Arsenic Contamination in Water and its Removal by using Different Low Cost Adsorbents

NASEEM ZAHRA
PITMAEM, PCSIR Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan.

(Received on 24th August 2009, accepted in revised form 6th January 2010)

Summary: Industrial waste constitutes the major source of various kinds of pollution in natural water and toxicity from heavy metals has been reported worldwide. The presence of arsenic in water is major problem these days. High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. Arsenic pollution also has emerged as a serious public health concern in Pakistan also. The presence of metal in drinking water is of special concern because of its persistence and toxicity. Different adsorbents are used to remove arsenic from water. In present review paper arsenic contamination, its toxicity and its removal from drinking water using different adsorbents is described.

Introduction

Arsenic occurs in rocks, soil, water, air and in biota. It is present in the environment in several forms but in natural waters, it is mostly found as trivalent arsenite, As(III) or pentavalent arsenate, As (V). Organic arsenic species, abundant in seafood, are very much less harmful to health and are readily eliminated by the body. Arsenic is also used commercially, in alloying agents and wood preservatives. Combustion of fossil fuels is a source of arsenic in the environment through atmospheric deposition. The greatest threat to public health arises from arsenic in drinking water. Exposure at work, mining and industrial emissions may also be significant locally [1].

Arsenic is introduced into the aquatic environment from both natural and man-made sources. Typically, however, arsenic occurrence in water is caused by the weathering and dissolution of arsenic-bearing rocks, minerals and ores. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. Although arsenic exists in both organic and inorganic forms, the inorganic forms are more prevalent in water and are considered more toxic. Arsenic chemistry in aquatic system is quite complicated as the element can be stable in four oxidation states (+5), (+3), (0) and (-3) under different redox condition but in groundwater only two valence states (+3) and (+5) are common. The toxicity of arsenic varies greatly with its oxidation states as (+3) is much more toxic and mobile than (+5). A variety of methods have been used in the past for arsenic removal from drinking water and waste water. Existing methods of arsenic removal include precipitation [2-4], adsorption [5-8], ion exchange [9] and ultrafiltration [10].

Level of Arsenic in Drinking Water

Exposure to arsenic leads to an accumulation of arsenic in tissues such as skin, hair and nails, resulting in various clinical symptoms such as hyperpigmentation and keratosis. There is also an increased risk of skin, internal organ and lung cancers. Cardiovascular disease and neuropathy have also been linked to arsenic consumption. Arsenic in drinking water can affect human health and is considered as one of the most significant environmental causes of cancer in the world [11]. Therefore, it is necessary to mention the levels of As in drinking water and its chemical speciation [12]. The FAO health limit for As in groundwater was until recently 50 $\mu g/L$, but in view of recent incidences of As poisoning in the Indian subcontinent, a decrease to 5–10 $\mu g/L$ is being considered by a number of regulatory bodies throughout the world. The temporary WHO guideline for As in drinking water is 10 $\mu g/L$. This is based on a $6\times10{-}4$ excess skin cancer risk, which is 60 times higher than the factor normally used to protect human health. However, the WHO states that the health-based drinking water guideline for As should in reality be 0.17 $\mu g/L$. Previously, such low levels were not feasible to determine as many analytical techniques had detection limits of 10 μg/L, that is why the less protective guideline was adopted [13-15].

Arsenic Removal by Adsorption

Consequently, attempts have been made in order to find new simple and efficient techniques. For dilute concentrations, adsorption is one of the suitable methods for removal of heavy metal ions. Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement [16, 17]. The use of carbon extends far back into history. Its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 b.c. [18]. Modern activated carbon industrial production was established in 1900–1901 to replace bone-char in sugar refining [19]. Powdered activated carbon was first produced commercially from wood in Europe in the early 19th century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930 [20]. Activated carbon is a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions [21]. Active carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc. Wood (130,000 tons/year), coal (100,000 tons/year), lignite (50,000 tons/year), coconut shell (35,000 tons/year) and peat (35,000 tons/year) are most commonly used [22]. Carbon surface chemistry has been reviewed [23, 24]. This surface chemistry depends upon the activation conditions and temperatures employed. Activation refines the pore structure. Mesopores and micropores are formed yielding surface areas up to 2000m^2/g [25]. Acidic and basic activation carbon exists according to the Steenberg's classification [26]. The acidic groups on activated carbons adsorb metal ions [27]. Surface area may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity [28]. The adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges affect removal kinetics from solution. Adsorption capacity depends on adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated carbons are available commercially but few are selective for heavy metals. They are also expensive. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery. Adsorption and ion exchange: [29] various solid materials, including iron and aluminum hydroxide flocks have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds and are less easily reversed.

Different Adsorbents for Arsenic Adsorption

In some areas of the world, arsenic presence in drinking water systems is a serious human health hazard. Serious adverse health effects [30] including human mortality, from arsenic contamination of drinking water are well documented. Arsenic (III) compounds are primarily non-ionic [31] whereas arsenic (V) compounds are primarily ionic at normal drinking water pH levels. A simple and economical domestic arsenic removal kit [32] has been designed and successfully evaluated in laboratory using sand-iron scrap mixture as media for the removal of arsenic from water. Removal of arsenic (V) from wastewater [33] by bentonite and D202 resin was studied. The peak adsorption appears at pH 4 and 7. For treatment of wastewater containing arsenites and arsenates [34] were treated with grey bentonite modified with $FeSO_4.7H_2O$, $FeCl_3.6H_2O$, $MgSO_4$ or $Al(NO_3)_3.9H_2O$.The best results were obtained in the range of pH 6 and 7 with bentonite modified with ferrous salts. Studies on removal of arsenic (III) by adsorption [35] on groundnut husk and carbon were carried out at room temperature. Maximum adsorption capacity was observed at pH 7.0. Arsenate adsorption [36] by a natural manganese oxide was studied. The affinity order was determined: arsenates >> phosphates > hydrogen carbonates ~ sulfate .The effectiveness of the use of special clays for heavy metal removal from waste water was evaluated. The sepiolite and the magnesic bentonite were effective in reducing the [37] heavy metal concentration of the industrial wastewater samples. Photocatalytic oxidation of arsenite and simultaneous removal of the generated arsenate [38] from aqueous solution was investigated Goethite was synthesized from the oxidation of ferrous carbonate. The optimum pH of adsorption [39] was found to be 5.0. Biosorption of arsenic using algae as sorbent was studied. Maximum adsorption [40] capacities were estimated to 45.2 mg/g (pH = 2.5), 33.3 mg/g (pH = 4.5) and 28.2 mg/g (pH = 6.5) indicating better adsorption at the lower pH. The removal of arsenic (III) on iron oxide-coated sand in batch studies [41] conducted as a function of pH, time, initial arsenic concentration and adsorbent dosage. An adsorption process for the removal of As (V) and As (III) was evaluated using zirconium (IV) loaded chelating resin. Arsenate ions strongly adsorbed in the pH range from 2 to 5, [42] while arsenite was adsorbed between pH 7 and 10.5. Adsorption of arsenite and arsenate versus pH was studied on goethite, amorphous iron hydroxide and clay pillared with titanium (IV), iron (III) and aluminum (III) synthesized from a bentonite with a montmorillonitic-pillared fraction [43].

Activated carbon is an example of efficient sorbents, that its application is limited by high cost of production and regeneration. Thus searching for new, low-cost and ecofriendly sorbents has been considered. Various types of biological materials such as non-living biomass of algae, aquatic ferns and seaweeds, waste biomass originated from plants, *etc.* have been cited as efficient biosorbents [44-57]. Arsenic from wastewater was removed by batch adsorption technique using bentonite. Bentonite contains montmorillonite which has the quality to adsorb inorganic and organic materials. Percentage adsorption was determined for bentonite-arsenic solution system as a function of i) contact time, ii) pH iii) temperature iv) mesh size and v) adsorbate dose. Bentonite is suitable for removal of arsenic from wastewater [58].

Effects of Temperature and pH, Reaction Kinetics and Nature of Link between Arsenic and Surface of Media

Effect of temperature on arsenic adsorption [58] was noted at various temperature ranges (20, 40, 60, 80, 100 °C). Maximum adsorption was observed at 20 °C room temperature. At higher temperature the percentage adsorption decreases because there may be breakdown of the forces by which arsenic ions were adsorbed on bentonite.

The mean metal ion sorbed by the coconut fiber at each temperature was determined using a mass balance equation expressed as:

$$qe = (Co-Ce) V / m$$

where;

qe = metal ion adsorption per unit weight of biomass (mg gG1 biomass) at equilibrium,

Ce = metal ion concentration in solution (mg LG1) at equilibrium;

Co = initial metal ion concentration metal in solution used (mg LG1);

V = volume of initial metal ion solution used (L);

M = mass of biomass used (g).

The amount of As (III) adsorbed increased from 293K to 303K and then decrease when the temperature increased to 323K. This means that the optimum temperature of adsorption is within 303K to 313K. Therefore, increasing the temperature beyond this point will not favor the adsorption. This is similar to the results obtained by various researches [59-61]. However, Horsfall and Spiff found out that the magnitude of the increase in amount as temperature is increased continues to decline as temperature is increased from 303K to 353K. Their findings also reveal that most metal ions were removed between the temperatures of 303k to 323k. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases. The negative values of ΔG° [60] indicate the spontaneous nature of adsorption of the metal ion by the biomass. Also, at high temperature, the thickness, of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a decrease in adsorption as temperature increases [62]. It has been reported that ΔG° up to -20 kJg/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than -40 kJg/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) [63]. The adsorption of arsenic by *Lessonia nigrescens* could be explained satisfactorily both by the Freundlich and the Langmuir isotherms. Maximum adsorption capacities were estimated to 45.2 mg/g (pH = 2.5), 33.3 mg/g (pH = 4.5) and 28.2 mg/g (pH = 6.5) indicating better adsorption at the lower pH. These values are high in comparison with other arsenic adsorbents reported.

The sorption kinetics of arsenic by *Lessonia nigrescens* could be modelled well by Lagergren's first order rate equation. The kinetics were observed to be independent of pH during the first 120 minutes of adsorption with the Lagergren first order rate constant of around $1.07 \cdot 10^{-3}$ min^{-1}[64]. Langmuir equation best fit the adsorption isotherm (Lakshmipathiraj *et al.*, 2006). The diffusion and adsorption coefficients of arsenate ion were 3.84×1011 cm^{2} s^{-1} and 1941 mol^{-1}, respectively. The activation energy of adsorption reaction was of the order of 20 kJ mol^{-1} to 43 kJ mol^{-1} and maximum adsorption capacity was 4.7 mg g^{-1} goethite [65]. Adsorption kinetics for removal of arsenic was carried out by red mud and its mixture with haematite, china clay and fly ash. Adsorption follows first order reaction kinetics [66]. The sorption kinetics and intraparticulate diffusivity of As (III) bioremediation from aqueous solution using modified and un-modified coconut fiber was investigated. The amount adsorbed increased as time increased, reaching equilibrium at about 60 minutes. The kinetics studies showed that the sorption rates could be described by both pseudo- first order and pseudo-second order process with the later showing a better fit with a value of rate constant of $1.16\text{x } 10^{-4}$ min^{-1}.The mechanism of sorption was found to be particle diffusion controlled [67]. The activation energy of adsorption reaction was of the order of 20 kJ mol^{-1} to 43 kJ mol^{-1} and maximum adsorption capacity was 4.7 mg g^{-1} goethite. The adsorption of arsenate by goethite increase as pH decreases and maximum adsorption was observed around pH 5 [68, 69].

Effect of Contact Time on Adsorption of Arsenic

Adsorption of arsenic on bentonite [58] as a function of time was determined and equilibrium was reached after mixing for 30 minutes, indicates that surface precipitation as well as ion exchange may be the possible adsorption mechanism. The amount of arsenic adsorbed on coconut fiber increased as time increased, reaching equilibrium at about 60 minutes [67]. The kinetic test was performed to investigate the effect of time on adsorption of arsenic. Increasing of the shaking time helps mineral bauxite [70] to remove the largest amount of arsenic. The highest value of the adsorbed arsenic was 4996.8 mg kg-1 after 48 h of shaking which means that 99.9% of the arsenic was removed. The lowest value was 4966.95 mg kg-1, i.e., 99.3% of arsenic removed after 1 min shaking. It is noted that the removal of arsenic increases with time.

Arsenic Contamination in Drinking Water Supply in Pakistan

In view of the health concerns outlined above and alerted by the magnitude of the problem afflicting nearby Bangladesh and West Bengal, the Public Health.

Engineering Department (PHED) and the Local Government and Rural Development Department (LGRDD) of Pakistan, in conjunction with UNICEF, recently undertook a survey of arsenic concentration in groundwater from drinking water supply wells in Pakistan [71]. In Punjab over 20% of the population is exposed to arsenic contamination of over 10 ppb in drinking water while nearly 3% of the population is exposed to over 50 ppb. In Sindh, the situation is even worse with 36% and 16% of population exposed to arsenic contaminated water over 10 ppb and 50 ppb respectively. Both shallow and deep sources have arsenic contamination [72].

Conclusion

It is very necessary to detect the arsenic concentration in drinking water supply and also to provide a suitable, environment friendly and cost effective arsenic removal process to save millions of people in Pakistan and all over the world from arsenic poisoning. Adsorption is a useful tool for controlling the extent of aqueous arsenic pollution. A definite need exists for low-cost adsorbents, which exhibit superior adsorption capacities and local availability. The purpose of this review was to show that several materials have equal or greater adsorption capacities to remove arsenic from water. Therefore, additional/preventive steps must be applied to utilize these adsorbents for arsenic adsorption. Clays, silica, sand, etc. are in fact low-cost adsorbents which are available worldwide and can also be regenerated.

References

1. World Health Organization (W.H.O.) Technical Report, *Arsenic in drinking water* (2001).
2. W. Chow, *Pollution Engineering*, **19**, 54 (1997).
3. T. R. Harper and N. W. Kingham, *Water Environment Research*, **64**, 200 (1992).
4. A. Ramana and A. K. Sengupta, *Journal of Environmental and Engineering*, **118**, 755 (1992).
5. M. P. Elizalde, *Chemical Engineering Journal*,

81, 187 (2001).

6. J. Gregor, *Water Research*. **35**, 1659 (2001).
7. S. K. Gupta and K. Y. Chen, *Journal of Water Pollution Control Federation*, **50**, 493 (1978).
8. C. P. Huang and P. L. K. Fu, *Journal of Water Pollution Control Federation*, **56**, 233 (1984).
9. D. Clifford and C.C. Lin, *EPA/600/S2-91/011* (1991).
10. E. Bellack, *Journal of American Water Works Association*, **63**, 454 (1971).
11. A. H. Smith, C. Hopenhayn-Rich, M. N. Bates, H. M. Goeden, I. Hertz-Picciotto, H. M. Duggan, R. Wood, M. J. Kosnett, M. T. Smith, *Environmental Health Perspectives*, **97**, 259 (1992).
12. A. H. Welch, D. B. Westjohn, D. R. Helsel, R. B. Wanty, *Ground Water*, **38**, 589 (2000).
13. W.H.O. *Guidelines for Drinking-Water Quality, Volume 1* Recommendations. 2nd Edition, Geneva (1993).
14. W.H.O. *Guidelines for Drinking-Water Quality Addendum to Volume 1: Recommendations*, 2nd edition. Geneva (1998).
15. World Health Organization (W.H.O.) Technical Report, Arsenic contamination of drinking water in Bangladesh, Fact sheet No. 210 (1999).
16. M. M. Benjamin, R. S. Sletten, R. P. Bailey and T. Bennett, *Water Research* **30**, 2609 (1996).
17. L. Dambies, T. Vincent and E. Guibal, *Water Research*, **36**, 3699 (2002).
18. P. N. Cheremisinoff and C. M. Angelo, Carbon adsorption applications, in: *Carbon Adsorption Handbook*, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1–54, (1980).
19. R. P. Bansal, J.-P. Donnet and F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, (1988).
20. C. L. Mantell, *Carbon and Graphite Handbook*, John Wiley & Sons, Inc., New York, (1968).
21. Y. Hamerlinck, D. H. Mertens, in: E. F. Vansant (Ed.) *Activated Carbon Principles in Separation Technology*, Elsevier, New York, (1994).
22. S. J. T. Pollard, G. D. Fowler, C. J. Sollars and R. Perry, *Science of the Total Environment*, **116**, 31 (1992).
23. R. C. Bansal and M. Goyal, *Activated Carbon Adsorption*, CRC Press, (2005).
24. L. R. Radovic (Ed.), *Chemistry and Physics of Carbon*, **vol. 27**, Marcel Dekker, Inc., New York, (2000).
25. D. Mohan, K. P. Singh, Granular activated carbon, in: J. Lehr, J. Keeley, J. Lehr (Eds.), *Water Encyclopedia:* Domestc, Municipal and Industrial Water Supply and Waste Disposal, Wiley–Interscience, New York, (2005).
26. J. S. Mattsom and H. B. Mark, Activated Carbon: Surface Chemistry and Adsorption from Aqueous Solution, Marcel Dekker, New York, (1971).
27. M. O. Corapcioglu and C. P. Huang, *Carbon* **25**, 569 (1987).
28. J. R. Perrich, *Activated Carbon Adsorption for Wastewater Treatment*, CRC press, Inc., Boca Raton, FL, (1981).
29. R. Johnston and H. Heijnen, Safe Water Technology for Arsenic Removal, A compilation of papers presented at the International Workshop on Technologies for Arsenic Removal from Drinking Water organized by Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh and The United Nations University (UNU), Tokyo, Japan, (2001).
30. National Research Council, *Arsenic in drinking water*, Washington DC, National Press Academy (1999).
31. S. Arivar, A. Gupta, R. K. Biswas, A. K. Deb, E. Greenleaf and A. K. SenGupta, *Water Research Journal*, **39**, 2196 (2005).
32. R. Goel, S. K. Kapoor, K. Misra and R. K. Sharma, *Indian Journal of Chemical Technology*, **11**, 518 (2004).
33. C. Hong, Fang, Shi, *Zhejiang Daxue Xuebao*, Peop. Rep. China, **34**, 547 (2000).
34. E. K. Velcheva and I. I. Kulev, *Khimi Kotekhnol*, Inst. Burgas, **24**, 85(1995).
35. P. B. Nagrnaik, A. G. Bhole and G. S. Natarajan, *Journal of Ecotoxicology and Environmental Monitoring*, **14**, 93 (2004).
36. S. Ouvard, M. O. Simonnot and M. Sardin, *Water Science and Technology: Water Supply*, **1**, 167 (2001).
37. L. Andrade, E. F. Covel and F. A., Vega, *Information Technologia*, **16**, 3 (2005).
38. F. Shen, Zhang and Hideaki, *Chemosphere*, **65**, 125 (2006).
39. P. Lakshmipathiraj, B. R. V. Narasimhan, S. Prabhakar and G. Bhaskar Raju, *Journal of Hazardous Materials*, **136**, 281(2006).
40. H. K. Hansen, A. Ribeiro and E. Mateus, *Minerals Engineering*, **19**, 486 (2006).
41. V. K. Gupta, V. K. Saini and Neeraj, *Journal of Colloid and Interface Science*, **55**, 288 (2005).
42. T. Balaji, T. Yokoyama and Hideyuki, *Chemosphere*, **59**, 1169 (2005).

43. V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, J.-C. Bollinger, *Journal of Colloid Interface Science*, **255**, 52 (2002).
44. E. Luef, T. Prey and C. P. Kubicek, *Applied Microbiology and Biotechnology*, **34**, 688 (1991).
45. M. Nourbakhsh, Y. Sag, D. Ozer, Z. Aksu, T. Katsal and A. Calgar, *Process Biochemistry*, **29**, 1 (1994).
46. P. Puranik and K. M. Paknikar, *Bioresource Technology*, **70**, 269 (1999).
47. B. Verma and N. P. Shukla, *Indian Journal of Environmental Health*, **42**, 145 (2000).
48. R. Say, A. Denizli and M.Y. Arica, *Bioresource Technology*, **76**, 67 (2001).
49. R. Apiratikul, T.F. Marhaba, S. Wattanachira and P. Pavasant. *Journal of Science Technology*, **26**, 199 (2004).
50. N.R. Bishnoi, M. Bajaj, N. Sharma and A. Gupta, *Bioresource Technology*, **91**, 305 (2004).
51. P. Lodeiro, B. Cordero, J.L. Barriadh, R. Herrero and M.E.S. deVicente, *Bioresource Technology*, **96**, 1796 (2005).
52. K. Chandrasekhar, C. T. Kamala, N. S. Chary and Y. Anjanuyulu, *International Journal of Mineral Process*, **68**, 37 (2003).
53. Y. S. Ho, C. T. Huang and H. W. Huang, *Process Biochemistry*, **37**, 1421 (2002).
54. M. I. Kandah, *Chemical Engineering Technology*, **25**, 921 (2002).
55. R. Naseem and S. S. Tahir, *Water Research*, **35**, 3982 (2001).
56. F. F. O. Orumwense, *Journal of Chemical Technology and Biotechnology*, **65**, 363 (1996).
57. A. Kapoor, T. Viraraghavan and D. Roy Cullimore, *Bioresource Technology*, **70**, 95 (1999).
58. N. Zahra, S.T. Sheikh, A. Mahmood, K. Javed, *Bangladesh Journal of Science and Industrial Research*, **44**, 81 (2009).
59. Y.S. Ho, *Water Research*, **37**, 2323 (2003).
60. Horsfall, M. Jnr and A. I. Spiff, *Electronic Journal of Biotechnology*, **8**, 1 (2005).
61. G. Mckay, Y. S. Ho and J.C.P. Ng, *Electronic Journal of Biotechnology*, **28**, 87 (1999).
62. Z. Aksu and T. A. Kutsal, *Journal of Chemical Technology and Biotechnology*, **52**, 108 (1991).
63. M. Horsfall, A. I. Spiff, *Electronic Journal of Biotechnology*, **7**, 1 (2004).
64. H. K. Hansen, A. Ribeiro and E. Mateus, *Minerals Engineering*, **19**, 486 (2006).
65. P. Lakshmipathiraj, , B. R. V. Narasimhan, S. Prabhakar, G. B. Raju, *Journal of Hazardous Materials*, **36**, 281 (2006).
66. A. P. Singh, k.k. Srivastava and H. Shekhar, *Journal of Scientific and Industrial Research*, **66**, 952 (2007).
67. J. C. Igwe and A. A. Abia, *Electica Quimica*, **31**, 23 (2006).
68. A. Dimirkou, Z. Ioannou, E. E. Golia, N. Danalatos and I. K. Mitsios, *Communication in Soil Science and Plant Analysis*, **40**, 259 (2009).
69. J. Gimenez, M. Martinez, J. de Pablo, M. Rovira and L. Duroc, *Journal of Hazardous Materials* **141**, 575 (2007).
70. F. Y. Alshaebi, W. Zuhairi, W. Yaacob, A. R. Samsudin and E. Alsabahi, *American Journal of Applied Sciences*, **6**, 1826 (2009).
71. B. Shrestha, Drinking water quality: Future directions for UNICEF in Pakistan. Consultancy Report 2 of 3, Water Quality, SWEET Project, UNICEF Pakistan, Islamabad (2002).
72. T. Ahmad, M. A. Kahlown, A. Tahir and H. Rashid, Arsenic an Emerging Issue: Experiences from Pakistan, 30th WEDC International Conference, Vientiane, Lao PDR, 459-466 (2004).