**Arsenic contamination in water and the recent removal techniques**

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**ABSTRACT**

Arsenic is considered as one of the most hazardous element in the chemical world and its presence in drinking water is a matter of great concern. Severe and widespread contamination by arsenic (As) in groundwater as well as in drinking water has been recently revealed in rural and sub-urban areas where expensive water treatment techniques are not affordable. Arsenic exists in organic as well as inorganic forms with varying valence states which plays an important role in its behaviour and toxicity in aqueous system.Chronic arsenic exposure has devastating health effects such as cardiovascular diseases, cancer and the eventual death. Thus, the removal of arsenic from drinking water is strongly recommended. Many methods of arsenic removal have been studied, but every available process has its own limitations and it can serve to a limited extent only. This chapter summarizes the effects caused by arsenic contamination and the technologies currently being investigated for its removal from drinking water.

**Keywords** – toxicity, arsenic, water

1. **INTRODUCTION**

Arsenic is a crystal shape metalloid which is brittle in nature and greyish white in colour. It rarely occurs in free state and is found mostly in combination with sulphur, oxygen and iron. Unlike other heavy metalloids, arsenic can be mobilized under a wide range of pH values typically found in groundwater (pH =6.5-8.5). Arsenic has four main chemical forms having oxidation states -3, 0, +3 and +5, but mostly found in earth’s crust as trivalent arsenite, AsO33-,As(III) and pentavalent arsenate, AsO43-, As(V). Arsenic in both the forms is poisonous in nature1(Fig. 1).



**Fig. 1: Structures of (a) arsenite and (b) arsenate.**

1. **SOURCES**

Release of arsenic in the environment is a result of both natural and man-made activities. Naturally sources of arsenic include volcanic ash, weathering of arsenic containing minerals and ores which get dissolved in groundwater. Most of its dispersion in the environment comes from man-made sources including mining and commercial uses. The main uses of metallic arsenic are for strengthening alloys of copper and lead used in car batteries and in smelting processes for ores of many metals such as cobalt, gold, lead and zinc. It is also used as wood preservatives. In addition, combustion of fossil fuels is also a source of arsenic and the greatest threat to public health arises mainly from arsenic contaminated in drinking water2.

1. **EFFECTS OF ARSENIC POISONING**

In recent decades, a huge number of effects have been reported on the widespread presence of arsenic in groundwater. Human exposure to arsenic occurs through ingestion, inhalation or skin adsorption among which, ingestion is the most predominant form of arsenic intake. High doses of arsenic can cause acute toxic effects with gastrointestinal symptoms such as poor appetite, vomiting, diarrhoea etc., disturbance in cardiovascular and nervous system functions such as muscle cramps, heart complains or death. The toxic effects are strongly dependant on the form in which arsenic is present.

The presence of arsenic, even at high concentrations, is not accompanied by any change in taste, odour or visible appearance of water. The detection of arsenic in drinking water is therefore very difficult and require some particular analytical techniques. In most of the developing countries, the drinking water used is with high arsenic concentrations even several times higher than the recommended limit of 10 millionths of a gram per litre of water (10 μg/L)3 by World Health Organization (WHO).

 The first visible symptom caused by arsenic poisoning is abnormal black-brown skin pigmentation known as *melanosis* and hardening of palms and soles known as *keratosis*. Prolong exposure to arsenic may result skin de-pigmentation developing white spots that looks like raindrops known as *leukomelanosis*. Long-term ingestion of arsenic in water can lead to problems with kidney and liver function followed by damage to the internal organs including lungs, kidney, liver and bladder which are togetherly called as *arsenicosis* and may develop when arsenic contaminated water is consumed for more than ten years. However it may lead to variant forms of cancer on more than 20 years of exposure3,4.Thus, strategies to avoid and alleviate arsenic contamination in ground water need to be developed to reduce the health risk associated with it.

1. **MECHANISM OF ARSENIC POISONING**

The mechanism of arsenic poisoning can be described with the help of the following ways:

1. **Glycolysis**

In this reaction mechanism, arsenate (AsO43-) takes the position of phosphate (PO43-) of the Glycolysis cycle and produces 1-arseno-3-phosphoglycerate instead of 1,3-bisphosphoglycerate (Scheme 1). Generally, in glycolysis process, the enzyme phosphoglycerokinase converts 1,3-bisphosphoglycerate to 3- phosphoglycerate by producing ATP. Here arsenate producing 1-arseno-3- phosphoglycerate undergo non-enzymetic hydrolysis to 3-phosphoglycerate by short change glycolysis one ATP per arsenate5.



 ***↓***

 Short- change glycolysis

 1 ATP per Arsenate

**Scheme 1: Glycolysis cycle, arsenate takes the position of phosphate4.**

1. **TCA Cycle**

In this mechanism, two thiol groups actually attach to the arsenic and form arsenite chelate on enzyme by removal of water as shown in scheme 2. The arsenite chelate on enzyme is very much poisonous and it stops the TCA cycle. Here 2,3- dimercaptopropanol acts as a antidote and restores the enzyme6.



**Scheme 2: TCA Cycle in which arsenite act as a poisoning5.**

1. **REMOVAL TECHNIQUES**

Various treatment methodologies have been developed for arsenic removal from drinking water. The commonly used physical methods include ion-exchange, adsorption, electrochemical techniques and membrane process whereas the chemical methods involve coagulation, ozone oxidation, filtration and precipitation. Some biological methods such as bacterial removals and phytoremediation have been also adopted7.

1. **Adsorption**

Adsorption is one of the most effective methods to remove arsenic from drinking water. In this process, the most commonly used adsorbents are activated alumina, activated carbon, functional resin and metal oxide. In this process of adsorption, purification of water depends on specific surface area and surface energy of the adsorbent. Strong adsorption ability depends on the properties of the material which is being used as the adsorbent. Therefore several researchers are involved in developing high performance adsorbents.

Xiao *et al.*­8 used activated alumina for arsenic removal. The principle is that the soluble arsenic in the water can be adsorbed on the surface and occupies the aluminous octahedron crystal lattice sites. The maximum adsorptive capacity of activated alumina is 5-24 mg As adsorbed/g media at equilibrium arsenic concentrations of 0.05-0.2 ppm. Huang and Vane9 and Reed *et al*.10 used activated carbon for arsenic adsorption with various metal compounds—impregnating iron compound and zirconium onto activated carbon. Metal oxides show strong adsorption capability due to their high surface area in comparison to many inorganic ions. Manning *et al.*11used amorphous hydrous ferric oxide, Raven *et al.*12 used crystalline hydrous ferric oxide (ferrihydrite), Jackson and Miller13 used α-FeOOH, Jain and Loeppert14 used hematite, Goldberg15 used magnetite and Goethite for arsenate and arsenite removal.

Altundogan *et al.*16 used liquid phase of red mud, Brunori *et al.*17 used red mud and Fuhrman *et al.*18 used seawater-neutralized red mud (bauxsol), activated bauxsol (ferric sulfate or aluminum sulfate) and normal bauxsol19 and chemically modified and activated bauxsol-coated sand20 as adsorbents for arsenic removal. Natural zeolites, volcanic stone, cactaceous powder and clinoptilolite-containing rocks are also applied for arsenic removal20. Lorenzen *et al*.21 used coconut-shell carbon and coconut-shell carbon pretreated with Fe(III) as adsorbent for As(III) and As(IV).

Buswell22 first reported the arsenic removal with the help of metal salts. The most commonly used metal salts are aluminium salts such as alum and ferric salts such as ferric chloride or ferric sulphate out of which, ferrous sulphate is found to be less effective. Excellent arsenic removal is possible with either ferric or aluminium salts, with laboratories reporting over 99% removal under optimal conditions23-25. Bajpai and Chaudhuri reported that 54–57% of arsenic can be removed by oxidizing As(III) to As(V) in contaminated groundwater using air, pure oxygen or ozone26.

1. **Ion exchange**

Various synthesized ion-exchange resins are available among which strong base anion exchange resins can be effectively used to remove arsenic from water, with less than 1ppm concentration. Several resins are developed by different groups in this regard, for example Matsunaga27 and Balaji28 used an iron(III) and zirconium(IV)-loaded chelating resin containing lysine and diacetic acid based functional groups for the adsorption of As(III) and As(V). Peleanu *et al*.29 used iron-loaded iminodiacetate chelating resin and a silica/iron (III) oxide composite material for As(V) remediation. Wasay *et al*.30 used La(III) and yttrium carbonate resin to remove As(III) and As(V) between pH 4 and 9 with 98% and 100% efficiency. Chanda *et al.*31 used impregnated iron whereas Lenoble *et al*.32 used manganese dioxide, loaded on a polystyrene matrix anionic commercial resin for simultaneous removal of both arsenite and arsenate forms.

1. **Coagulation**

Aluminium based coagulation disinfected with chlorination is one of the commonly used arsenic treatment methods7. However, Yuan et al.33 investigated on a combination system of ferric sulphate coagulation and sand filtration which were established as economic and effective. Scott *et al*.34 reported the full-scale study of the coagulation process by using ferric sulfate at the Metropolitan Water District of Southern California and achieved high arsenic removal of over 95%. Similarly, Liu *et al*.35 reported the enhanced co-precipitation of arsenite by the coupling of FeCl3 with permanganate as the coagulant.



**Fig. 2: Removal of Arsenic through coagulation36.**

1. **Filtration**

The conventional filtration process uses sand, activated carbon or paper that retains the solid on its surface and allows the liquid to pass through it. In case of filtration processes for arsenic removal, red soil (rich in oxidized iron), clay minerals, iron ore, scrap iron or fillings and cellulose materials (containing jute and cotton fibers) are generally used. Nikolaidis and Lackovic37 reported iron filing filter system with 95% efficiency.

1. **Membrane process**

Several natural and synthetic membranes are highly used for arsenic removal as they are easy to produce, simple to operate and even easy to maintain. These membranes have billions of pores or microscopic holes that act as selective barriers and allow only some particular constituents to pass through it. Membrane filtrations are classified on the basis of applied pressure. High driven pressure (50 to 1,000 psi) processes include Reverse Osmosis (RO) and Nano Filtration (NF), while low-pressure processes (5 to 100 psi) include Micro Filtration (MF) and Ultra Filtration (UF).

Clifford *et al.*38, Fox39 and Waypa *et al*.40 used cellulose acetate based RO membrane for the removal of arsenic. Similarly, Sato *et al.*41 alsoused cellulose acetate and polyamide type membrane. However, Waypa *et al.*42 reported arsenic removal by a thin-film composite film NF membrane which is found to be more efficient in removing the dissolved arsenic from water due to the small size of the membrane pores. Vrijenhoek and Waypa43 also used porous polyamide thin-film composite membrane (NF-45) for the removal of arsenic.

Han *et al*.44 reported the use of mixed ester of cellulose acetate and cellulose nitrate MF membrane with pore size of 0.22 and 1.22 μm combined with both ferric chloride and ferric sulfate and cationic polymeric flocculants to investigate the arsenic removal efficiency.

1. **Electrocoagulation**

Electrocoagulation is a simple, efficient and promising technique where flocculating agent is generated by electrooxidation on anode, which is made up of metal, generally iron or aluminum. Parga *et al*.45 and Hansen *et al*.46 reported maximum arsenic removal (more than 99.6%) by aluminum and iron electrodes. Maldonado-Reyse *et al.*47 reported a system with the combined use of both aluminum and iron in the same electrochemical cell. The efficiency varied from 78.9% to more than 99.6% at different initial arsenic concentrations. Kumar *et al.*48 and Parga *et al.*49 reported the removal efficiency of both arsenic species with the help of iron electrode forming amorphous iron oxide and hydroxide complexes which was more than 90% at different pH values at a constant current of 0.5-30 μA.

1. **Oxidation methods**

Oxidation involves the conversion of soluble arsenite to arsenate in the solution, after which a removal technique such as adsorption, coagulation or ion exchange has to be applied. Particularly, for groundwater, oxidation is an important step since arsenite is the most prevalent form. In addition to atmospheric oxygen, different oxidants have already been used to oxidize arsenite in water. Kim *et al*.50 reported oxygen and ozone for the oxidation of As(III). A large number of oxidants such as activated chlorine, chlorine dioxide, hydrogen peroxide etc. have been used51-53. Miller et al synthesised a TiO2 coated chitosan bead and applied for oxidation as well as removal of arsenic from aqueous solution. They observed a higher amount of adsorption of arsenic with UV radiation as compared to the solution that was not exposed to UV light(Fig. 3)54.



**Fig. 3: As removal by TiO2 beads using UV rays54.**

Criscuoli et al.found that the oxidation of As(III) by MnO2 coated nanostructured capsules had higher efficiency than conventional oxidation methods when the arsenic concentration of the water is low. More than 99% oxidation was obtained at 100 to 300 ppb of initial arsenic concentration by this method. However, increasing the concentration to 700 and 1000 ppb results in a decreased oxidation efficiency55.

1. **Bioremediation**

There are two types of biological methods for the removal of arsenic from water. The first of these uses cultured bacteria to oxidize and the second method uses anaerobic, sulphate-reducing bacteria and other reducing bacteria to precipitate arsenic as insoluble arsenic sulphide complexes. Elson *et al*.56 and Mcafee *et al*.57 used chitosan, chitin, chitosan/chitin mixture and biomass from *Rhizopus oryzae* for the removal of arsenic from contaminated drinking water.

Dead fungal biomass of *Lessonia nigrescens* (an algae), *Aspergillus niger* (fungus) coated with iron oxide, *Penicillium purpurogenum* were used for arsenic removal and the pre-treatment with hexadecyl-trimethyl ammonium bromide dodecylamine and a cationic polyelectrolyte was carried out to improve arsenate biosorption58-63. Bacterial species which treat arsenic with anaerobic oxidation are known as dissimilatory arsenate reducing bacteria or arsenate respiring bacteria such as *Geospirillum arsenophilus, Geospirillum barnesi, Desulfutomaculum auripigmentum, Bacillus arsenicoselenatis and Crysiogenes arsenates*64-68. Specific indigenous bacteria known as “iron and manganese oxidizing bacteria” are highly used for the biological arsenic oxidation directly in continuous ground water treatment69-71(Fig. 4). The biological oxidation by two bacteria, *Gallionella ferruginea and Leptothrix ochracea,* has also been found to be a promising way for the effective removal of arsenic from groundwater72.



**Fig. 4: Removal of arsenic by using coliform bacteria73.**

1. **Phytoremediation**

Phytoremediation is a new approach for arsenic removal from groundwater where certain plant species are used to accumulate high concentrations of arsenic in their aerial tissue. Visoottiviseth *et al*.74 used cottonwood, sunflower, Indian mustard, maize, ryegrass, prairie grasses and hyper-accumulating ferns in this process. Young plants of water lettuce, *Garcinia combogia* (indigenous plant), *Pista stratiotes* L. (aquatic plant), water hyacinths (*Eichhornia crassipes*) and dried roots of water hyacinths (harvested from a pollution free pond and hydroponically cultured) are also used for the simultaneous and rapid remediation of arsenic along with other heavy metals from polluted water at effective concentration75,76.

Recently *Pteris vittata,* *P. cretica,* orange juice waste (containing cellulose, pectins, hemicellulose, chlorophyll pigments and other low molecular weight compounds like limonene) residue and phosphorylated cross-linked orange waste are also used for arsenic removal77-79. Murugesan *et al*.80 reported the use of industrial waste autoclaved tea fungal mats and tea fungal with pretreated FeCl3 for As(III) and As(V) removal from groundwater samples. Wasiuddin *et al*.81 reported the use of human hair to remove arsenic due to their ability to absorb arsenic from contaminated water.

1. **Nanotechnology**

Now-a-days, nano particles are highly used in the arsenic removal in drinking water. Tang *et al*.82 synthesized ultrafine α-Fe2O3 nanoparticles using a solvent thermal process and used in the treatment of water samples contaminated with arsenic. The kinetics study revealed that As(III) and As(V) removal can be achieved very rapidly and effectively with the help of these nanoparticles.

1. **CONCLUSION**

Arsenic contamination in drinking water is an alarming problem on a global scale. As the arsenic in drinking water is having a major human impact in several part of the world, in present literature survey, we tried to elaborate various remediation method based on conventional, modern and hybrid technologies for the removal of arsenic. But we should bear in mind that the various approaches described have their own advantages and disadvantages. The technologies discussed are quite effective and are safe for arsenic removal from water, but need promotion for wider implementation in acute arsenic problem areas. In addition, care must be taken in cleaning the arsenic removing filters regularly and disposing off the sledge generated by these filters properly.

Arsenic-free drinking water is a necessity for human health, so we should emphasize on the purification of water through the several discussed techniques. Among all the techniques, the polymeric support technique is found to be more effective which offers innovative materials for arsenic separation. In this technique, designing functional polymers is a key requirement; it can be assisted by chemical modification and graft modification as well. High degree of binding groups may be incorporated through this technique. However, research efforts are still needed to develop cost-effective, rapid, beneficial and reproducible technologies for arsenic removal.

REFERENCES

[1] P. L. Smedly, D. G. Kinniberg, *Applied Geochemistry* **2002**, 17, 517-568.

[2] A. Georges, O. Bersillon, J. Blachot, A. H. Wapstra, *Nuclear Physics A* **2003**, 729: 3–128.

[3] D. Mohan, C. U. Pitmann Jr., Arsenic removal from water/wastewater using adsorbents, a critical review, *Elsevier* **2007**, 1-42.

[4] US Environmental Protection Agency (EPA), Research plan for Arsenic in drinking water-Treatment, Technologies and Costs for Removal of Arsenic from drinking water, National Primary Drinking Water Regulation, Office of Ground Water and Drinking Water (**1998, 1999, 2000, 2001**).

[5] F. Dickens, F. Simer, *Biochem J* **1929**, 23(5), 936-958*.*

[6] R. K. Crane, F. Lipmann, *J. Biol. Chem.* **1953**, 201-235.

[7] T. S. Y. Choong, T. G. Chuah, Y. Robiah, F. L. G. Koay, I. Azni, *Desalination* **2007**, 217, 139-166.

[8] T. F. Xiao, B. Hong, Z. H. Yang, *Geological Science and Technology Information*, **2001**, Vol. 20, No. 1, pp. 71-76.

[9] C. P. Huang, L. M. Vane, *J. Water Pollution. Contr. Federation*, **1989**, Vol. 61, pp. 1596-1603.

[10] B. Reed, E. R. Vaughan, L. Q. Jiang, *J. Environ. Eng. Div.,* Am. Soc. Civ. Eng., **2000**, Vol. 126, pp. 869-873.

[11] B. A. Manning, S. E. Fendorf, S. Goldberg, *Environmen. Sci. Technol.*, **1998**, Vol. 32, pp. 2383-2388.

[12] K. P. Raven, A. Jain, R. H. Loeppert, *Environ Sci.Technology*, **1998**, Vol. 32, pp. 344-349.

[13] B. P. Jackson, W. P. Miller, *Soil Sci. Soc. Am.* *Journal*, **2000**, Vol. 64, pp. 1616-1622.

[14] A. Jain, R. H. Loeppert, *J. Environ. Quality*, **2000**, Vol. 29, pp. 1179-1184.

[15] S. Goldberg, *Soil Sci. Soc. Am. Journal*, **2002**, Vol. 66, pp. 413-421.

[16] H. S. Altundogan, S. Altundogan, F. Tumen, M. Bildik, “Arsenic Adsorption from Aqueous Solutions by Activated Red Mud Waste Management”, **2002**, Vol. 22, pp. 357-363.

[17] C. Brunori, C. Cremisini, P. Massanisso, *J. Hazard. Material*, **2005**, Vol. 117, No. 1, pp. 55-63.

[18] H. G. Fuhrman, J. C. Tjell, D. McConchie, O. Schuiling, *J. Colloid Interf. Sciences*, **2003**, Vol. 264, pp. 327-334.

[19] H. G. Fuhrman, J. C. Tjell, D. McConchie, *J. Colloid Interf. Sci*., **2004**, Vol. 271, No. 2, pp. 313-320.

[20] H. G. Fuhrman, J. C. Tjell, D. McConchie, *Environ. Sci. Technol.*, **2004**, Vol. 38, No. 8, pp. 2428-2434.

[21] L. Lorenzen, J. S. J. Deventer, W. M. Landi, *Miner. Eng.*, **1995**, Vol. 8, No. 45, pp. 557-569.

[22] A. M. Buswell, *Journal American Water Works Association* **1943**, 35(10), 1303.

[23] P.-Y. Chen, J. G. Hering, J. Wilkie, M. Elimelech, *Journal of Environmental Engineering* **1997**, 123(8), 800-807.

[24] M. R. Jekel, *Removal of arsenic in drinking water treatment*, John Wiley & Sons, Inc., New York, **1994**.

[25] J. G. Hering, P. Y. Chen, J. A. Wilkie, M. Elimelech, S. Liang, *Journal of the American Water Works Association* **1996**, 88(4), 155-167.

[26] S. Bajpai, M. Chaudhuri, *Journal of Environmental Engineering* **1999**, 125, 8, 782–784.

[27] H. Matsunaga, T. Yokoyama, R. J. Eldridge, B. A. Bolto, *React. Polymer*, **1996**, Vol. 29, pp. 167-174.

[28] T. Balaji, T. Yokoyama, H. Matsunaga, *Chemosphere*, **2005**, Vol. 59, No. 8, pp. 1169-1174.

[29] I. Peleanu, M. Zaharescu, I. Rau, M. Crisan, A. Jitianu, A. Meghea, *Sep. Sci. Technol*., **2002**, Vol. 37, No. 16, pp. 3693-3701.

[30] S. A. Wasay, M. J. Haron, A. Uchiumi, S. Tokunaga, *Water* *Res.*, **1996**, Vol. 30, No. 5, pp. 1143-1148.

[31] M. Chanda, K. F. Driscou, G. L. Rempel, *Reactive Polymers*, **1988**, Vol. 8, pp. 85-89.

[32] V. Lenoble, C. Laclautre, B. Serpaud, *Science of the Total Environment*, **2004**, Vol. 326, pp. 197-207.

[33] T. Yuan, Q. F. Luo, J. Y. Hu, S. L. Ong, W. J. Ng, *J*. *Environ*. *Science* *&* *Health*; *Part* *A*, *Toxic*/*Hazardous* *Sub*. *Environ*. *Eng*. **2003**, 38, 1731-1744.

[34] K. N. Scott, J. F. Green, H. D. Do, S. J. Mclean, *Journal of American Water Work Association*, **1995**, pp. 114-126.

[35] R. P. Liu, X. Li, S. J. Xia, *Environment Science*, **2005**, Vol. 26, No. 1, pp. 73-76.

[36] M. Edwards, *Chemistry of Arsenic removal during coagulation and Fe-Mn oxidation,* **2002**, 98.

[37] N. P. Nikolaidis, J. Lackovic, “Arsenic Remediation Technology: AsRT”, International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effect and Remedies, Dhaka, **1998**, pp. 8-12.

[38] D. A. Clifford, C. C. Lin, “As(III) and As(V) Removal from Drinking Water”, Project Summary EPA/600/S2-91/011, US Environmental Protection Agency Risk Reduction Engineering Laboratory, Lincinnati, **1991**.

[39] K. R. Fox, *J. of AmericanWater Works Associations*, **1989**, Vol. 81, pp. 94-101.

[40] J. J. Waypa, M. Elimelech, J. G. Hering, *Journal of American Water Works Association*, **1997**, Vol. 89, No. 10, pp. 102-114.

[41] Y. Sato, M. Kang, T. Kamei, Y. Magara, *Water Res*., **2002**, Vol. 36, pp. 3371-3377.

[42] J. J. Waypa, A. Seidel, M. Elimelech, *Environ. Eng. Sci*., **2001**, Vol. 18, No. 2, pp. 105-113.

[43] E. M. Vrijenhoek, J. J. Waypa, *Desalination*, **2000**, Vol. 130, pp. 262-277.

[44] B. Han, T. Runnells, J. Zimbron, R. Wickramasinghe, *Desalination*, **2002**, Vol. 145, pp. 293-298.

[45] J. R. Parga, D. L. Cocke, J. L. Valenzuela, *J. Hazard. Material,* **2005**, Vol. 124, Nos. 1-3, pp. 247-254.

[46] A. R. Hansen, E. Mateus, *Miner. Eng.*, **2006**, Vol. 19, No. 5, pp. 486-490.

[47] A. Maldonado-Reyse, C. Montero, O. Solorzo-Ferea, *Journal of Env. Monitoring*, **2007**, Vol. 9, pp. 1241-1247.

[48] P. R. Kumar, S. Chaudhari, K. C. Khilar, S. P. Mahajan, *Chemosphere*, **2004**, Vol. 55, No. 9, pp. 1245-1252.

[49] J. R. Parga, D. L. Cocke, J. L. Valenzuela, *J. Hazard. Material,* **2005**, Vol. 124, Nos. 1-3, pp. 247-254.

[50] M. Kim, J. Nriagu, *Sci. Total. Environ*. **2000**, 247, 71–79.

[51] C. Hu, H. Liu, G. Chen, W. Jefferson, J. Qu, Environ. Sci. Technol. **2012**, 46, 6776–6782.

[52] S. Sorlini, F. Gialdini, Water Res. **2010**, 44, 5653–5659.

[53] M. Pettine, L. Campanella, F. J. Millero, Geochim. Cosmochim. Acta **1999**, 63, 2727–2735.

[54] S. M. Miller, J. B. Zimmerman, *Water Research* **2010**, 44, 19, 5722–5729.

[55] A. Criscuoli, S. Majumdar, A. Figolietal, *Journal of Hazardous Materials* **2012**, 211-212, 281–287.

[56] C. M. Elson, D. H. Davies, E. R. Hayes, *Water Res.*, **1980**, Vol. 14, No. 9, pp. 1307-1311.

[57] B. J. Mcafee, W. D. Gould, J. C. Nedeau, A. C. da Costa, *Sep. Sci. Technol.*, **2001**, Vol. 36, No. 14, pp. 3207-3222.

[58] A. I. Zouboulis, I. A. Katsoyiannis, *Ind. Eng. Chem. Res.*, **2002**, Vol. 41, No. 24, pp. 6149-6155.

[59] M. X. Loukidou, K. A. Matis, A. I. Zouboulis, M. Liakopoulou-Kyriakidou, *Water Research*, **2003**, Vol. 37, No. 18, pp. 4544-4552.

[60] S. Ridvan, Y. Nalan, D. Adil, *Sep. Sci. Technol.*, **2003**, Vol. 38, No. 9, pp. 2039-2053.

[61] A. R. Hansen, E. Mateus, *Miner. Eng.*, **2006**, Vol. 19, No. 5, pp. 486-490.

[62] G. S. Murugesan, M. S. Kumar, K. Swaminathan, *Bioresour. Technology*, **2006**, Vol. 97, No. 3, pp. 483-487.

[63] D. Pokhrel, T. Viraraghavan, *Water Res.*, **2006**, Vol. 40, No. 3, pp. 549-552.

[64] R. S. Oremland, J. F. Stolz, *Trends in Microbiology* **2005**, 13, 2, 45–49.

[65] R. S. Oremland, C. W. Saltikov, F. Wolfe-Simon, J. F. Stolz, *Geomicrobiology Journ*a*l* **2009**, 26, 7, 522– 536.

[66] F. Battaglia-Brunet, M.-C. Dictor, F. Garrido et al., *Journal of Applied Microbiology* **2002**, 93, 4, 656–667.

[67] J. M. Santini, L. I. Sly, R. D. Schnagl, J. M. Macy, *Applied and Environmental Microbiology* **2000**, 66, 1, 92–97.

[68] E. O. Kartinen Jr., C. J. Martin, *Desalination* **1995**, 103, 1-2, 79–88.

[69] A. I. Zouboulis, I. A. Katsoyiannis, *Industrial & Engineering Chemistry Research* **2002**, 41, 24, 6149–6155.

[70] Katsoyiannis, A. Zouboulis, H. Althoff, H. Bartel, *Chemosphere* **2002**, 47, 3, 325–332.

[71] I. A. Katsoyiannis A. I. Zouboulis, *Water Research* **2004**, 38, 1, 17–26.

[72] I. A. Katsoyiannis, A. Zikoudi, S. J. Hug, *Desalination* **2008**,224, 1–3, 330–339.

[73] P. Xiaohong, G. Qinghaihua *, Journal of Hazardous Material* **2012**, 215 -216, 1-16.

[74] P. Visoottiviseth, K. Francesconi, W. Sridokchan, *Environ. Pollution*, **2002**, Vol. 118, pp. 453-461.

[75] M. Misbahuddin, A. Fariduddin, *Arch. Environ. Health*, **2002**, Vol. 57, No. 6, pp. 516-518.

[76] C. T. Kamala, K. H. Chu, N. S. Chary, *Water Res.*, **2005**, Vol. 39, No. 13, pp. 2815-2826.

[77] J. W. Huang, C. Y. Poynton, L. V. Kochian, M. P. Elless, *Environ.* *Sci. Technology*, **2004**, Vol. 38, No. 12, pp. 3412-3417.

[78] M. Srivastava, L. Q. Ma, J. A. G. Santos, *Sci. Total Environ*., **2006**, Vol. 364, pp. 24-31.

[79] K. N. Ghimire, K. Inoue, K. Makino, T. Miyajima, *Sep. Sci. Technol.*, **2002**, Vol. 37, No. 12, pp. 2785-2799.

[80] G. S. Murugesan, M. Sathishkumar, K. Swaminathan, *Bioresour. Technology*, **2006**, Vol. 97, No. 3, pp. 483-487.

[81] N. M. Wasiuddin, M. Tango, M. R. Islam, *Energy Sources*, **2002**, Vol. 24, pp. 1031-1041.

[82] W. Tang, Q. Li, S. Gao, J. Shang, Mater. **2011**, 192, 131–138.