Removal of fluoride and arsenic by pilot vertical-flow constructed wetlands using soil and coal cinder as substrate

Juan Li, Xinchun Liu, Zhisheng Yu, Xin Yi, Yiwen Ju, Jing Huang and Ruyin Liu

ABSTRACT

This study evaluated the performance of soil and coal cinder used as substrate in vertical-flow constructed wetlands for removal of fluoride and arsenic. Two duplicate pilot-scale artificial wetlands were set up, planted respectively with cannas, calamus and no plant as blank, fed with a synthetic sewage solution. Laboratory (batch) incubation experiments were also carried out separately to ascertain the fluoride and arsenic adsorption capacity of the two materials (i.e. soil and coal cinder). The results showed that both soil and coal cinder had quite high fluoride and arsenic adsorption capacity. The wetlands were operated for two months. The concentrations of fluoride and arsenic in the effluent of the blank wetlands were obviously higher than in the other wetlands planted with cannas and calamus. Fluoride and arsenic accumulation in the wetlands body at the end of the operation period was in range of 14.07–37.24% and 32.43–90.04%, respectively, as compared with the unused media.

Key words | arsenic, coal cinder, constructed wetlands, fluoride, soil

Juan Li
Xinchun Liu (corresponding author)
Zhisheng Yu
Xin Yi
Jing Huang
Ruyin Liu
College of Resources and Environment,
University of Chinese Academy of Sciences,
Beijing 100049,
China
E-mail: *xcliu@ucas.ac.cn*

Yiwen Ju
College of Earth Science,
University of Chinese Academy of Sciences,
Beijing 100049,
China

INTRODUCTION

Fluoride is a natural element that is considered a beneficial nutrient at an optimal level and is important to the integrity of bone and teeth (Palmer *et al.* 2012). However, due to its strong electronegativity, fluoride is attracted by positively charged calcium ions in teeth and bones. Excessive intake may result in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis followed by skeletal fluorosis (Hussain *et al.* 2012). As Seraj *et al.* (2012) report, high water fluoride concentration has great influence on the intellectual development of children. Arsenic and arsenic compounds are listed by the International Agency for Research on Cancer as an evident human carcinogen. High concentrations of arsenic in drinking water may result in skin cancer, bladder cancer, lung cancer and so on (Guo & Tseng 2000). Fluoride and arsenic are classified as contaminants of water for human consumption by the World Health Organization (2006), in addition to nitrate, which causes large-scale health problems. Over the past decade, the contamination of groundwater by fluoride and arsenic has recently increased. Significant increase in the concentration levels of arsenic and fluoride in surface water has been reported (Kumar *et al.* 2011). This will be a serious threat to human health. Therefore, study on the removal of fluoride and arsenic is extremely urgent.

During the last decade, vertical-flow constructed wetlands have become a common treatment selection of urban wastewaters. They are attractive in specific cases, due to the relatively small surface requirement and their high purification efficiency compared with other natural systems. However, most application cases of wetlands have mainly focused on the removal of organic matter (Vymazal 2007) and phosphorus (Prochaska & Zouboulis 2006). There are few studies on the removal of fluoride and arsenic.

The present study examines the use of soil and coal cinder as a potential constructed wetland substrate to remove fluoride and arsenic from aqueous solution. The objectives of this study were (1) to evaluate the maximum adsorption capacity of soil and coal cinder and (2) to compare the fluoride and arsenic removal performance of six pilot-scale vertical-flow constructed wetland systems. The

doi: 10.2166/wst.2014.273

six systems were respectively planted with cannas, calamus and no plant as blank, all in duplicate. The present results concern 2 months of operation, which followed the construction and the establishment of the wetlands.

MATERIALS AND METHODS

Vertical-flow constructed wetland construction and operation

Six glass vessels, each with a surface of 0.12 m^2 and 60 cm in height, were filled with four successive layers of the following materials: an upper layer (10 cm, soil), followed by the second layer (10 cm, 0–3 mm soil: 0–3 mm coal cinder at a ratio 3.5: 1, w/w), the third layer (10 cm, 3–15 mm coal cinder) and a lower drainage layer (10 cm, 20–30 mm pebbles). For the collection of the treated effluents, a drainage pipe was placed at the bottom of each vessel. This pipe had an internal diameter of 5 cm and 15 cm length (Figure 1).

The wetlands were located in the balcony of the main building on the campus of the University of Chinese Academy of Science. The six wetlands were planted in autumn, two of them planted with cannas (A), two of them with calamus (B), and the remaining two with no plants (C) as blank. All wetlands were kept flooded for a week with tap water and a week with synthetic sewage, and then synthetic sewage was applied to each wetland for the experiment. The plants in four wetlands reached 30–40 cm in height and a density of four to six stems per wetland when we began the operation.

Synthetic sewage solution was used as the influent for the wetlands for health and safety reasons and in order to minimize variability of composition during the experiments. The synthetic wastewater contained approximately 10 mg/L fluorine and 1 mg/L arsenic. The required chemicals were mixed with a mechanical mixer in a 100-L polyethylene container, using tap water. The residual chlorine content of tap water was controlled and eliminated by setting the tap water in the open polyethylene container for approximately 48 h.

The batch applied wastewater volume was kept constant at 15 L, while the application times were kept at 72 h. The synthetic sewage was applied onto the wetlands surface in a batch mode; the entire volume was applied within less than 10 min. The wastewater was allowed to drain by gravity and sampled for fluorine and arsenic analytical determination through the respective drainage pipe when it achieved the application time.

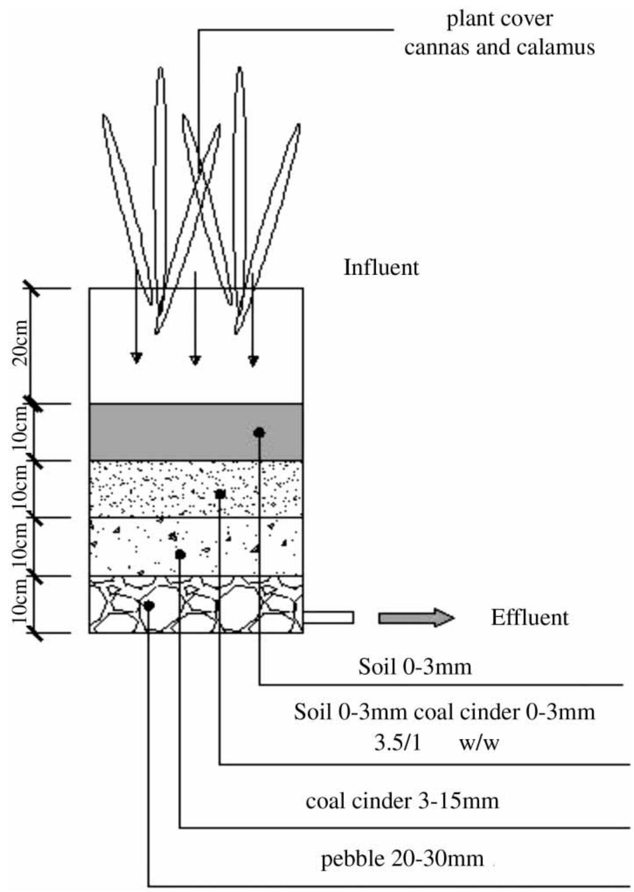

Figure 1 | Schematic diagram of semi-pilot scale vertical-flow constructed wetland.

Vertical-flow constructed wetland substrate materials

The specific materials selected for substrates were soil from the campus of the University of Chinese Academy of Science and coal cinder from a restaurant (near the University of Chinese Academy of Science); after grinding, it can be divided into two parts, with diameter 0–3 mm and 3–12 mm. The soil and coal cinder were provided free of charge. For the construction of the vertical-flow constructed wetlands, pebbles were used.

The elemental composition of coal cinder was determined by X-ray fluorescence spectroscopy (XRF). The pH of the materials was determined with a pH meter (METROHM 632) after mixing 2 g of material with 20 mL of 0.01 M $CaCl_2$ (Drizo *et al.* 1999). Table 1 presents the main chemical composition of coal cinder. Table 2 presents the main physical-chemical properties of substrate soil used in the experiment.

Table 1 | The main chemical composition of coal cinder XRF analysis (%, w/w)

C	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	TiO_2	SO_3	MgO
5.24	50.50	25.46	5.7	4.42	2.79	1.82	1.10	1.08	0.99

Table 2 | The main physical-chemical properties of substrate soil

Available phosphorus (mg/kg)	Total phosphorus (g/kg)	Effective nitrogen (mg/kg)	Organic matter(g/kg)	pH
15.6	0.49	134.77	9.31	8.92

The measurement of fluoride and arsenic

Fluoride was measured in the filtrate using fluorine ion selective electrode method (Gao *et al.* 1984). Arsenic was measured in the filtrate using ICP-MS (inductively coupled plasma mass spectrometry) (Zheng *et al.* 2003).

Fluoride and arsenic adsorption capacity experiments

These experiments were conducted for the coal cinder and soil, using batch incubation technique. Each medium was ground to less than 0.15 mm and equilibrated for 24 h with 100 ml solution, containing different concentrations of fluoride and arsenic, with continuous shaking in a reciprocal shaker at 160 rpm, at 25 ± 2 °C. The equilibrated samples were centrifuged at 3500 rpm for 10 min and filtered through a 0.45 μm membrane filter. Fluoride and arsenic were measured in the filtrate. The fluoride and arsenic content which was not recovered in the solution was considered as the amount adsorbed by the media. The obtained data were expressed as fluoride (F^-) and arsenic (As) adsorbed per unit weight of materials under equilibrium conditions.

Fluoride and arsenic accumulation experiments in wetlands substrate

Fluoride and arsenic accumulation in wetlands substrate was assessed. This analysis was performed on samples received from the two replicate wetlands. Unless otherwise stated, all experiments were conducted in triplicate and the mean values were reported.

RESULTS AND DISCUSSION

Maximum arsenic and fluoride adsorption capacity

To understand the involved processes of arsenic, the main adsorption equations (i.e. Langmuir and Freundlich equations) were applied. The concentration of As in the equilibrium solution was related to adsorption quantity of As, as shown in Figure 2. The data of As obtained in this

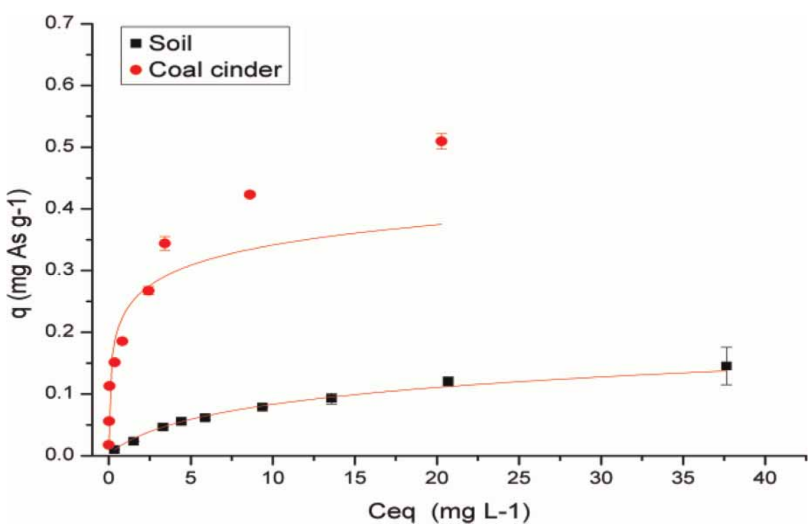

Figure 2 | Relation between equilibrium solution As and adsorbed As for soil and coal cinder.

study were found to fit both Langmuir and Freundlich equations, while the coal cinder fit is only good up to an equilibrium concentration of around 3 mg/L. The regression values for these equations and the respective constants were different for the two materials, indicating variations in the As adsorption characteristics, with coal cinder presenting higher adsorption capacity (Table 3). According to the coefficients of the Langmuir isotherm, the maximum adsorption capacity of the soil was 0.18 mg As/g and of coal cinder 0.52 mg As/g.

The relationship between concentration of F^- in the equilibrium solution and the adsorption of F^- is shown in Figure 3. The data of F^- for soil obtained were found to fit both Langmuir and Freundlich equations, while the data of F^- for coal cinder were found to fit the Langmuir equation better than the Freundlich equation when the concentration of F^- was more than 100 mg/L. The regression values for these equations and the respective constants were also different for the two materials, indicating variations in the F^- adsorption characteristics, with coal cinder presenting higher adsorption capacity (Table 4). According to the coefficients of the Langmuir isotherm, the maximum adsorption capacity of the soil was 0.78 mg F^-/g and of coal cinder was 7.25 mg F^-/g. The maximum adsorption capacity of the coal cinder was found to agree with the respective maximum adsorption capacity values of three coal-based sorbents (6.9–7.44 mg/g) (Sivasamy *et al.* 2001).

The above estimations compare favorably with estimations quoted in the literature for other wetland substrates.

Activated alumina has been an absorbent of interest for years among researchers for fluoride and arsenic removal. As tested by Ku & Chiou (2002), activated alumina had a fluoride adsorbing capacity of 16.3 mg/g. Saturation adsorption capacity of As(III) in activated alumina was 0.0041 g of As (III)/g (Manjare *et al.* 2005). But the adsorption of fluoride and arsenic by activated alumina was quite influenced by pH (Pietrelli 2005). Its application was limited to a great extent. Some other materials had also been examined and had an extremely high fluoride and arsenic adsorbing capacity, such as some industrial by-products (Kanel *et al.* 2006; Nigussie *et al.* 2007), agricultural wastes (Amin *et al.* 2006; Parmar *et al.* 2006) and other metal oxides (Kim *et al.* 2003; Streat *et al.* 2008) and so on. However, the adsorption capacities of these materials were

Table 3 | Langmuir and Freundlich adsorption constants and correlation coefficients for arsenic

Material	Soil	Coal cinder
Langmuir		
q_0(mg g^{-1})	0.18	0.52
K_L(L mg^{-1})	0.10	0.98
R^2	0.97	0.98
Freundlich		
K_L	0.02	0.20
1/n	0.59	0.37
R^2	0.99	0.93

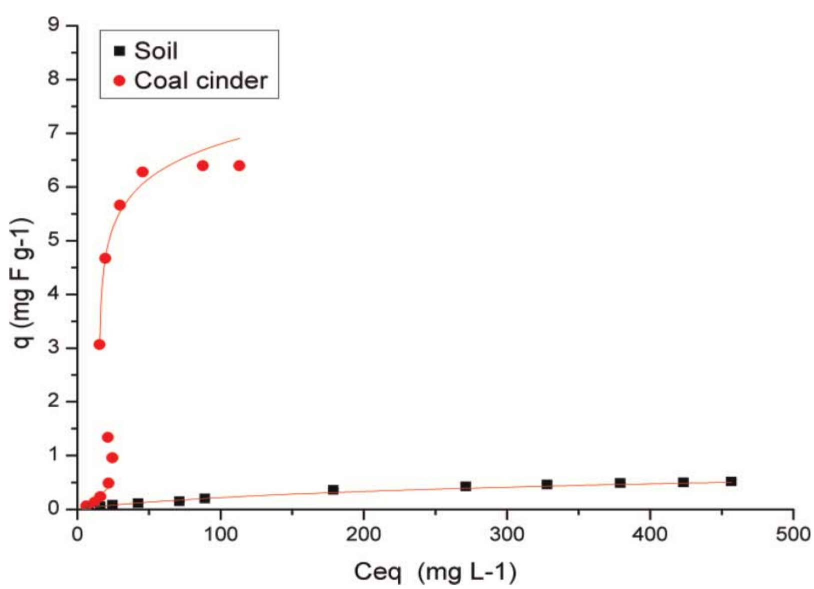

Figure 3 | Relation between equilibrium solution F^- and adsorbed F^- for soil and coal cinder.

Table 4 | Langmuir and Freundlich adsorption constants and correlation coefficients for fluoride

Material	Soil	Coal cinder
Langmuir		
q_0 (mg g^{-1})	0.78	7.25
K_L (L mg^{-1})	0.004	0.08
R^2	0.97	0.98
Freundlich		
K_L (L mg^{-1})	0.01	0.91
1/n	0.69	2.28
R^2	0.99	0.68

rather limited and influenced by pH (Mohan & Pittman 2007).

Fluoride and arsenic removal efficiency

The six wetlands were operated in autumn. The air temperature was in the range of 10–33°C during the operation, which is not unusual for the season in China. The temperature favors the soil microorganisms' growth. The pH values in effluent of wetlands ranged between 7.50 and 8.28. Figures 4(a) and 4(b), respectively, present the concentrations of fluoride and arsenic in the effluent of the wetlands planted with cannas (A), calamus (B) and the blank (C). The concentrations of fluoride and arsenic in the effluent of the wetlands followed the order: $C + A > B$. The wetlands C were capable to remove 31.22% of initially applied fluoride and 88.60% of initially applied arsenic at the end of the operation period. The corresponding data for wetlands A were 50.94 and 95.34%, and those of wetlands B were 59.09 and 96.40%.

Because plants can absorb fluoride and arsenic, and the roots of the plants can adjust the conditions of wetlands substrate, which may regulate biological activities (Lavelle 2002), the wetlands A and B can remove fluoride and arsenic better than wetlands C. The wetlands A and B can operate for a longer time than wetlands C before saturation.

Fluoride and arsenic accumulation in wetlands body

Fluoride and arsenic accumulation in wetlands substrate were assessed by comparison to corresponding values of unused materials (i.e. soil and coal cinder unused in the wetlands). The results are presented in Figure 5.

An increase of F accumulation in the range of 14.07–37.24% and As in the range of 32.43–90.04% was found, as compared with the unused media. The accumulation of fluoride in the wetlands was the second layer > the first layer > the third layer, while the accumulation of arsenic was the first layer > the second layer > the third layer, as is shown in Figure 5. This indicated that the substrate in different layers had different adsorption capability for fluoride and arsenic. The accumulation of fluoride and arsenic was found higher in wetlands A and B than the corresponding layers of wetlands C. This indicated that the growth of plants was beneficial to the substrates' adsorption, which had been reported in the literature (Tanner 2001; Weis & Weis 2004). And, since calamus had a better-developed root system than cannas, the accumulation of fluoride and

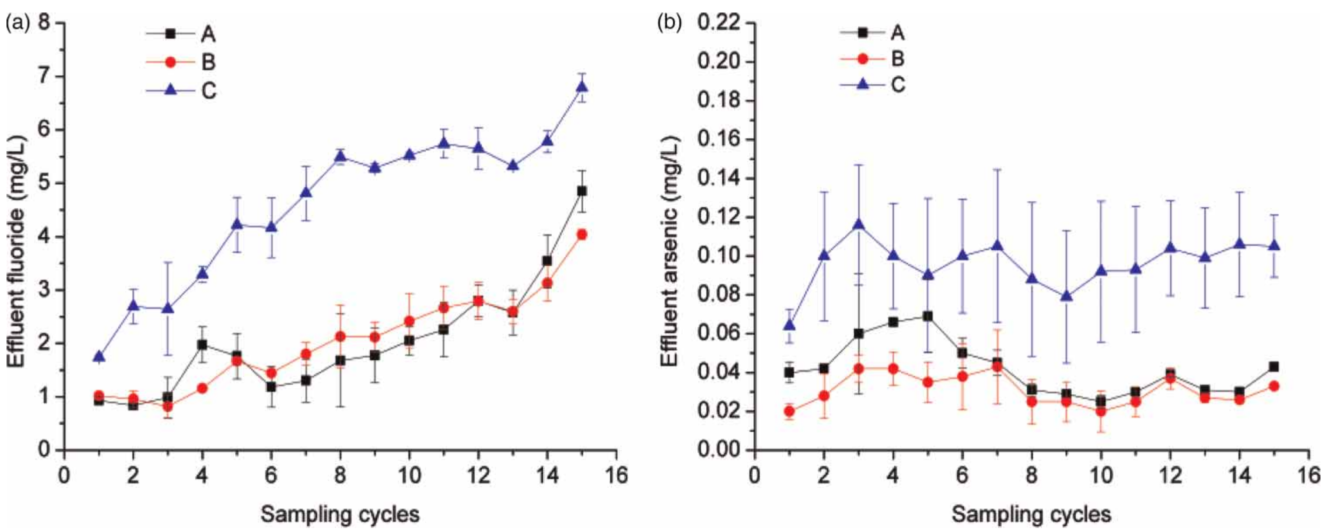

Figure 4 | Outlet concentrations of fluoride and arsenic.

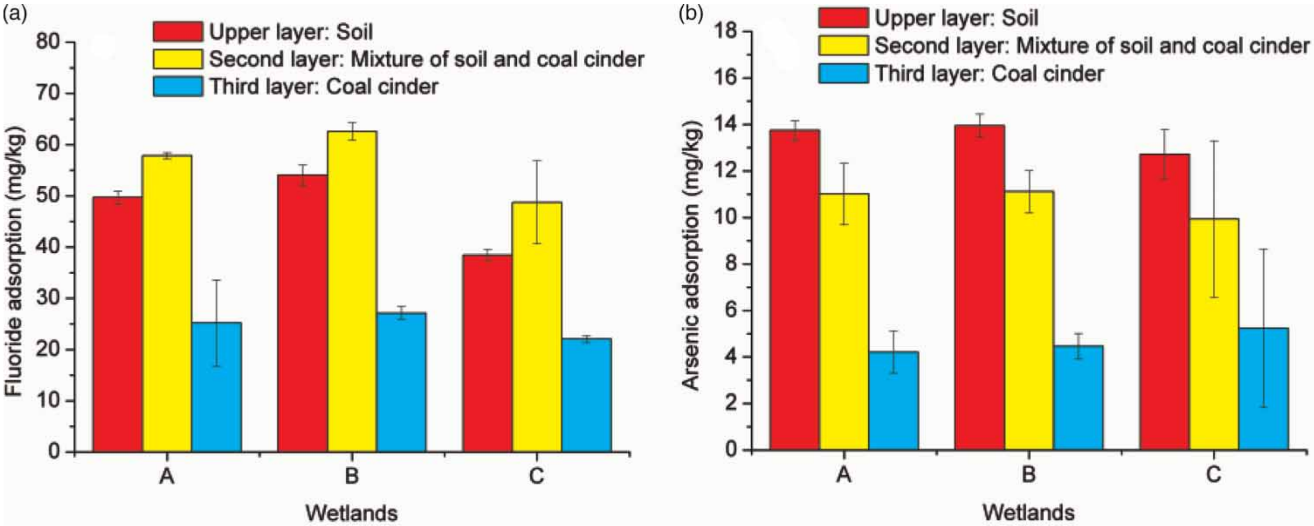

Figure 5 | Fluoride and arsenic adsorption of wetland substrates.

arsenic were found higher in wetlands B than A. Besides the retained F^- and As in the wetlands substrate, the remaining fluoride and arsenic may be absorbed by the plants or micro-organism or flushed as outflow.

CONCLUSIONS

In the present study soil and coal cinder were used as substrate of vertical-flow constructed wetlands. The results of laboratory (batch) incubation experiments showed that the maximum arsenic adsorption capacity of the soil was 0.18 mg As/g and of coal cinder 0.52 mg As/g. The maximum fluoride adsorption capacity of the soil was 0.78 mg F^-/g and of coal cinders 7.25 mg F^-/g.

The wetlands planted with cannas and calamus could obtain better removal efficiency for fluoride and arsenic than the blank wetlands. The accumulation analysis performed on substrate samples showed that the substrate in different layers had different adsorption capability for fluoride and arsenic. And the growth of plants was beneficial to the substrates' adsorption.

Although the results presented in this study cannot be directly applied to the potential performance of examined soil and coal cinder in a full-scale wetland, due to certain difficulties and problems specific to the relatively short-term operation period and the use of synthetic instead of real wastewater, this study may provide an indication that the use of coal cinder should be the subject of further investigation in larger-scale projects.

ACKNOWLEDGEMENT

This work was supported by National Science and Technology Major Projects (2011ZX05060–005).

REFERENCES

Amin, M. N., Kaneco, S., Kitagawa, T., Begum, A., Katsumata, H., Suzuki, T. & Ohta, K. 2006 Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. *Industrial & Engineering Chemistry Research* **45** (24), 8105–8110.

Drizo, A., Frost, C., Grace, J. & Smith, K. 1999 Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research* **33** (17), 3595–3602.

Gao, G., Yan, B. & Yang, L. 1984 Determination of total fluorine in coal by the combustion-hydrolysis/fluoride-ion selective electrode method. *Fuel* **63** (11), 1552–1555.

Guo, H.-R. & Tseng, Y.-C. 2000 Arsenic in drinking water and bladder cancer: comparison between studies based on cancer registry and death certificates. *Environmental Geochemistry and Health* **22** (2), 83–91.

Hussain, I., Arif, M. & Hussain, J. 2012 Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India. *Environmental Monitoring and Assessment* **184** (8), 5151–5158.

Kanel, S. R., Choi, H., Kim, J.-Y., Vigneswaran, S. & Shim, W. G. 2006 Removal of arsenic(III) from groundwater using low-cost industrial by-products–blast furnace slag. *Water Quality Research Journal of Canada* **41** (2), 130–139.

Kim, J.-Y., Davis, A. P. & Kim, K.-W. 2003 Stabilization of available arsenic in highly contaminated mine tailings using iron. *Environmental Science & Technology* **37** (1), 189–195.

Ku, Y. & Chiou, H.-M. 2002 The adsorption of fluoride ion from aqueous solution by activated alumina. *Water, Air, and Soil Pollution* **133** (1–4), 349–361.

Kumar, V., Talreja, N., Deva, D., Sankararamakrishnan, N., Sharma, A. & Verma, N. 2011 Development of bi-metal doped micro – and nano multi-functional polymeric adsorbents for the removal of fluoride and arsenic(V) from wastewater. *Desalination* **282**, 27–38.

Lavelle, P. 2002 Functional domains in soils. *Ecological Research* **17** (4), 441–450.

Manjare, S. D., Sadique, M. H. & Ghoshal, A. K. 2005 Equilibrium and kinetics studies for As(III) adsorption on activated alumina and activated carbon. *Environmental Technology* **26** (12), 1403–1410.

Mohan, D. & Pittman Jr., C. U. 2007 Arsenic removal from water/wastewater using adsorbents – A critical review. *Journal of Hazardous Materials* **142** (1–2), 1–53.

Nigussie, W., Zewge, F. & Chandravanshi, B. S. 2007 Removal of excess fluoride from water using waste residue from alum manufacturing process. *Journal of Hazardous Materials* **147** (3), 954–963.

Palmer, C. A., Gilbert, J. A. & Academy of Nutrition and Dietetics 2012 Position of the Academy of Nutrition and Dietetics: the impact of fluoride on health. *Journal of the Academy of Nutrition and Dietetics* **112** (9), 1443–1453.

Parmar, H. S., Patel, J. B., Sudhakar, P. & Koshy, V. 2006 Removal of fluoride from water with powdered corn cobs. *Journal of Environmental Science & Engineering* **48** (2), 135–138.

Pietrelli, L. 2005 Fluoride wastewater treatment by adsorption onto metallurgical grade alumina. *Annali Di Chimica* **95** (5), 303–312.

Prochaska, C. A. & Zouboulis, A. I. 2006 Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecological Engineering* **26** (3), 293–303.

Seraj, B., Shahrabi, M., Shadfar, M., Ahmadi, R., Fallahzadeh, M., Eslamlu, H. F. & Kharazifard, M. 2012 Effect of high water fluoride concentration on the intellectual development of children in Makoo/Iran. *Journal of Dentistry (Tehran, Iran)* **9** (3), 221.

Sivasamy, A., Singh, K. P., Mohan, D. & Maruthamuthu, M. 2001 Studies on defluoridation of water by coal-based sorbents. *Journal of Chemical Technology and Biotechnology* **76** (7), 717–722.

Streat, M., Hellgardt, K. & Newton, N. L. R. 2008 Hydrous ferric oxide as an adsorbent in water treatment. *Process Safety and Environmental Protection* **86** (1), 21–30.

Tanner, C. 2001 Plants as ecosystem engineers in subsurface-flow treatment wetlands. *Water Science and Technology* **44** (11–12), 9–17.

Vymazal, J. 2007 Removal of nutrients in various types of constructed wetlands. *The Science of the Total Environment* **380** (1–3), 48–65.

Weis, J. S. & Weis, P. 2004 Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environment International* **30** (5), 685–700.

World Health Organization 2006 Guidelines for drinking-water quality [electronic resource]: incorporating first addendum. Recommendations, Vol. 1, WHO, Geneva.

Zheng, J., Hintelmann, H., Dimock, B. & Dzurko, M. S. 2003 Speciation of arsenic in water, sediment, and plants of the Moira watershed, Canada, using HPLC coupled to high resolution ICP-MS. *Analytical and Bioanalytical Chemistry* **377** (1), 14–24.

First received 26 February 2014; accepted in revised form 29 May 2014. Available online 14 June 2014