

ARSENIC REMOVAL FROM REAL-LIFE GROUNDWATER BY ADSORPTION ON NEEMBARK (*Azadirachta indica*)

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ABSTRACT

The adsorption characteristics of arsenic on Neem bark, a low-cost natural adsorbent, were studied in the laboratory scale using real-life sample. Neem bark has tremendous potential as a remediation material for the removal of arsenic from groundwater. The present work investigates the possibility of the use of neem bark adsorption technology without any pretreatment in the removal of arsenic from aqueous media. Various conditions that affect the adsorption/desorption of arsenic are investigated. Adsorption column methods show the maximum removal of As (III) under the following conditions: initial As concentration, 100 $\mu\text{g/L}$; neem bark amount, 5 g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min; and pH, 6.9 respectively. The desorption efficiencies with 1M of HCL after the treatment of groundwater were in the range of 79%. The present study might provide new avenues to achieve the arsenic concentration for drinking water recommended by Bangladesh and the World Health Organization (WHO).

Key Words: arsenic (III), adsorption, neem bark, aqueous solution

1. INTRODUCTION

Arsenic (As) is mostly found in the earth's core and in clay- and sulphide-rich portions of the earth's crust (Henken, 2009b). Being a metalloid in group 15 on the periodic table (along with antimony, bismuth, nitrogen and phosphorus), arsenic is well known for its chronic toxicity, particularly when exposure occurs over prolonged periods (Katherine et al., 2011). Arsenic exposure via drinking-water is related to lung, kidney, bladder and skin cancer. For example, drinking-water arsenic concentrations in excess of 50 $\mu\text{g/L}$ have been associated with increased risks of cancer in the bladder and lung, whilst drinking-water arsenic levels even below 50 $\mu\text{g/L}$ have been associated with precursors of skin cancer (IPCS, 2001). Therefore, the presence of arsenic in water supply poses a serious risk to human health. Surface and ground waters in many parts of the world have been found to naturally contain As concentrations that make these waters unsuitable for human use. Significant concentrations of As have been reported in various countries such as Bangladesh, Chile, USA, China, and India. In Bangladesh, for example, about 100 million people currently drink water with As concentrations up to 100 times the World Health Organisation (WHO) drinking water guideline, which is 10 $\mu\text{g/L}$ (Mohan and Pittman Jr., 2007).

To remove As from potential drinking water sources, a variety of conventional and non-conventional technologies have been studied, and these technologies have been reviewed by several authors (Mohan and Pittman Jr., 2007). However, it is known that conventional engineered treatment technologies are costly and create problems of sludge generation and

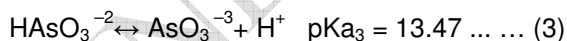
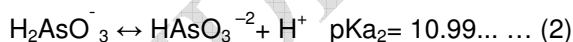
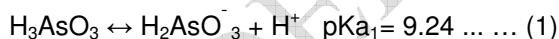
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disposal (Kosolapov et al., 2004; Cohen, 2006; Nelson et al., 2006). In addition, these systems often become sources of As-rich effluents and are typically located in remote isolated areas (such as mining sites), thus precluding the transportation of the effluents to large centralised treatment facilities. As such, to prevent As pollution of water courses, it is essential to find onsite, decentralised treatment systems that are robust and have low maintenance requirements and operating costs.

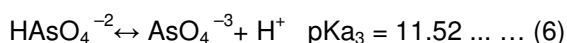
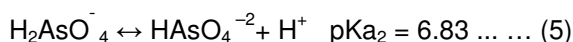
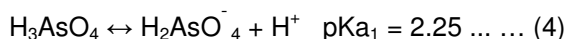
Many technologies, including coprecipitation with iron or alum, adsorption onto coagulated floc, ion-exchange resin, reverse osmosis, and membrane techniques, have been used to remove As from aqueous solution (Katsoyiannis et al., 2004; Kim and Benjamin, 2004; Jay et al., 2004; Hege et al., 2004; Balasubramanian and Madhavan, 2001). In these methods, however, the adsorption techniques are simple and convenient and have the potential for regeneration and sludge-free operation. So far, various adsorbents for arsenic removal have been developed that include such materials as metal-loaded coral limestone, (Maeda et al., 1992; Ohki et al., 1996) hematite and feldspar, (Singh et al., 1996) activated carbon, (Manjare et al., 2005; Huang and Fu, 1984) activated alumina, (Ghosh and Yuan, 1987; Hathaway and Rubel, 1987) and hydrous zirconium oxide (Suzuki et al., 1997). However, most of these adsorbents entail several problems in terms of efficiency and cost. The present work was performed to evaluate the use of neem bark without any pretreatment as an alternate adsorbent for removing arsenite from aqueous mediums. Moreover, the neem bark was applied to the removal of arsenic from Bangladeshi As-contaminated drinking water samples in a single-step column operation.

2. ARSENIC CHEMISTRY

Arsenic is a highly reactive metalloid that can be found in oxidation states -3, 0, +3 and +5. In natural waters, arsenic occurs as arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}), referred to as As (III) and As(V). As (III) mostly exists in reducing groundwaters and hydrothermal waters, whilst As(V) is more often present in surface waters and oxidising groundwaters (Henken and Hutchison, 2009). The main factors that control arsenic speciation are the oxidation state and pH. As(III) commonly hydrates to arsenious acid; therefore its chemistry depends strongly on pH. The predominant As (III) species is arsenious acid, H_3AsO_3 , due to the high value of $\text{pK}_{\text{a}1}$ (pK_{a} values reported by Wolthers et al. 2005) under the condition of 25 °C and 1 bar pressure). The reactions of the dissociation of arsenious acid and its respective anions are shown below, along with the associated pK_{a} values (where $\text{pK}_{\text{a}} = -\log(\text{K}_{\text{a}})$, and K_{a} = equilibrium constant of the reaction):



As (V) commonly hydrates to arsenic acid, and its chemistry also depends on pH. The most common species are H_2AsO_4^- and HAsO_4^{-2} , due to the low $\text{pK}_{\text{a}1}$ value (pK_{a} values reported by Wolthers et al., 2005). The reactions of dissociation of arsenic acid and its respective anions are shown below along with the associated pK_{a} values:



The toxicity of arsenic depends on its speciation; for example, arsenite is significantly more toxic than arsenate (APHA et al., 2005). It is typically more difficult to remove arsenite than arsenate from contaminated water; this is because in natural waters, under normal pH conditions (6)–(9), arsenite is mostly found as an uncharged species (H_3AsO_3), and negatively charged species (H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-}) are found only at high pH (>9). On the other hand, arsenate is commonly found as negatively charged species ($\text{H}_2\text{AsO}_4^{2-}$ and HAsO_4^{2-}); which are easier to remove than are uncharged species, because the charges of the As(V) oxyanions allow them to be removed by sorption, anion exchange or precipitation/coprecipitation (Henken and Hutchison, 2009).

3. MATERIALS AND METHODS

3.1 Reagent

All reagents used throughout this work were of analytical-grade purity. NaOH, KOH, KI, HCl, HNO_3 , and H_2SO_4 were obtained from E. Merck, Germany. Individual standard solution of As (III) was supplied by Varian Inc, USA with highest purity level (99.98%). Dilute standard solutions were prepared daily before use. Pure water was purified with an ultrapure water system (Barnsted E-Pure, USA) resulting in a resistivity of >18 MΩ cm.

3.2 Preparation of Adsorbent

The Neem bark used in the present work was obtained from Bangladesh. The chemical composition of Neembark has been reported as 3.43 wt % protein, 0.68 wt % Alkaloids, 4.16 wt % Mineral,. The collected materials were washed with pure water several times to remove dust and fines. The washing process was repeated until the color of the wash water was transparent. The washed materials were then dried in a hot-air oven at 60°C for 24 h. The dried material was sieved into the following five size fractions: 0.105mm, 0.25mm, 0.595mm, 1.41mm, and 2.3 mm. The materials were used for the removal of arsenic without further physical or chemical treatment.

3.3 Adsorption and Analytical Procedures

Neembark was added to the treatment glass columns (2 x 30 cm). The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column eluate flow rate (treatment rate). Adsorption factors including the amount of duckweed (1-5 g), average particle size (0.105-2.3mm), treatment flow rate (3.3-0.41 mL/min), initial sample concentration (50-500 µg/L), and pH (2.3-12) were evaluated. After the pH had been adjusted to the desired value with HCl and NaOH solutions, the sample solution (100 mL) was passed through the adsorption column at a given flow rate. The treatment flow rates of 0.41, 0.55, 0.83, 1.67 and 3.3, mL/min correspond to 5 g of neem bark. The packing density of the treatment column was 0.32 g/cm³. A small piece of tissue paper was inserted into the bottom of the column to prevent the loss of neem bark during the treatment. The flow rate was kept constant by controlling the stopper valve. The removal treatment was performed at ambient temperature. The number of experiments for the removal of As was greater than five. Analyses were performed by Varian Atomic Absorption Spectrometer (Model SpectraAA 240). The instrument is equipped with a Hydride generation system (Model VGA-77) and controlled with software Version 5.01. Samples were analyzed with HG-AAS using three-point calibration.

In the analysis time, acid container contains 5M HCl and reductant container contain 0.6 % Sodium borohydride (NaBH_4) in 0.5 % (w/v) sodium hydroxide.

The removal (adsorption) efficiency was calculated using the equation,

$$\text{Removal (adsorption) efficiency} = \frac{C_o - C_t}{C_o} \times 100$$

Where C_o and C_t are the concentration of As in the sample solution before and after treatment, respectively.

4. RESULTS AND DISCUSSION

First, the performances of eight adsorbents (Coconut shell, Neem bark, Orange peel, Nut shell, Flax, Saw dust, Wheat stalk, News paper) were evaluated for the removal of As (III) from aqueous solutions. The removal efficiencies with coconut shell, Neem bark, Orange peel, Nut shell, Flax, Saw dust, Wheat stalk and Newspaper were 18.79%, 19.23%, 3.8%, 14.26%, 12.89%, 14.2%, 12.3%, 32.3% respectively. Although the absorption capacity of news paper was highest, neem bark was taken as adsorbent because the main component of neem bark is carbon, neem bark has the potential to be used as an adsorbent. It was chosen for use as an adsorbent material because of its granular structure, insolubility in water, chemical stability, and high mechanical strength. Neem bark was selected as a suitable adsorbent. Of the adsorption neem bark gives the highest desorption and regeneration. Apart from this neem bark is widely available through the country.

4.1 Effect of Adsorbent Amount

The effect of the amount of neem bark on the removal of As (III) was investigated. The results are presented in Figure 1. The removal efficiencies of As (III) increased gradually with increasing amount of neem bark. It is readily understood that the adsorption capacity of neem bark depends on the surface activity, that is, the specific surface area available for As-surface interactions that is accessible to the As. Hence, increasing the amount of neem bark will increase removal capacity of As. Until now, various kinds of adsorbents have been studied for the removal of arsenic. The maximum As(III) removal efficiency achieved was 99% for iron oxide-coated sand at an adsorbent dose of 20 g/L with an initial As concentration 100 µg/L in batch studies (Gupta et al.,2005) The removal efficiencies for As(III) from an aqueous solution (100 µg/L, 100 mL) by 0.1 g of modified fungal biomass were 75%, respectively, after a 12-h batch treatment (Pokhrel and Viraraghavan,2006) When an aqueous As(III) solution of 10 mg/L concentration was stirred in the presence of both 1.0 g/L TiO_2 and 1.0 g/L activated alumina under sunlight irradiation, the arsenic removal increased with time and reached 89% after 24 h (Nakajima et al.,2005). Although the removal efficiencies in the proposed system were similar to those obtained with the other adsorbents, the treatment time was very short because of the flow method (column system).

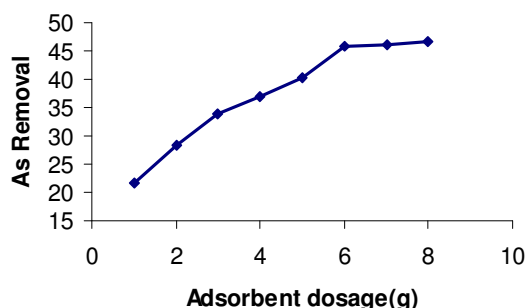


Figure1: Effect of adsorbent amount on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 µg/L. pH 2.36. Treatment flow rate 1.67mL/min)

4.2 Effect of Flow Rate

Flow rate is one of the effective factors in column adsorption process. The effect of the treatment flow rate on the removal of As (III) is illustrated in Figure 2. The removal efficiency for As (III) increased gradually with decreasing treatment flow rate. This is because, when the flow rate was slow, As (III) in the sample solution got more contact time with the active surface of the adsorbents.

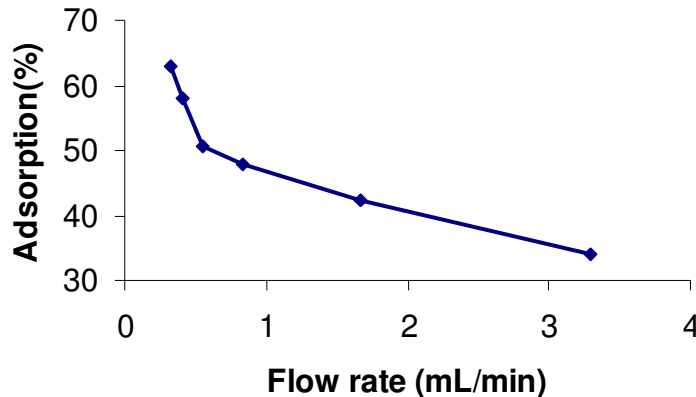


Figure 2: Effect of treatment flow rate on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 $\mu\text{g/L}$. pH 2.36. Amount of adsorbent 5g.)

4.3 Effect of Initial Concentration

The removal efficiency is highly dependent on the initial concentrations of As (III) in the sample solution. The effect of the initial sample concentration on the removal of arsenic with neem bark was investigated. The initial concentration was evaluated in the range of 50-500 $\mu\text{g/L}$, and the results are illustrated in Figure 3. The removal efficiency decreased with increasing adsorbate concentration in the solutions. It is because, at low concentration, most of As (III) in the sample solution gets contact with active sites. With increasing arsenic concentration in solution, active sites on the adsorbents were not increased. Therefore arsenic removal efficiencies were decreased.

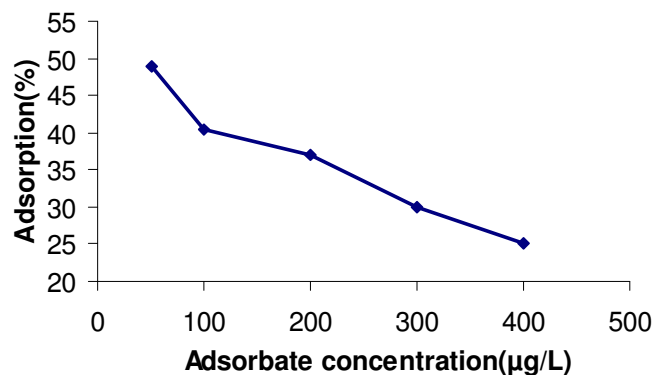


Figure 3: Effect of initial adsorbate concentration on the removal of As (III) by adsorption onto neem bark (pH 2.36. Amount of adsorbent 5g. Treatment flow rate 1.67mL/min)

4.4 Effect of pH

pH is one of the most important parameters controlling the metal ion sorption process (Munaf and Zein, 1997; Wong et al., 2003). Figure 4 depicts the effect of pH on As(III) removal with neem bark. For the removal of As (III), the efficiency curve was essentially nearly a plateau in the pH range of 4-7, and then, the efficiency tended to decrease with increasing pH. The poor As removal efficiencies at high pH can be attributed to the following factors: First, chemical species for As (III) in this pH region are oxyanions. Next, hydroxyl groups are more plentiful on the surface of neem bark with increasing pH. The maximum removal efficiency for As (III) was observed in comparatively neutral region (at pH 7). This result should be of great advantage for the practical implementation of arsenic removal from groundwater.

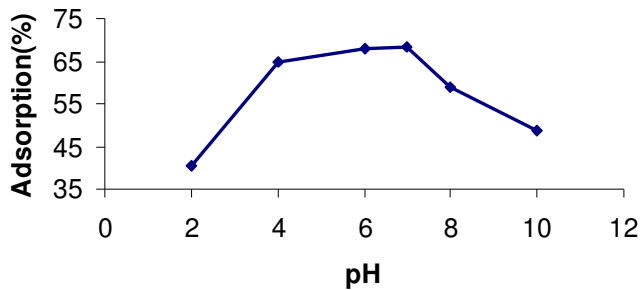


Figure 4: Effect of pH on the removal of As (III) by adsorption onto neem bark (initial As (III) concentration, 100 µg/L. Amount of adsorbent 5g. Treatment flow rate 1.67mL/min)

4.5 Effect of Particle Size

Column adsorption experiments were carried out for the removal of arsenic from aqueous solution using five different particle sizes (0.105mm, 0.25mm, 0.595 mm, 1.41mm, and 2.3 mm). The results are shown in Figure 5. With decreasing particle size, the removal increased from 68.23% to 96% for As (III). Munaf and Zein reported that, when the size of adsorbent particles increased, the adsorption of metal ions decreased (Munaf and Zein, 1997). Similar trends have been reported by Wong et al. (Wong et al., 2003). These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

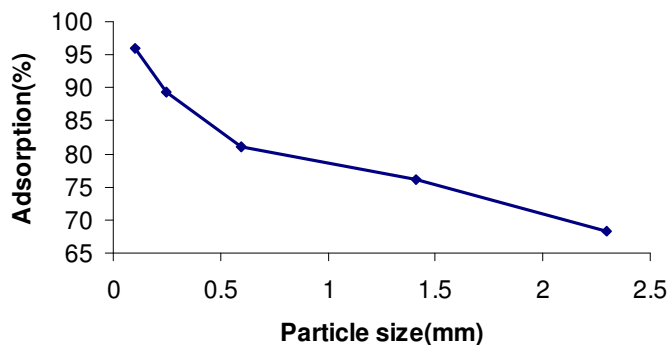
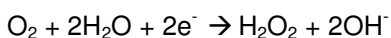


Figure 5: Effect of particle size on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 µg/L. pH 7. Amount of adsorbent 5g. Treatment flow rate 1.67mL/min)

5. ADSORPTION MECHANISM

Arsenic removal by adsorption onto neem bark can be supposed to occur mainly through two routes: (i) affinity adsorption and (ii) anion exchange between the arsenic in the water and the carbon surface of the neem bark. Affinity adsorption is related to the surface behavior of neem bark, whereas anion exchange relates to the existing forms of the arsenic species. OH groups are created on the carbon surface during the activation process (Corapcioglu and Huang, 1987; Manju et al., 1998). The mechanism of adsorption of metal anions onto activated carbon is generally well explained by electrochemical theory: Carbon in contact with water reduces oxygen to a hydroxyl group [44]



And thus, the carbon loses electrons and become positively charged. Electrical neutrality is maintained with hydroxyl ions, resulting in their adsorption. Although the neem bark used in the present work was not subjected to any chemical or physical activation treatment, a large number of OH groups will remain on the surface of the neem bark after the drying process. The physical adsorption and interaction between the H_3AsO_3 species and the neem bark surface might be partly responsible for the removal of As (III).

6. DESORPTION

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb As (III) from the neem bark surface with various eluents, such as hydrochloric, sulfuric, and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide.

This desorption process was performed using the column method. For each experiment, 100 mL of desorption solution was added to the column and held there for a fixed period of time. After the standing time, the solution was passed through the column. The results are presented in Table 1. Although the achievement of arsenic elution using strong acidic or alkaline solutions has been reported in the literature, (Lorenzen et al., 1995) the present work showed that effective desorption was obtained with acidic solutions. These phenomena are consistent with the results observed for the effect of pH. Consequently, hydrochloric acid solution was useful for the desorption of arsenic from the surface of neem bark.

Table1: Influence of the Eluent on the Desorption of As (III)

Desorption agent	Desorption (%)
NaOH (1M)	38.0
KOH(1M)	42
HCl(1M)	79
H ₂ SO ₄ (1M)	48.08
HNO ₃ (1M)	51.63

Adsorption process: initial As(III) concentration, 100 µg/L; neem bark 5g; average particle size, 0.595mm; treatment flow rate, 1.67mL/min. Volume of desorption agent, 100mL.

7. APPLICATION OF THE DEVELOPED TREATMENT SYSTEM

The utility of the neem bark was evaluated for the treatment of As contaminated Bangladeshi groundwater samples. The concentrations of total arsenic in the samples was 233.032 µg/L. It

has been reported that the total arsenic concentration in the tubewell water is in the range 0.25-1 mg/L, with 60-90% of the arsenic present as As (III) species (Khoe et al., 1997). Because the pH of these groundwater samples was around 7, the arsenic species might be H_3AsO_3 for As (III) (Meng et al., 2000; Ghimire et al., 2003; Wickramasinghe et al., 2004). The treatment results are presented in Table 2. Although 10 g of adsorbent was applied in the treatment, the concentration of arsenic in the treated sample water could be lowered to 60 µg/L. The desorption efficiencies with 100 mL of 1 M HCL was 89.63%. From the present results, the arsenic was successfully removed from practical As-contaminated groundwater, and the adsorbed As could be recovered from the surface of neem bark.

Table 2: Removal and Desorption of As from the Contaminated Groundwater of Bangladesh

	Sample
pH	7.5
initial As conc. (µg/L)	233.032
final As conc. (µg/L)	60
removal ^a (%)	74.25
desorption ^b (%)	89.63

^a Removal: neem bark 10g, treatment flow rate 1.67mL/min, average particle size 0.595mm

^b Desorption: 1M HCL, 100mL, flow rate 1.67mL/min.

8. CONCLUSIONS

The presence of arsenic in groundwater has been recognized as a major problem for Bangladesh. Due to its high toxicity, even in low concentrations, it is a threat to human health. There are many techniques, which can be effectively applied to remove arsenic from water streams. Moreover, some of the existing techniques are costly and they are not economically applicable in small community systems. Therefore, there is a need for developing cheap efficient methods for the removal of arsenic from drinking water. The proposed column treatment systems are appropriate and suitable home made approaches to arsenic removal in local areas, because of their simplicity and easy operation and handling. The present method is effective for a wide range of concentrations (i.e., 10-500 µg/L), which were quite similar to those observed in contaminated Bangladeshi groundwater. No secondary-pollution problem will occur, because desorption of the arsenic is possible. Direct removal of arsenic (III) can be achieved without first oxidizing arsenite to arsenate, whereas the traditional methods require the oxidation process. Based on the results of this research, neem bark can be considered as low cost, effective, available and natural adsorbent for removing arsenic from ground water.

REFERENCES

- APHA, AWWA, WEF, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, DC.
- Balasubramanian, N., Madhavan, K. (2001). Arsenic removal from industrial effluent through electrocoagulation. Chem. Eng. Technol, 24, 519.
- Cohen, R.R.H., 2006. Use of microbes for cost reduction of metal removal from metals and mining industry waste streams. J. Clean. Prod, 14, 1146–1157.

- Corapcioglu, M. O., Huang, C. P. (1987). The adsorption of heavy metals onto hydrous activated carbon. *Water Res*, 21, 1031.
- Ghimire, K. N., Inoue, K., Yamaguchi, H., Makino, K., Miyajima, T. (2003). Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. *Water Res*, 37, 4945.
- Ghosh, M. M., Yuan, J. R. (1987). Adsorption of inorganic arsenic and organoarsenicals on hydrous oxides. *Environ. Prog*, 6, 150.
- Gupta, V. K., Saini, V. K., Jain, N. (2005). Adsorption of As (III) from aqueous solutions by iron oxide-coated sand, *J. Colloid Interface Sci*, 55, 288.
- Hathaway, S. W., Rubel, F. J. (1987). Removing arsenic from drinking water. *J. Am. Water Works Assoc*, 79, 61.
- Hege, K. V., Verhaege, M., Verstraete, W. (2004). Electro-oxidative abatement of low-salinity reverse osmosis membrane concentrates. *Water Res*, 38, 1550.
- Henken, K.R., Hutchison, A. (2009). Arsenic chemistry. In: Henken, K.R. (Ed.), *Arsenic Environmental Chemistry, Health Threats and Waste Treatment*. John Wiley & Sons Ltd., Chichester, 9–68.
- Henken, K.R., 2009b. Introduction. In: Henken, K.R. (Ed.), *Arsenic Environmental Chemistry, Health Threats and Waste Treatment*. John Wiley & Sons Ltd. Chichester, 1–7.
- Huang, C. P., Fu, P. L. K. (1984). Treatment of arsenic(V)-containing water by the activated carbon process. *J. Water Pollut. Control Fed*, 56, 233.
- IPCS, (2001). *Arsenic and Arsenic Compounds*. World Health Organisation, International Programme on Chemical Safety (Environmental Health Criteria224), Geneva.
- Jay, J. A., Blute, N. K., Hemond, H. F., Durant, J. L. (2004). Arsenic sulfides confound anion exchange resin speciation of aqueous arsenic. *Water Res*, 38, 1155.
- Katherine, L. A., Tim, D. F., Guangzhi S., (2011). Removal processes for arsenic in constructed wetlands. *Chemosphere*, 84, 1032–1043.
- Katsoyiannis, I. A., Zouboulis, A. I. (2004). Application of biological processes for the removal of arsenic from groundwaters, *Water Res*, 38, 17.
- Khoe, G. H., Emmett, M. T., Robins, R. G. (1997). Photoassisted Oxidation of Species in Solution; U.S. Patent 5, 688, 378.
- Kim, J., Benjamin, M. M. (2004). Modeling a novel ion exchange process for arsenic and nitrate removal. *Water Res*, 38, 2053.
- Kosolapov, D.B., Kuschik, P., Vainshtein, M.B., Vatsourina, A.V., Wießner, A., Kästner, M., Müller, R.A., 2004. Microbial processes of heavy metal removal from carbon deficient effluents in constructed wetlands. *Eng. Life Sci.* 4, 403–411.
- Lorenzen, L., Deventer, J. S. J. V., Landi, W. M. (1995). Factors affecting the mechanism of the adsorption of arsenic species on activated carbon. *Miner. Eng*, 8, 557.

- Maeda, S., Ohki, A., Saikoji, S., Naka, K. (1992). Iron(III) hydroxide loaded coral limestone as an adsorbent for arsenic(III) and arsenic(V). *Sep. Sci. Technol*, 27, 681.
- Manjare, S. D., Sadique, M. H., Ghoshal, A. K. (2005). Equilibrium and kinetics studies for As(III) adsorption on activated alumina and activated carbon. *Environ. Technol*, 26, 1403.
- Manju, G. N., Raji, C., Anirudhan, T. S. (1998). Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res.* 32, 3062.
- Meng, X., Bang, S., Korfiatis, G. P. (2000). Effect of silicate, sulfate and carbonate on arsenic removal by ferric chloride. *Water Res.* 34, 1255.
- Mohan, D., Pittman Jr., C.U. (2007). Arsenic removal from water/wastewater using adsorbents – a critical review. *J. Hazard. Mater*, 142, 1–53.
- Munaf, E., Zein, R. (1997). The use of rice husk for removal of toxic metals from wastewater. *Environ. Technol*, 18, 359.
- Nakajima, T., Xu, Y. H., Mori, Y., Kishita, M., Takanashi, H., Maeda, S., Ohki, A. (2005). Combined use of photocatalyst and adsorbent for the removal of inorganic arsenic(III) and organoarsenic compounds from aqueous media. *J. Hazard. Mater*, 120, 75.
- Nelson, E.A., Specht, W.L., Knox, A.S., 2006. Metal removal from water discharges by a constructed treatment wetland. *Eng. Life Sci.* 6, 26–30.
- Ohki, A., Nakayachigo, K., Naka, K., Maeda, S. (1996). Adsorption of inorganic and organic arsenic compounds by aluminium-loaded coral limestone. *Appl. Organomet. Chem*, 10, 747.
- Pokhrel, D., Viraraghavan, T. (2006). Arsenic removal from an aqueous solution by a modified fungal biomass, *Water Res.* 40, 549.
- Singh, D. B., Prasad, G., Rupainwar, D. C. (1996). Adsorption technique for the treatment of As(V)-rich effluents, *Colloids Surf. A: Physicochem. Eng. Aspects*, 111, 49.
- Suzuki, T. M., Bomani, J. O., Matsunaga, H., Yokoyama, T. (1997). Removal of As(III) and As(V) by a porous spherical resin loaded with monoclinic hydrous zirconium oxide, *Chem. Lett.* 11, 1119.
- Wickramasinghe, S. R., Han, B., Zimbron, J., Shen, Z., Karim, M. N. (2004). Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination*, 169, 231.
- Wolthers, M., Charlet, L., van Der Weijden, C.H., van der Linde, P.R., Rickard, D., (2005). Arsenic mobility in the ambient sulfidic environment: sorption of arsenic(V) and arsenic(III) onto disordered mackinawite. *Geochim. Cosmochim. Acta*, 69, 3483–3492.
- Wong, K. K., Lee, C. K., Low, K. S., Haron, M. J. (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemosphere*, 50, 23.