Strategies for Low-Cost Water Defluoridation of Drinking Water-A Review of Progress

[1]AMIR HAIDER MALIK, [1]SADIA NASREEN, [1]QAISAR MAHMOOD*,
[1]ZAHID MAHMOOD KHAN, [1]RIZWANA SARWAR, [2]GHULAM JILANI AND [3]AFSAR KHAN
[1]Department of Environmental Sciences, COMSATS Institute of Information Technology, Abbottabad, Pakistan.
[2]Department of Soil Sciences & Water Conservation, PMAS Arid Agriculture University, Rawalpindi, Pakistan.
[3]Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad 22060, Pakistan.

(Received on 25th July 2009, accepted in revised form 1st March 2010)

Summary: One of the biggest challenges of 21st century is to ensure safe drinking water-supplies and environmental sanitation which are vital for protecting the environment, improving health and alleviating poverty. Natural contamination of groundwater sources by fluoride, arsenic and dissolved salts is the main health menace at present in many parts of Pakistan and other countries. Most of the fluoride in drinking water, either occurring naturally or added will be in the form of the free fluoride ion. It is a big challenge to investigate appropriate, low cost methods and technologies to be applied in developing countries to make fluoride contaminated water drinkable. In this paper low cost fluoride removal methods have been discussed and compared for application in developing countries.

Introduction

The consequences of previous exponential human population growth and industrialization will have to be faced by present generations. One of the biggest challenges of 21st century is to ensure safer drinking water-supplies and environmental sanitation which are vital for protecting the environment, improving health and alleviating poverty. The widespread drinking water shortage, gradual deterioration and aggravated pollution of freshwater resources in many regions of the World, along with the progressive encroachment of incompatible activities demand integrated water resources planning and management [1-2].

According to the World Water Assessment Programme issued by United Nations, the average water availability per person is expected to drop by one-third over next 20 years [3], so one-third of humanity (about 2.7 billion) will be under the shadow of acute water shortage by the year 2025 [4]. The situation will be too acute in the years to come, as the world population is expected to increase by 74.8 million every year [5]. The access to "closer and cleaner drinking water" is still a distant dream for about one-sixth of humanity on this planet [6]. It is predicted that this increasing shortage, and competition over water resources in the first quarter of the 21st century, will dramatically change the way we value and use water. The general objective is to make certain that adequate water supplies of good quality are maintained for the entire population of this planet, while preserving the hydrological, biological and chemical functions of ecosystems, adapting human activities within the capacity limits of nature and combating vectors of water-related diseases [7-10]. An estimated 80 per cent of all diseases and over one third of deaths in developing countries are caused by the consumption of contaminated water, and on average as much as one tenth of each person's productive time is sacrificed to water-related diseases. To reduce the incidence of water-borne diseases and make the water suitable for human consumption, the removal of pathogenic organisms, fecal matter, suspended solids, algae, organic matter and harmful chemicals is absolutely necessary [11]. Among the various undesirable and naturally occurring pollutants in water, coliform bacteria, fluoride and arsenic are very important as these cause serious health problems [12]. On the contrary, the lower concentration of fluoride in water like 1 mg/L, is even found to be beneficial in preventing dental caries. However, excessive fluoride concentration in drinking water causes dental fluorosis, skeletal fluorosis and crippling skeletal fluorosis [12-14]. Innovative technologies, including the improvement of indigenous technologies, are

*To whom all correspondence should be addressed.

needed to fully utilize limited water resources and to safeguard those resources against pollution.

Pakistan's current population of 150 million is expected to grow to about 221 million by the year 2025. This increase in population will have direct impact on the water sector for meeting the domestic, industrial and agricultural needs. The per capita water availability has dropped from 5,600 m^3 in 1953 to 1,000 m^3 to present situation. Pakistan has now essentially exhausted its available water resources and is on the verge of becoming a water deficit country [15]. The quality of groundwater and surface-water is low and is further deteriorating because of unchecked disposal of untreated municipal and industrial wastewater and excessive use of fertilizers and insecticides in agricultural fields. Water pollution is a serious problem in Pakistan as almost 70% of its surface water resources and a growing number of its groundwater reserves are already contaminated by biological, organic and inorganic pollutants [16]. In many cases, these sources have been rendered unsafe for human consumption as well as for other activities such as irrigation and industrial needs. This illustrates that water quality decline in effect contributes to water scarcity as it limits the availability of water for both human use and their ecosystem [17-19].

Nitrate and fluoride, and other pollutants concentrations in ground water exceed the recommended levels at various places throughout the world. Water quality monitoring and information management is lacking in Pakistan which is crucial to any water quality improvement program. One hundred million cases of diarrhea are being registered for treatment in hospitals of Pakistan each year. A survey conducted by Pakistan Council for Research on Water Resources (PCRWR) showed that 81,996 cases of water related diseases were registered in Basic Health Units of Rawalpindi division in Pakistan alone [18]. Chemical composition of surface or subsurface water is one of the prime factors on which the suitability of water for domestic, industrial or agricultural purpose depends [18].

Fluoride in Nature and its Pollution

Fluoride is recognized as the thirteenth most common element in the earth's crust. It is widely distributed in the lithosphere mainly as fluorspar, fluorapatite and cryolite. The emissions of volcanoes, marine aerosols, weathering and dissolution of rock minerals release fluorides into the environment naturally [20-21]. Fluoride pollution of drinking water is very common in subcontinent and other parts of Asia [22-26]. The major source of fluoride pollution is the natural weathering process. As per a conservative estimate, populations to the tune of 200 million from more than 35 nations appear to be at risk of different forms of "fluorosis" due to excess fluoride in drinking water [19, 27]. The World Health Organization has stipulated the minimum concentration of fluoride in drinking water as 1 mg/L to prevent dental decay, though this is still a subject of intense scientific debate. Hence, the development of sustainable defluoridation technologies has been a critical problem confronting the global scientific community for long [20, 28].

Fluoride contaminates water by weathering of fluoride-bearing mineral rocks from volcanic and fumarolic activities, from industrial emissions, and by precipitation from snow, or dry fall-out. It is found in seawater at a concentration of around 1.2-1.4 mg/L, in groundwater at concentrations up to 67 mg/L, and in most surface waters at concentrations less than 0.1 mg/L [28-29]. Fluoride is also found in foods particularly in fish and tea whilst almost all foodstuffs contain at least traces of fluoride. Generally, higher proportions of dissolved constituents are found in groundwater than in surface water because of the greater exposure to soluble materials in geologic strata. Soluble salts found in groundwater originate primarily from solution of rock materials. Fluoride is also a common geogenic contaminant of drinking water and it has deleterious effect on the health of human being. There are more than 20 developed and developing nations that are endemic for fluorosis. These are Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Pakistan, Persian Gulf, Sri Lanka, Syria, India, *etc* [30].

The absence of fluoride in drinking water causes a disease called "Osteoporosis" in which bones and teeth degenerate with increasing age [31]. However, its excessive intake may result in slow, progressive crippling scourge known as fluorosis. Under normal conditions, when fluoride is present in water supply, most of the ingested fluoride ions get incorporated into the appetite crystal lattice of calciferous tissue enamel during its formation. The hydroxyl ion gets substituted by fluoride ion since fluorapatite is more stable than hydroxyl appetite [32, 33]. Thus, a large amount of fluoride gets bound in these tissues and only a small amount is excreted through sweat, urine and stool [34]. The intensity of fluorosis is not merely dependent on the fluoride content in water, but also on the fluoride from other sources, physical activity and dietary habits [26].

Fluorine is highly reactive and is found naturally as CaF_2. It is an essential constituent in minerals like topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite, etc. [35]. The fluoride is found in the atmosphere, soil and water. It enters the soil through weathering of rocks, precipitation or waste run off. Surface waters generally do not contain more than 0.3 mg/L of fluoride unless they are polluted from external sources. Though drinking water is the major contributor (75–90% of daily intake), other sources of fluoride poisoning are food, industrial exposure, drugs, cosmetics, etc. [36]. Fluorine being a highly electronegative element has extraordinary tendency to get attracted by positively charged ions like calcium. Hence the effects of fluoride on mineralized tissues like bones and teeth leading to develop mental abnormalities are of clinical significance as they have highest amount of calcium and thus attract the maximum amount of fluoride that gets deposited as calcium–fluorapatite crystals [37].

The severe fluoride pollution has been identified in three cities of Pakistan i.e. Kasur, Loralai and Quetta. However, fluoride in drinking water has been observed in some isolated places of Bahawalpur, Faisalabad Karachi and Ziarat. According to PCRWR 2002-2003 fluoride hazard in water, the cities are (in descending order of percentage sample found with fluoride contamination) Quetta (29%), Kasur (20%), Karachi (14%), Loralai (10%), Faisalabad (8%) and Bahawalpur (4%) [38].

It is a big challenge to investigate low cost appropriate methods and technologies to be applied to make fluoride contaminated water drinkable. In this paper few of the low cost and appropriate methods & technologies are discussed and compared for potential application in developing countries with special reference to Pakistan.

Defluoridation Technologies

It is highly desirable to explore both technically and economically feasible fluoride removal techniques for the regions having high fluoride concentration in their water supplies [39, 40]. Defluoridation techniques have been extensively studied in many countries. During the years following the discovery of fluoride as the cause of fluorosis, extensive research was done on various methods for removal of fluoride from water and wastewater [41]. Following are the methods used for defluoridation of contaminated waters

1. Use of alternate water sources
2. Adsorption
3. Ion-exchange
4. Coagulation and precipitation
5. Membrane process
6. Biological treatment or integrated biological and physiochemical treatment

Processes such as desalination will virtually remove all fluoride from wastewater. In terms of using such sources for drinking water, the implications for public health will strongly depend on local circumstances. However, the public health requirement is to maximize the beneficial effects of fluoride in drinking water supplies for caries prevention, whilst minimizing the unwanted dental and potential general health effects [42].

Use of Alternative Water Sources

It is common practice of general public that they ignorantly use drinking water containing higher fluoride contents. It is highly desirable that ground water that is used for drinking should be characterized throughout the Pakistan and other developing countries. The Governments should develop baseline data regarding the drinking water quality in the developing nations. More emphasis should be placed on the use of surface waters like freshwater rivers and streams after purification. Even sea water can be use for drinking after desalination. Since surface water is often heavily contaminated with biological and chemical pollutants, it cannot be used for drinking purposes without treatment and disinfection that make the process too expensive and complex for application in poor communities [43]. The rain water may be harvested and purified for drinking purpose in the regions with high fluoride contents in groundwater. Harvesting the rainwater is usually a much cleaner water source and may provide a low-cost simple solution to the problem [44]. However, the un-even distribution of rain, limited amount and expensive storage capacity in communities or households are big bottlenecks in harvesting rain water for drinking purposes. The fact that fluoride is unevenly distributed in groundwater and its concentration keeps on changing with time both vertically and horizontally demands the testing of every well and regular monitoring which are not always possible in rural areas [45]. Vitamin C safeguards against the fluoride risk though measures to improve the nutritional status of an affected population might be an effective supplement to the technical solutions of the problem.

Adsorption

Defluoridation of drinking water is the only practicable option to overcome the excessive fluoride in drinking water, where alternate source is not available [9, 46]. One of the promising option for defluoridation of drinking water is the use of various adsorbents. Following adsorption techniques were used by various workers for defluoridation of drinking and mineral water.

- Adsorption by powdered activated carbon
- Adsorption by activated alumina and locally produced raw alumina
- Adsorption by tricalcium phosphate
- Adsorption by bone char
- Adsorption by anionic exchange resin [26, 47-49]

The other approach is to filter water down through a column packed with a strong adsorbent, such as activated alumina (Al_2O_3), activated charcoal, or ion exchange resins. Adsorbents such as alumina fly ash and carbon are used to adsorb fluoride from wastewater [26, 50-53]. When the adsorbent becomes saturated with fluoride ions, the filter material has to be backwashed with a mild acid or alkali solution to clean and regenerate it [54-56]. It has been reported that passing contaminated water with high fluoride content through columns containing different adsorbents (e.g. calcium three phosphate, activated alumina, bone flour and activated carbon) is an efficient method of fluoride removal [57]. It is already known that ion exchange, coagulation with alum, and softening of water are also suitable for defluoridation purposes [58-59].

Ion-Exchange

Fluoride can be removed from water supplies with a strongly basic anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction [60-65].

$$\text{Matrix-NR}_3^+\,Cl^- + F^- \rightarrow \text{Matrix-NR}_3^+\,F^- + Cl^-$$

The fluoride ions replaced the chloride ions of the resin [66]. This process continues until all the sites on the resin are occupied [67-68]. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electro negativity of the fluoride ions [69-70].

Coagulation and Precipitation

Lime and alum silicate the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water upto 11–12 [71-72].

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^-$$

As lime leaves a residue of 8.0 mg/L, it is used only in conjunction with alum treatment to ensure the proper fluoride removal. As a first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. When alum is added to water, essentially two reactions occur [22, 73-75]. In the first reaction, alum reacts with some of the alkali to produce insoluble aluminium hydroxide [$Al(OH)_3$]. In the second reaction, alum reacts with fluoride ions present in water. The best fluoride removal is accomplished at pH range of 5.5–7.5 [8-9, 76-81]. Due to use of aluminium sulfate as coagulant, the sulfate ion concentration increases tremendously and in few cases; it crosses the maximum permissible limit of 400 mg/L, which causes cathartic effects in human beings and the residual aluminum in excess of 0.2 mg/L in treated water causes dangerous disease of dementia as well as physiological path, neuronal behavior, structural and biochemical changes. It also affects musculo-skeletal, respiratory, cardiovascular, endocrine and reproductive systems [82-84].

Membrane Process

Although various conventional techniques like membrane process of water purification are being used at present to solve the problem of groundwater pollution none of them is user-friendly and cost-effective technique due to some or the other limitation and may have very long pay back period. In the recent years, reverse osmosis (RO) through membrane process has emerged as a preferred alternative to provide safe drinking water without causing the problems associated with other conventional methods [85-89]. RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semi permeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charges. The factors that influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment [90].

Efficiency of the process is governed by different factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance, etc. In the past, the use of membrane technology for water treatment, particularly for drinking water production had been considered un-economical in comparison with conventional means, but in the recent years the increased demand and contamination of water, rise in water quality standards and the problems associated with other methods have led to reconsideration of membrane technology for water purification. The progressive technical improvements in design and materials of the membranes have made the water treatment process economically competitive and highly reliable. Also, the capital and operational costs of RO plant go on decreasing with increasing plant capacity [91-94].

Biological and Physiochemical Treatment

Integrated biological and physiochemical water treatment process for nitrate and fluoride removal has been evaluated and it was concluded that the conventional processes of fluoride removal has been limited because of their expensive operation and subsequent problem of disposing of the waste being generated. *Eichhornia crassipes* and the activated carbon were tested for removal of fluoride from wastewater by batch techniques. Systematic batch studies were conducted on fluoride adsorption equilibrium and kinetics by *E. crassipes* and low-cost activated carbons prepared from *E. crassipes*. Different parameters were studied at different temperature, pH, time dose and size of adsorbent. The adsorption of fluoride on noncarbonized and carbonized *E. crassipes* increased with increasing temperature (25, 35, 45 °C), thereby indicating that the process was endothermic in nature in all of the cases examined. Carbonized *E. crassipes* showed better removal efficiency than the noncarbonized plant. The activation temperatures in the preparation of activated carbon played an important role. Carbon activated at 600 °C exhibited better performance than activated at 300 °C. Column studies were also performed with an initial concentration of 15 ppm. The effluent volume at breakthrough was found to be 100 bed volumes, and the column capacity was calculated as 4.4 mg/g [95].

Drawbacks and advantages of different defluoridation processes are given in Table-1.

The major techniques which are used for defluoridiation of water include coagulation, adsorption and/or ion exchange, electrochemical methods, and membrane techniques. Adsorption and precipitation methods are mostly used defluoridation techniques all over the worlds. Magnesium oxide, calcium oxide, alum and lime are cheap and more efficiently remove soluble fluorides in the form of fluoride precipitates. Fluoride removal is accomplished through solids separation from liquid. Various other chemicals involved in the precipitation process are polyaluminium chloride, polyaluminium hydroxy sulphate and polyelectrolytes. Chemical coagulants are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Though coagulation methods are generally effective in defluoridation, they are unsuccessful in bringing fluoride to desired concentration levels. Ion exchange and/or adsorption and sorption methods are more effective in reducing fluoride concentration than precipitation methods; in which adsorbents like

Table-1: Drawbacks and advantages of different defluoridation process.

Process	Advantages	Drawbacks
Adsorption	Fluoride removal is up to 90%. Treatment is cost-effective.	Highly dependent on pH. The pH range require(5–6). High concentration of total dissolved salts (TDS) results. Presence of sulfate, phosphate or carbonate results in ionic competition. Pretreatment require Because of low adsorption capacity, poor integrity. The regeneration is required after every 4–5 months and effectiveness of adsorbent for fluoride removal reduces after regeneration each time.
Ion-exchange.	Removes fluoride removal is up to 90–95%. Retains the taste and color of water intact.	Efficiency is reduced in presence of other ions like sulfate, carbonate, phosphate and alkalinity. Regeneration of resin is a problem because it leads to fluoride rich waste, which require proper treatment. The technique is expensive because of the cost of resin, pretreatment required to maintain the pH, Treated water has a very low pH and high levels of chloride.
Coagulation–precipitation	Most effective technique for fluoride removal based on combined use of alum and lime	Large amount of sulfate ion produce due to use of aluminium sulfate as coagulant. Due to organoleptic reasons, users do not like the taste of treated water. Maintenance cost of plant is very high. Large space is required for drying of sludge. Temperature also affects the defluoridation capacity.
Membrane process	Highly effective for fluoride removal. One step process and it ensures constant water quality. It works under wide pH range. No interference by other ions is observed.	It removes all the ions present in water, though some minerals are essential for proper growth, remineralization is required after treatment. The process is expensive in comparison to other options. The water becomes acidic and needs pH correction. Lot of water gets wasted as brine. Disposal of brine is a problem.

alumina and bone char were reported successful at the implementation level all over the world [96-98].

Conclusion

Natural contamination of groundwater sources by fluoride, arsenic and dissolved salts is a serious menace in many parts of Pakistan and other countries. Most of the fluoride in water, either naturally occurring or added, will be in the form of the free fluoride ion. It is big challenge to investigate low cost appropriate methods and technologies to be applied in developing countries to make fluoride contaminated water drinkable. The literature survey and the laboratory experiments have indicated that various techniques can remove fluoride under specified conditions. The fluoride removal efficiency varies according to many site-specific chemical, geographical and economic conditions, so actual applications may vary from the generalizations made. Any particular process, which is suitable for a specific region, may not meet the requirements for some other place. Therefore, any technology should be tested or before using for the actual water to be treated.

References

1. M. N. Bhutta, M. Ramzan and C. A. Hafeez, *Revue des Sciences de l'Eau*, **l**, 671 (2002).
2. M. J. Haron AND W. M. Z. W. Yunus, *Journal of Environmental Science and Health, Part A: Environmental Science and Engineering & Toxic and Hazardous Substance Control*, **36**, 727 (2001).
3. IPCS (Institute of Peace and Conflict Studies) (2002) Environmental Health Criteria 227 Fluorides. World Health Organization, Geneva.
4. WHO, Guidelines for Drinking Water Quality. Draft or review and comment, World Health Organization, Geneva, Switzerland, September, 2004.
5. R. Ahmed, Impact of Environmental Pollution in Rawalpindi and Islamabad, 24^{th} WEDC Conference, Islamabad, Pakistan (1998).
6. UNDP, United Nations Development Programme. Human Development Report—Beyond scarcity: Power, poverty and the global water crisis, New York (2006).
7. A. Agarwal, K. Rai and R. Shrivastav, *Journal of Cleaner Production*, **11**, 439 (2003).
8. C. Çengeloğlu, E. Kir and M. Ersoz, *Journal of Colloid and Interface Science*, **244**, 342 (2001).
9. C. Çengeloğlu, E. Kir and M. Ersoz, *Separation and Purification Technology*, **28**, 81 (2002).
10. D. R. R. Sarma and S. L. N. Rao, *Bulletin of Environment Contamination and Toxicology*, **58**, 241 (1997).
11. C. K. Agarwal, K. S. Gupta and B. A. Gupta, *Water Science and Technology*, **40**,167(1999).
12. E. K. Mroczek, *Geothermics*, **34**, 218 (2005).
13. F. Frey, D. M. Owen and S. K. Chowdhury, *Journal American Water Works Association*, **90**, 89 (1998).
14. Gupta and M. Chaudhuri, *Water Research*, **29**, 511 (1995).

15. M. J. Haron and W. M. Z. W. Yunus, *Journal of Environmental Science and Health, Part A: Environmental Science and Engineering & Toxic and Hazardous Substance Control*, **36**, 727 (2001).
16. Y. Joshi and M. Chaudhuri, ASCE *Journal of Environmental Engineering*, **122**, 769(1996).
17. R. C. Meenakshi, *Journal of Hazardous Materials*, **137**, 456 (2006).
18. M. A. Tahir and A. Bhatti, Survey of Drinking Water Quality in the Rural Areas of Rawalpindi District. Pakistan Council of Research in Water Resources, Islamabad (unpublished).Technical Digest, National Environmental Engineering Research Institute, Nagpur, NEERI Manual (1994).
19. C. S. Zhu, G. L. Bai and X. L. Liu, *Water Research*, **40**, 3015 (2006).
20. A. Oren, Y. Yechieli, J. K. Bohlke and A. Dody, *Journal of Hydrology*, **290**, 312 (2004).
21. A. Kass, Y. Yechieli, A. Gavrieli and A. Vengosh, *Journal of Hydrology*, **300**, 314 (2005).
22. G. Singh, B. Kumar, P. K. Sen and J. Majumdar, *Water Environment Research*, **71**, 36 (1999).
23. G. Garmes, F. Persin, J. Sandeaux, *Desalination*, **145**, 87 (2002).
24. http://bch.minambiente.it/EN/Documents/RioDecl.pdf, accessed on 23rd April 2009.
25. J. O. Hem, Study and interpretation of chemical characteristics of natural water, U.G. Geological Survey *Water Supply Paper* (1959).
26. K. Chaturvedi, K. P. Yadava, K. C. Yadava, K. C. Pathak and V. N. Singh, *Water Air Soil Pollution*, **49**, 51(1990) .
27. WHO Guidelines for Drinking Water Quality (vol. II): Health Criteria and Supporting Information, World Health Organization, Geneva, Switzerland (1984).
28. A. Agarwal, K. Rai and R. Shrivastav, *Journal of Cleaner Production*, **11**, 439 (2003).
29. C. K. Agarwal, K. S. Gupta and B. A. Gupta, Development of new low cost defluoridation technology, *Water Science and Technology*, **40**, 167 (1999).
30. N. Shengji, N. Jun, L. Ruiping and L. Guibai, *Desalination*, **1**, 41 (2004).
31. C. Bell, T. C. Ludwig, The supply of fluoride to man: Ingestion from water, in: Fluorides and Human Health, WHO Monograph Series 59, World *Health* Organization, Geneva, (1970).
32. T. C. Huang, C. J. Liu, Treatment of Semiconductor wastewater by dissolved air flotation, *Journal of Environmental Engineering*, **128**, 974 (2002).
33. D. J. John, Water Treatment, Handbook of Drinking Water Quality Standards and Controls, Van Nostrand Reinhold, New York pp 407–490 (1985).
34. J. J. Murray, J. Dent, *Brazilian Dental Journal*, **134**, 250 (1973).
35. R. C. Meenakshi, *Journal of Hazardous Materials*, **137**, 456 (2006).
36. B. Apambire, D. R. Boyle, F. M. Michel, *Environmental Geology*, **33**, 13 (1997).
37. A. Ayoob and A. K. Gupta, *Critical Reviews in Environmental Science and Technology*, **36**, 433 (2006).
38. A. Azbar and A. Turkman, *Water Science and Technology*, **42**, 403 (2000).
39. J. L. Bahena, A. R. Cabrera, A. L. Valdivieso and R. H. Urbina, *Separation Science and Technology*, **37**, 1973 (2002).
40. M. Murugananthan, G. Bhaskar and S. Prabhakar, *Separation and Purification Technology*, **40**, 69 (2004).
41. M. Hichour, M. Persin, F. Sandeaux and J. C. Gavach, *Separation and Purification Technology*, **18**, 1 (2000).
42. N. Parthasarathy, J. Buffle and W. C. Haerdi, *Water Research*, **4**, 443 (1986).
43. WHO. World Health Organization, Geneva, Ground water and public health, chapter 1, p2. (2004). (www.who.int/entity/water sanitation health/ resourcesquality/En/groundwater1.pdf)
44. M. I. Rorabaugh, *Transaction of American Geophysical Union*, **37**, 436 (1996).
45. Dahi, The State of Art of Small Community Defluoridation of Drinking Water, Dahi, E., Rajchagool, S., and Osiriphan, N., Eds., Proceedings of the *3rd* International Workshop on Fluorosis Prevention and Defluoridation of Drinking Water, Chiang Mai, Thailand, p.137–167 (2000). http://www.icoh.org/download/3rdproceeding.pdf
46. M. I. Hardisson, A. Rodriguez, A. Burgos, L. D. Flores, R. Gutierrez and H. Varela, Spain, *Bulletin of Environment Contamination and Toxicology*, **67**, 163 (2001).
47. J. A. Blackwell and P. W. Carr, *Journal of Chromatography*, **549**, 43 (1991).
48. A. K. Chaturvedi, K. C. Pathak, V. N. Singh and *Applied Clay Science*, **3**, 337 (1988).
49. N. I. Chubar, V. F. Samanidou and V. S. Kouts,

Journal of Colloid and Interface Science, **291**, 67 (2005).

50. B. S. N. Murty, V. Ravi and P. J. Reddy, *Pollution Research*, **16**, 177 (1997).
51. H. Lounici, L. Addour and D. Belhocine, *Desalination*, **114**, 241 (1997).
52. R. Peikos and S. Paslawska, *Fluoride*, **32**, 14 (1999).
53. R. Weerasooriya, H. U. S. Wickramarathne and H. A. Dharmagunawardhane, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **144**, 267 (1998).
54. D. Dieye, B. Larchet, C. Auclair and Mar-Diop, *European Polymer Journal*, **3**, 467 (1998).
55. A. Li and J. M. Wang, *Journal of Applied Polymer Science*, **92**, 596 (2004).
56. S. Abe, T. wasaki and N. Tokimoto, *Journal of Colloid and Interface Science*, **275**, 35(2004).
57. S. K. Adhikari, U. K. Tipnis, W. P. Harkare and K. P. Govindan, *Desalination*, **71**, 301 (1989).
58. T. S. Bhakuni and C. A. Sastry, *Environmental Health*, **4**, 246 (1969).
59. G. H. Swope and R. S. Hess, *Industrial and Engineering Chemistry*, **29**,110 (1997).
60. Z. Amor, B. Bariou, N. Mameri, M. Toky, S. Nicolas and A. Elmidaoui, *Desalination*, **133**, 215 (2001).
61. M. Castel, M. O. Schweizer, M. Simonnot and M. Sardin, *Chemical Engineering Sci*ence, **55**, 334 (2000).
62. S. T. Hwang and K. Kammermeyer, *Techniques of Chemistry*, **99**, 123 (1975).
63. R. Liu, O. Ming and G. Ankumah, *Science of the Total Environment*, **3**, 112 (2005).
64. E. J. Reardon and Y. Wong, *Environmental Science and Technology*, **34**, 3247 (2000).
65. R. M. Wallace, *Industrial & Engineering Chemistry Process Design and Development*, **6**, 423 (1967).
66. C. Wang, R. Strojek and J. W. T. Kuwana, *Journal of Physical Chemistry*, **91**, 3606 (1987).
67. Z. Ogumi, T. Kuroe and Z. Takehara, *Journal of the Electrochemical Society*, **132**, 2601 (1985).
68. A. Uragami, R. Nakamura and M. Sugihara, *Polymer*, **24**, 559 (1983).
69. Z. Ogumi, T. Takehara and S. Yoshizawa, *Journal of the Electrochemical Society*, **131**, 769 (1984).
70. Z. Ogumi, K. Toyama, Z. Takehera, K. Katakura and S. Inuta, *Journal of Membrane Science*, **165**, 205 (1992).
71. Y. Hu, Lo SL and W. Kuan, *Water Research*, **37**, 4513 (2003).
72. F. Shen, X. Chen, P. Gao and G. Chen, *Chemical Engineering Science*, **58**, 987 (2003).
73. F. Durmaz, H. Kara and Y. Cengeloğlu, *Desalination*, **177**, 51 (2005).
74. M. Hichour, M. Persin, F. SandeauxJ and C. Gavach, *Desalination*, **122**, 53 (1999).
75. M. Hichour, M. Persin, F. Sandeaux and J. C. Gavach, *Separation and Purification Technology*, **18**, 1 (2000).
76. A. Tor, T. Büyükerkek, Y. Çengeloğlu and M. Ersöz, *Desalination*, **171**, 233 (2004).
77. J. Gregory and J. Duan, *Pure and Applied Chemistry*, **73**, 2017 (2001).
78. S. R. Grobler, A. G. Dreyer and R. J. Blignaut, *Journal of the South African Dental Association*, **56**, 557 (2001).
79. H. Hagmeyer, and R. Gimbel, *Desalination*, **117**, 247 (1998).
80. J. H. Kennedy, *Analytical Chemistry Principles* (2nd Ed.), W.B. Saunders Company, New York. (1990)
81. D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry* (7th Ed.), Saunders College Publisher, USA (1996).
82. M. Y. A. Mollah, R. Schennach, J. R. Parga and D. L. Cocke. *Journal of Hazardous Materials*, **84**, 29 (2001).
83. N. Mameri, A. R. Yeddou and H. Lounici, *Water Research*, **32**, 604 (1998).
84. J. Q. Jiang, N. Graham, C. Andre, G. H. Kelsall and N. Brandon, *Water Research*, **36**, 4064 (2002).
85. S. Saha, *Water Research*, **27**, 1347 (1993).
86. D. Babra, and S. Caputi, *Desalination*, 11 (2002).
87. S. Culp and H. Stolenberg, *Journal of American Water Works Association*, **3**, 423 (1958).
88. Nayak, *Environmental Research Sec* A, **89**, 101 (2005).
89. J. H. Potgieter, A. M. Heyns and W. Skinner, *Journal of Applied Electrochemistry*, 20 (1990).
90. L. Parker and C. C. Fong, *Industrial Wastes*, 23 (1975).
91. A. M. RaichuR and M. Y. Basu, *Separation and Purification Technology*, **24**, 121 (2001).
92. B. Amer, N. Bariou and M. Mameri, *Desalination*, **13**, 215 (2001).
93. W. G. Nawalakhe, D. N. Kulkarni, B. N. Pathak and K. R. Bulusu, *Indian Journal of*

Environment and Health, **1**, 16 (1974).
94. Anwar, *Waste Management*, **9**, 817(2003).
95. S. Sinha, K. Pandey, D. Mohan and K. P. Singh, *Industrial and Engineering Chemistry Research*, **42**, 6911 (2003).
96. S. Ayoob, A. K. Gupta and V. T. Bhat, *Environmental Science and Technology*, **38**, 401 (2008)
97. A. V. Jamode, V. S. Sapkal and V. S. Jamode, *Journal of the Indian Institute of Science*, **84**, 163 (2004)
98. R. H. Yao, F. P. Meng, L. J. Zhang, D. D. Ma and M. L. Wang, *Journal of Hazardous Materials*, **165**, 454 (2009).