

Removal of Heavy Metals From Drinking Water Supplies Through the Ion Exchange Membrane Bioreactor- A Review

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Abstract

Arsenic (As) and mercury (Hg) are two highly toxic heavy metals that must be removed to very low levels in drinking water supplies. A novel treatment method for the removal of both compounds is the ion exchange membrane bioreactor (IEMB) process, which incorporates pollutant transport through an ion exchange membrane by Donnan dialysis, with biological removal of the pollutant. As detailed in this study, the IEMB process has a high potential for use in drinking water treatment systems, and offers numerous advantages over currently implemented processes, such as minimising the risk of secondary pollution of the drinking water.

Keywords: Anion exchange membrane (AEM); Cation exchange membrane (CEM); Arsenate ($H_2AsO_4^-$); Arsenite ($H_2AsO_3^-$); Ionic mercury (Hg^{2+}); Biological removal

1. Introduction

Heavy metals have been found in potentially harmful concentrations in numerous drinking water systems due to natural or industrial pollution sources. Two of the most toxic heavy metals are arsenic (As) and mercury (Hg), and thus each compound must be removed to very low levels in order to prevent health problems. The maximum concentrations of arsenic and mercury recommended by the World Health Organization are 10 ppb and 1 ppb, respectively. The main limitations of existing treatment technologies are secondary contamination by microbial cells, nutrients, and metabolic by-products in biological processes; difficulties in disposing the brine solution from pressure driven membrane processes; high energy demands in distillation processes; competition for adsorption sites in ion-exchange systems by other ions that are usually present in much higher concentrations; and the undesirable addition of chemicals, as well as difficulties in achieving very low limits, in coagulation processes. One possible means of overcoming these problems is through the ion exchange membrane bioreactor (IEMB) [1],

Mercury is a highly volatile and highly toxic heavy metal present in the environment. Inorganic mercury in water is mainly seen in the +2 oxidation state. Mercury is released into the atmosphere through a variety of natural and anthropogenic sources [4]. Natural sources include volcanic eruptions, mercury rich soil and forest fires. Mobilization of mercury from fossil fuels, incinerators, chlor-alkali industries, gold mining, processing and refining of mercury ores are few of the major anthropogenic sources [5]. Once released into the environment, it can undergo complex physical and chemical transformations. Released mercury vapour gets converted into soluble form and gets deposited in soil and water by rain. Due to microbial action, inorganic mercury gets converted into methyl mercury and enters the food chain of predatory species. Low dose mercury exposure can affect various organ systems of adults and children. In adults it can lead to memory loss, Alzheimer's like dementia, decreased rate of fertility, birth of abnormal offspring, etc. In children the effects include autism, late walking and deficit in memory and language [6]. In the world the first mercury pollution reported in Minamata City located on the Yatsushiro Sea coast in Kumamoto Prefecture of Japan in 1956, was due to the poisoning of the central nervous

system caused by methyl mercury which accumulated in fish and shellfish, as a result of mercury released into Minamata Bay [7, 8]. Due to the severe effects of mercury on mankind, World Health Organization (WHO) has set the limit for mercury in drinking water to be 0.001 mg/L [9]. Due to its diverse properties, mercury is still used in different areas like electrical industry, dentistry, mining, catalysis, etc. [10]. Studies show that mercury pollution is a threat to human beings in the developing countries even now [11]. Reports show that the concentrations of mercury in ground water in a few industrial areas of India are more than the standards set by WHO and the Bureau of Indian Standards [9, 12]. According to this, the concentration of mercury in a few industrial areas in the states of Gujarat, West Bengal, Orissa, Haryana and Andhra Pradesh are ten or twenty times higher than the maximum permissible limit. These alarming levels are mainly due to the discharge of mercury bearing effluents having concentrations ranging from 0.058 to 0.268 mg/L. It is against the permissible limit of mercury (0.01 mg/L) set by Indian standards for effluent discharge [11]. Different technologies like adsorption, ion exchange; amalgamation and chemical precipitation are available for the removal of mercury from contaminated water [13-23].

2 VARIOUS OPTIONS FOR REMOVAL OF HEAVY METAL

2.1 Ion-Exchange Membrane Bioreactor (IEMB)

An advantageous alternative to the above-mentioned systems is the ion-exchange membrane bioreactor, which combines ion-selective membrane dialysis, also known as Donnan dialysis (2), and biological remediation. Compared to previously described systems, the advantage of the ion-exchange membrane bioreactor relies on the use of a nonporous membrane that keeps the water being treated segregated not only from the microbial culture, as in membrane-contactor systems, but also from the biomedium where the culture is suspended. The transfer of species between the water and the bioreactor depends on the characteristics of the membrane, which can thus be selected as to facilitate the extraction of the ionic pollutant from the water and to hinder the transfer of organic and inorganic pollutants present in the biomedium.

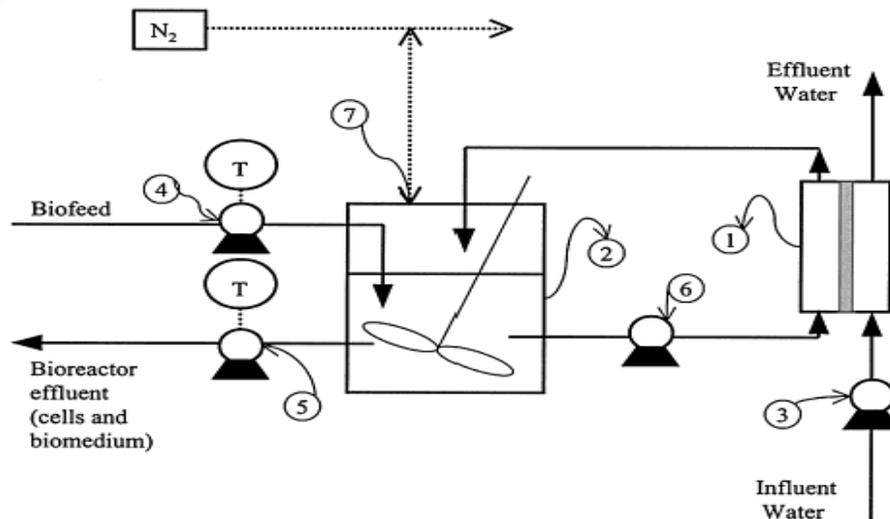


FIGURE 1. Schematic diagram of the ion-exchange membrane bioreactor. Key: 1, flow cell dialyzer; 2, anoxic bioreactor; 3, polluted water pump; 4, timer-switch operated biofeed pump; 5, timer-switch operated bioreactor effluent pump; 6, bioreactor recirculation pump; and 7, nitrogen gas line.

2.2 Removal of Trace Organic Compounds by a Membrane Bioreactor

WWTPs treating wastewater from municipalities and industries have been shown as major sources of many environmental pollutants. These pollutants usually originate from synthetic chemicals that have been used widely for industrial, agricultural, and household purposes. Compounds like pharmaceutically active compounds (PhACs), industrial chemicals, and pesticides are produced worldwide on a 100 000 t scale. After their usage for the intended purpose, a large fraction of these substances will be discharged into the wastewater unchanged or in the form of degradation products that are often hardly eliminable in conventional WWTPs. Depending on the efficiency of the treatment and chemical nature of a compound, they reach WWTP effluents and surface waters in certain concentration. In the worst case, they are present in drinking water, in spite of expensive treatment steps. Although the exact effect of consistent exposure to trace organic contaminants is still unclear, there is no more doubt that it has significant adverse consequences for public health. For example, antibiotics and their metabolites can significantly increase antibiotic resistance in the population. Synthetic hormones can act as endocrine disruptors by mimicking or blocking hormones and disrupting the body's normal functions. Due to their polarity, they can be eliminated during wastewater treatment only incompletely. Polar poorly degradable compounds were detected in high and comparable concentrations in the effluents of numerous WWTPs all over Europe. A proper wastewater treatment as mandatory in the European Union due to the Urban Wastewater Treatment Directive (91/271/EEC) will not eliminate polar pollutants completely [3]. Therefore, to avoid such contaminants, emissions with WWTP effluents would have to be reduced by their advanced treatment or by avoidance and replacement measures for the respective pollutant. One of the most promising technologies is MBR technology. The potential of MBR to efficiently remove hazardous substances from wastewater is often highlighted. Besides the fact that there is a physical retention of all the molecules larger than the molecular weight cut-off (MWCO) of the membrane, hydrophobic substances also tend to accumulate onto the sludge and therefore they are removed from the effluent. Furthermore, as all the bacteria are held back, there are better adapted to mineralizing of Micropollutants present in the reactor.

3 Arsenic Removals

In some areas source substitution may be impossible during part or all of the year, or may be very expensive. Arsenic removal may be more appropriate in these situations. Since arsenic removal is not covered in many standard texts, this chapter examines removal technologies in more detail.

3.1 Coagulation and filtration is the most common arsenic removal technology. By adding a Coagulant such as alum, ferric chloride, or ferric sulfate to contaminated water, much of the arsenic can be removed. If arsenic is present as arsenite, the water should be oxidized first, using chlorine, permanganate, ozone, or other oxidants. After adding the coagulant, the water should be stirred, allowed to settle, and filtered for best results. Coagulation improves parameters such as turbidity and color, and can reduce levels of organic matter, bacteria, iron, manganese, and fluoride, depending on operating conditions. Coagulation with ferric salts works best at pH below 8. Alum has a narrower effective range, from pH 6-7. If pH is above 7, removal may be improved by adding acid to lower pH. In general, the higher the coagulant dose, the better the arsenic removal. Typical doses are 5 to 30 mg/L ferric salts or 10 to 50 mg/L alum. If the source water has high levels of phosphate or silicate, coagulation may be less effective. However, sulfate, carbonate, and chloride have little effect on removal rates.

3.2 Ion exchange resins are commercially produced, synthetic materials that can remove some Compounds from water. Most commonly they are used in water softening, but some resins are very good at removing arsenic. These resins only remove arsenate, so if the raw water contains arsenite, it should be

oxidized first. Other compounds, including sulfate, nitrate, nitrite, and chromate, are also removed to some degree by most arsenic removal resins. Ion exchange resins usually come as sand-like grains, and are used in packed beds or columns, most often with an Empty Bed Contact Time (EBCT) of 1.5 to 3 minutes. A bed can typically treat several hundred to a thousand bed volumes before the resin must be regenerated. The amount of water a bed can treat is largely independent of arsenic concentration and pH. Instead, run lengths are largely determined by sulfate levels, since sulfate can quickly saturate the resin. For this reason, ion exchange resins are only appropriate in waters with under 120 mg/L sulfate, and work best with waters with under 25 mg/L sulfate. High levels of dissolved solids (TDS > 500 mg/L) will also shorten run times. Resins will not adsorb iron, but if the raw water contains high levels of dissolved iron, the iron can precipitate out and clog the filter. When the resin is saturated, it can easily be regenerated with a simple brine solution. Regenerated resin can be used over and over again.

3.3 Activated alumina, like ion exchange resins, is commercially available in coarse grains. Activated alumina is used in packed beds, with longer EBCTs (about 5 to 8 minutes) than ion exchange resins. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. Activated alumina works best in slightly acidic waters (pH 5.5 to 6) – above pH 7 removal efficiency drops sharply. The main factors controlling bed run length are pH and arsenic concentration. Concentrations of other solutes have a relatively small effect. For best results, raw water containing arsenite should be oxidized before treatment. Phosphate, sulfate, chromate and fluoride are also removed by activated alumina, but nitrate is not. Saturated activated alumina can be regenerated with flushing with strong base followed by strong acid. Regenerated media loses some volume and eventually must be replaced. Like ion-exchange resins, activated alumina beds can be clogged by precipitation of iron.

3.4. Membrane methods for arsenic removal include reverse osmosis and nanofiltration. These make use of synthetic membranes, which allow water through but reject larger molecules, including arsenic, chloride, sulfate, nitrate, and heavy metals. The membranes must be operated at high pressures, and usually require pretreatment of the raw water. Household level membrane units usually only treat about 10% of the water, resulting in a large waste stream. Municipal membrane units can achieve higher total recovery rates by using membranes in series. Currently available membranes are more expensive than other arsenic removal options, and are more appropriate in municipal settings, where very low arsenic levels are required. However, membrane technology is advancing rapidly, and it is conceivable that future generations of membranes could be used effectively in rural settings.

3.5 Other techniques exist for arsenic removal, but are less well documented. When arsenic-rich water also contains high levels of dissolved iron, iron removal will also remove much of the arsenic. Many new materials are being tested for arsenic removal, including low-tech iron coated sand and greensand, novel iron-based sorbents, and specially engineered synthetic resins. Some of this research is promising, but these technologies are still under development. All arsenic removal technologies generate some kind of arsenic-rich waste. These wastes are generally not hazardous to handle, but special care must be taken in disposing of them, especially at centralized plants. At the community or household level, the volume of waste generated is usually not enough to have a major environmental impact, and stabilized wastes can be disposed of with other solid wastes, solidified in concrete, buried, or discarded in sanitary latrines.

4. Conclusions

In both developing and industrialized countries that have faced arsenic contamination of drinking Water resources, source substitution, where possible, have been the preferred alternative. However, in some areas, arsenic removal may be a more practical, economically feasible strategy, at least for short-term supply of safe drinking water. Contaminated sources can still be safely used for purposes other than drinking and cooking, and should not be sealed unless safe water is conveniently available in the quantities required for all purposes.

5. REFERENCES

- [1] Adrian Oehmen, Rui Viegas, Svetlozar Velizarov, Maria A. M. Reis, João G. Crespo, Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor. *Desalination* 199 (2006) 405–407.
- [2] ANABELA D. FONSECA, JOAˆOG. CRESPO, JONASS. ALMEIDA, AND MARI A A. REIS, Drinking Water Denitrification Using A Novel Ion-exchange Membrane Bioreactor.
- [3] H. Schroeder, J. Munthes, *Atmos. Environ.*, 1998, **32**, 809
- [4] C.J. Lin, S.O. Pehkonen, *Atmos. Environ.*, 1999, **33**, 2067
- [5] F. Zahir, S.J. Rizwi, S.K. Haq, R.H. Khan, *Environ. Toxicol. Phar.*, 2005, **20**, 351
- [6] S. Ekino, M. Susa, T. Ninomiya, K. Imamura, T. Kitamura, *J. Neurol. Sci.*, 2007, **262**, 131
- [7] Study Group of Minamata Disease. *Minamata Disease*. Kumamoto: Kumamoto University, 1968
- [8] W.H.O., *Guidelines for Drinking Water Quality*, 3rd ed., 2004, Volume 1
- [9] USEPA, *Mercury Study Report to Congress*, December 1997, EPA-452/ R-97-003
- [10] Dr. R.C. Srivastava, *Guidance and Awareness Raising Materials under new UNEP Mercury Programs (Indian Scenario)*, 2004, Centre for Environmental Pollution Monitoring and Mitigation, India
- [11] <http://wbphed.gov.in>, as accessed on 19th July 2008
- [12] H.G. Park, T.W. Kim, M.Y. Chae, I.K. Yoo, *Process Biochem.*, 2007, **42**, 1371
- [13] V. Smuleaca, D.A. Butterfield, S.K. Sikdar, R.S. Varma, D. Bhattacharyya, *J. Membrane Sci.*, 2005, **251**, 169
- [14] S.M. Evangelista, E.D. Oliveira, G.R. Castro, L.F. Zara, A.G.S. Prado, *Surf. Sci.*, 2007, **601**, 2194
- [15] O. Olkhovik, M. Jaroniec, *Adsorption*, 2005, **11**, 205
- [16] M.E. Mahmoud, G.A. Gohar, *Talanta*, 2000, **51**, 77
- [17] C.B. Lopes, M. Otero, J. Coimbra, E. Pereira, J. Rocha, Z. Lin, A. Duarte, *Micropor. Mesopor. Mat.*, 2007, **103**, 325
- [18] A. Oehmen, R. Viegas, S. Velizarov, M.A.M. Reis, J.G. Crespo, *Desalination*, 2006, **199**, 405
- [19] A. Chojnacki, K. Chojnacka, J. Hoffmann, H. Gorecki, *Miner. Eng.*, 2004, **17**, 933
- [20] P. Huttenloch, K.E. Roehl, K. Czurda, *Environ. Sci. Technol.*, 2003, **37**, 4269
- [21] H. Biester, P. Schuhmacher, G. Mueller, *Water. Res.*, 2000, **34**, 2031
- [22] J. Kostal, A. Mulchandani, K.E. Gropp, W. Chen, *Environ. Sci. Technol.*, 2003, **37**, 4457
- [23] N. Savage, M.S. Diallo, *J. Nanopart. Res.*, 2005, **7**, 331