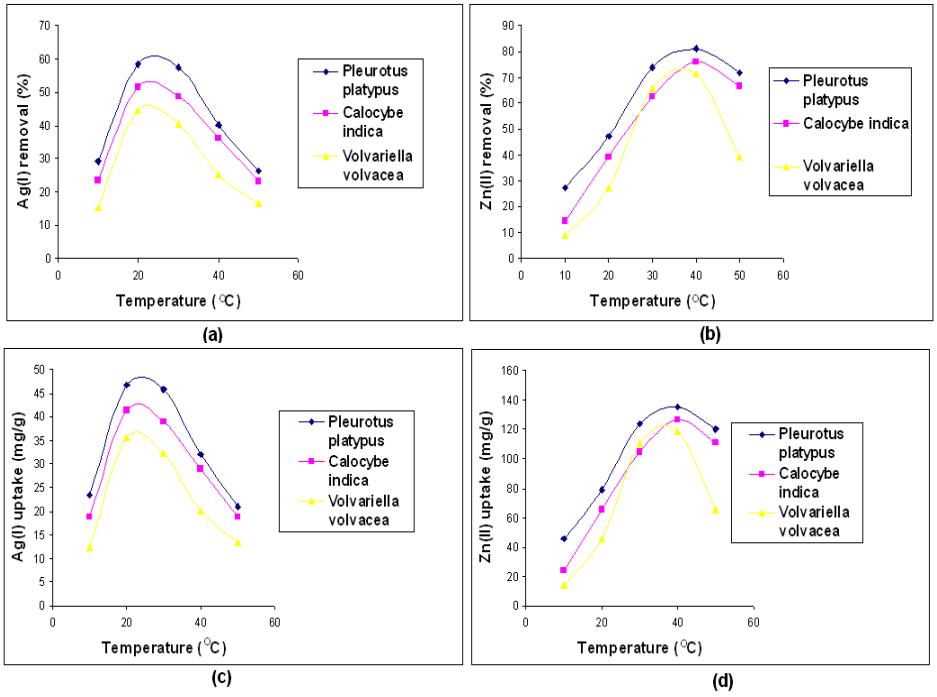


Figure 5: Effect of temperature on biosorption of Ag(I) and Zn(II) using macrofungi

On the contrary, a relatively high temperature of 40°C was found to be suitable in case of Zn(II) biosorption for all the three macrofungi. Similar results were reported in case of Zn(II) biosorption on *Penicillium simplicissimum* species [51]. This could be attributed to the exothermic (heat releasing) and endothermic nature (heat absorbing) of the former and latter process respectively [30] . Among the three macrofungi tested, maximum uptake of Ag (I) and Zn(II) by *P.platypus* was found to be 46.7 mg/g and 135.1 mg/g respectively at an optimum value of other parameters (Fig 5c,d).

ISSN: 0975-8585

CONCLUSION

Fruit bodies of macrofungi viz. oyster mushroom (*Pleurotus platypus*), milky mushroom (*Calocybe indica*) and paddy straw mushroom (*Volvariella volvacea*) were found to be effective for the development of biosorbent with metal uptake properties. The present study identified that *Pleurotus platypus* proved to be the most potential biosorbent for the removal of silver (I) and Zinc (II) ions from aqueous solution. A set of parameters relevant for effective comparison of biosorbents were evaluated to arrive this conclusion.

REFERENCES

[1] ATSDR. Toxicological Profile for Silver. Atlanta, GA, 1990.
[2] Pedroso MS, Pinho GLL, Rodrigues SC, Bianchini A. Aquat Toxicol 2007; 82 :173-180.
[3] Rosenman KD, Seixas N, Jacobs I. Br J Ind Med 1987; 44: 267-272.
[4] Eckelman MJ, Graedel TE. Environ Sci Technol 2007 ; 41 : 6283–6289.
[5] Hosoba M, Oshita K, Katarina RK, Takayanagi T, Oshima M, Motomizu S. Anal Chim Acta 2009; 639: 51–56.
[6] Chapman M, Peter E. Allen H, Godtfredsen K, Zgraggen MN. Environ Sci Technol 1995; 30: 448A-451 A.
[7] Areco MM, Hanela S, Duran J, Afanso MDS. J Hazard Mater 2012; 213-214:123-132.
[8] Joo J, Hassan SHA, Oh S. Int Biodeterior Biodegr 2010; 64: 374.
[9] WHO. Guidelines for Drinking Water Quality, 4th edn. WHO, Geneva, 2011.
[10] Norton L, Baskaran K, McKenzie ST. Adv Environ Res 2004; 8: 629-635.
[11] Chen JP, Lim LL. Chemosphere 2002; 49: 363–370.
[12] Norasikin O, Hanapi M, Masahiro G. J Membrane Sci 2006; 282: 171–177.
[13] Kononova, ON, Kholmogorov AG, Danilenko NV, Goryaeva NG, Shatnykh KA , Kachin SV. Hydrometallurgy 2007; 88: 189–195.
[14] Hanzlik J, Jehlicka J, Sebek O, Weishauptová Z, Machovic V. Water Res 2004; 38: 2178–2184.
[15] Su Y, Li Q, Wang Y, Wang H, Huang J , Yang X. J Hazard Mater 2009; 170: 1164-1172.
[16] Liu Q, Li YJ, Zhang J, Chi Y, Ruan XX, Liu JY, Qian GR. Chem Eng J 2011; 175:33-38.
[17] Aljendeel HA. Journal of Engineering 2011; 17: 647-658.
[18] Jha VK, Matsuda M, Miyake M. J Hazard Mater 2008; 160: 148–153.
[19] Dermentzis K, Christoforidis A, Valsamidou E. Int J Environ Sci 2011; 1:697-710.
[20] Monem MA, Zeftawy E, Mulligan CN. Sep Purif Technol 2011; 77: 120–127.
[21] Malamis S, Katsou E. J Hazard Mater 2013; 252–253: 428-461.
[22] Suazo-Madrid A, Morales-Barrera L, Aranda-García E, Cristiani-Urbina E. J Ind Microbiol Biotechnol 2011; 38: 51–64.
[23] Zhang A, Cui L, Pan G, Li L, Hussain Q, Zhang X, Zheng J ,Crowley D. Agri Ecosyst Environ 2010; 139: 469–475.
[24] Cordery J, Will AJ, Atkinson K,Wills BA. Miner Eng, Vol 1994; 7: 1003-1015.
[25] Pethkar AV, Kulkarni SK, Paknikar KM. Bioresource Technol 2001; 80: 211-215.
[26] Chen C, Wen D, Wang J. Bioresource Technol 2014; 156:380–383.
[27] Lin Z, Zhou C, Wu J, Zhou J, Wang L. Spec Acta A 2005b; 61:1195-1200.
[28] Diego M, Mauricio V, Torem L, Pino A H. Miner Eng 2013; 48: 44-50.
[29] Pandey AK, Jamaluddin AK, Awasthic , Pandey A. J Environ Sci Comp Sci Eng Technol 2013; 2: 385-393.
[30] Ahmad MF, Haydar S, Quraishi TA. Int Biodeterior Biodegr 2013; 83: 119-128.
[31] Muraleedharan TR, Iyengar L, Venkobachar C. Environ Technol 1994; 15:1015-1027.
[32] Mathialagan T, Viraraghavan T , Cullimore DR. Water Qual Res J Can 2003; 38: 499-514.
[33] Matheickal JT, Yu Q. Bioresource Technol 1999; 69:223-229.
[34] Malkoc E, Nuhoglu Y.(2005). J Hazard Mater 2005; 127: 120-128.
[35] Kapoor A, Viraraghavan T. Bioresource Technol 1997; 61: 221-227.
[36] Mesas ML, Navarette ER,Carrillo F, Palet C. Chem Eng J 2011; 174: 9-17.
[37] Lee YC, Chang SP. Bioresource Technol 2011; 102: 5297–5304.
[38] Vimala R, Das N. J Hazard Mater 2009; 168: 376-382.
[39] Azza MA, Nabila SA, Hany HAG, Ali RK. Journal of Advanced Research 2013; 4: 367–374.
[40] Balistrieri LS, Murray JW.(1984). Geochim Cosmochim Ac 1984; 46: 1253-1256.

[41] Rathinam A, Maharshi B, Janardhanan SK, Jonnalagadda RR ,Nair BU. Bioresource Technol 2010; 101: 1466–1470.
[42] Reddy DHK, Seshaiah K, Reddy AVR, Lee SM. Carbohyd Polym 2012; 88 :1077– 1086.
[43] Anastopoulos I, Massas I, Ehaliotis C. Chem Eng J 2013; 231: 245–254.
[44] Costa ACA, Leite SGF. Biotechnol Lett 1991; 13: 559-562.
[45] Tabaraki R,Ahmady- Asbchin S, Abdi O. J Environ Chem Eng 2013; 1: 604-608.
[46] Chatterjee SK, Bhattacharjee I, Chandra G. J Hazard Mater 2010; 175: 117-125.
[47] Colak F, Atar N, Yazıcıoglu D, Olgun A. Chem. Eng. J 2011; 173:422.
[48] Bulgariu D, Bulgariu L. Bioresource Technol 2012; 103: 489–493.
[49] Abd-Alla MH, Morsy FM , El-Enany AWE, Ohyama T. Int. Biodeter Biodegr 2012; 67 : 48-55.
[50] Das D, Das N, Mathew L. J. Hazard. Mater 2010; 184: 765 -774.
[51] Fan T, Liu Y, Feng B, Zeng G, Yang C, Zhou M, Zhou H, Tan Z, Wang X. J Hazard Mater 2008; 160: 655–661.