The Journal of Animal & Plant Sciences, 22(3): 2012, Page: 659-664
ISSN: 1018-7081

BIOSORPTION, SOLUTION TO AS (V) POLLUTION

S. Akhtar and A. Shoaib

Institute of Agricultural Sciences, University of the Punjab, Pakistan
Corresponding author: aamnaa29@yahoo.com

ABSTRACT

The study was focused on exploring role of six agricultural wastes viz., wheat (*Triticum aestivum* L.) and rice (*Oryza sativa* L.) husk, pea (*Pisum sativum* L.), peanut (*Arachis hypogaea* L.), and banana (*Musa acuminata* L.) peels and sohanjana (*Moringa oleifera* Lam.) leaves for adsorption of As (V) from aqueous solution. Batch experiments were performed by taking 0.1 g of oven dried biomass of biosorbent in 250 mL flask containing 100 mL of 1 mg L^{-1} of As(V) solution at 150 rpm for 1 hour. The experiment was laid out as a completely randomized design with three replicates. Results indicates that all six adsorbents hold significantly greater adsorption capacity (0.99 mg g^{-1}) and efficiency (99%) for capturing As(V) from the aqueous solution. Fourier Transformed Infrared Spectroscopy (FTIR) study revealed the involvement of carbohydrates and proteins groups like hydroxyl, amine, amide and carbonyl in metal sequestration. Adsorption based experiments summarized that agricultural wastes are potential easily available low-cost biomaterial for adsorption of As(V)ions from the aqueous phase.

Keyword: Metal, Arsenate, Adsorption, Agricultural waste.

INTRODUCTION

The name arsenic (As) is derived from the Greek word *arsenikon*, means yellow orpiment. This element is notorious as king of all poisons and in Pakistan it is recognized as Sinkhia. The most important inorganic species are arsenate (As V) and arsenite (As III). The inorganic arsenic caused death at fatal dose of 125 mg, therefore has been placed in Group 1 of humans carcinogen (IARC, 1987). The deadly poison has created an alarming and catastrophic crises world over due to drinking of toxic water and intake of contaminated crop. In this regard, serious health hazards have been recorded in Pakistan (Naseem, 2010), Bangladesh (Al Rmalli *et al*., 2005), USA (LinFu, 1980), India (West Bengal), Chile and Japan (Mandal and Suzuky, 2002; Roychowdhury *et al*., 2002). National Standard for maximum acceptable concentration (NEQS, 2000) of arsenic in drinking water is 0.05 mg As L^{-1}, that value is identical in several countries including India and Bangladesh based on an earlier WHO (1971) advice. Recommended guideline value of 0.01 mg As L^{-1} in drinking water now has been reduced to 0.005 mg As L^{-1} (WHO, 2001).

Remediation of arsenic contaminated water has thus become a major environmental issue. Several approaches for metal-treatment wastewater have been described including chemical and surface chemistry processes. Sensitive operating conditions, low efficiency, and production of secondary sludge demanding additional expensive disposal are inherent limitations in the application of these methods (Ahluwalia and Goyal, 2005; Kundu and Gupta, 2006; Thomas *et al*., 2007). These shortcomings, together with the need for more economical and efficient technique for removal of metal from wastewater, have focused interest towards other techniques. One such option is biosorption that is based binding ability of certain types of biomass with metals even from very dilute aqueous solution (Volesky, 2007). The adsorption technique can operate over wide range of pH and temperature exhibiting high efficiency, economic feasibility along with less chemical and biological sludge, therefore find niche in potential metal treatment technologies (Kratchovil and Volesky, 1998).

Extensive literature indicated that agricultural wastes either in natural form or modified form are highly efficient for the removal of arsenic ions from aqueous solution. Lignin and cellulose in agricultural material contained aldehydes, ketones, carboxylic, alcohols, ether and phenolic groups, which assist in binding with heavy metal ions (Pagnanelli *et al*., 2003; Ofomajaa and Ho, 2007; Demirbas, 2008). In this connection, most commonly used adsorbents for arsenic were *Moringa oleifera* (Kumari *et al*., 2005), rice husk (Amin *et al*., 2006), orange peels (Biplob, 2006), banana peels (Memon *et al*., 2008), jute stick (Israt *et al*., 2008) and rice polish (Ranjana *et al*., 2008) etc. Moreover, disposal issues associated with agricultural waste will also resolve to some extent. So far, easy availability, cheap and environmental friendly options inclined to select such agricultural waste as a metal scavengers.

Present study was designed to investigate the As(V) removal capacity of various agricultural wastes from aqueous solution. The adsorbent molecular groups-arsenic interactions was investigated on the basis of IR spectrum of native and exhausted (after metal sorption) biomass.

MATERIALS AND METHODS

Biosorbents: Wheat and rice husk, banana, pea and peanut peels, and sohanjana leaves were chosen as adsorbent material. After washing with tap water, these were dried in oven at 100°C for 24 hours and homogenized in a blender to utilize in adsorption experiments.

Experiment: 100 mL of 1 mg L^{-1} of As(V) solution was taken in the Erlenmeyer flasks (250 mL). pH of solution was adjusted to 7.8 with 0.1 M NaOH or 0.1M HCl measured with pH meter. 1 g of each biosorbent was added in metal solution and flasks containing this mixture (metal + adsorbent) were transferred to orbital shaker at 150 rpm for 1 hour at $25^{o}C$. After completion of each batch, the solution was filtered by Whatman No. 42 and filtrate was analyzed on atomic absorption spectrophotometer, to determine the quantity of residual metal ions concentration. All experiments were run in triplicates and control was conducted without biomass addition.

Data Evaluation: The amount of arsenic accumulated by biomass (q) and efficiency (E) of biosorption for each experiment was defined through following equations (Barros *et al.*, 2003).

$$q=\left(\frac{C_i - C_f}{m}\right)V \quad , \quad E=\left(\frac{C_i - C_f}{C_i}\right)*100$$

Where, $\mathbf{C_i}$ and $\mathbf{C_f}$ are initial and final concentrations of metal (mg L^{-1}), respectively; **m** = dried mass of the biosorbent in the reaction mixture (g); **V** = volume of the mixture (mL).

Statistical Analysis: Data regarding C_f (remaining metal concentration in the supernatant) values were analyzed through analysis of variance technique (Steel *et al.*, 1997) and means were compared by Duncan's Multiple Range Test (Duncan, 1955).

Fourier Transform Infrared Spectroscopy Analysis (FTIR): For the analysis on FTIR, sample preparations were carried out as described by Feist (2001). Samples were examined as a mull (a two phase mixture). Mulls were prepared by thoroughly grinding 2-5 mg of sample in a smooth mortar with a pestle of agate (a form of agate or silica). In this paste 1 to 2 drops of mulling agent (nujol) were added, grinding kept continuing to get a homogenous paste. The mull was then examined as a thin film between the NaCl plates. Spectra of the sorbents before and after As(V) sorption were studied by using hexachlorobutadiene and chlorofluorocarbon oils as complementary mulling agents.

RESULTS AND DISCUSSION

A highly significant difference was noticed amongst the C_f values of the different filtrates as compared to control (Table I). Whereas, all six adsorbents hold greater adsorption capacity (0.98-0.99 mg g^{-1}) and efficiency (~99%) for the arsenate at pH 7.8 (Fig. I). It has been documented that plant biomass have tremendous ability to accumulate a large concentration of poisonous metal on their surfaces. The surface of plant biomass contains number of metal binding functional groups that are available at optimum pH (Shafique *et al.*, 2011). Currently greater adsorption capacity and efficiency of the selected adsorbents could be due to the availability of maximum number (90%) of amino acids and other functional groups at highly basic pH 7.8 (Ghimire *et al.*, 2002). Positively charged functional groups along with amino acid groups probably bind with negatively charged monovalent arsenate species ($H_3AsO_4^{1-}$) (Kumari *et al.*, 2005) and that resulted in 99% adsorption of arsenate.

Table I. Remaining metal ion concentration in the supernatant (C_f).
Biosorption condition: Adsorbent amount: 1 g, Time duration: 1 hours, Stirring intensity: 150 rpm at 25˚C ± 3.

Biosorbents	**Remaining arsenic mg L^{-1}**
Control (without biosorbent)	1.0000 **a**
Rice (*Oryza sativa*)husk	0.0109 **b**
Wheat (*Triticum aestivum*)husk	0.0105 **c**
Banana (*Musa acuminata*)peels	0.0093 **d**
Peanut (*Arachis hypogaea*) peels	0.0085 **e**
Sohanjana (*Moringa oleifera*) leaves	0.0065 **f**
Pea (*Pisum sativum*) peels	0.0054 **f**

Note: Values with different letter shows significant ($p \leq 0.05$) difference among the treatments according to Duncan's Multiple Range Test.

The IR spectra were studied in mid-infrared region (3800-660cm^{-1}) for raw and As(V) laden biomass of different adsorbents. Table II shows the bands assignment to distinctive functional groups in the raw as well as in exhausted biomasses. Representative IR spectra of all six adsorbents (raw and metal-laden) were presented in Fig. II A-F. The IR findings revealed involvement of carboxyl (-COOH), hydroxyl (-OH), amides (-NH), amine (-NH), alkynes (CH), alkanes (CH$_2$, CH$_3$), ethers (C-O), ketones (C=O) and some other miscellaneous groups i.e. halides (C=O) and imines (C=N) in binding of As(V).

The IR spectra of almost all adsorbents displayed a band at 3791-3739 cm^{-1}, that corresponds to O-H stretching groups due to inter- and intra-molecular hydrogen bonding of polymeric compounds, such as alcohols, occasionally phenols, and carboxylic acids present in the cellulose and lignin in plants. In metal-loaded biomass of the adsorbents, disappearance or shift of the peaks in the region of 3791-3791 cm^{-1} revealed substantial contribution of OH group in metal-oxygen binding (Sigeel *et al*., 2002). These hydroxyl groups are integral part of all polysaccharides can act as negative scavenger thereby subsidizing metal adsorption to a substantial level (Gnanasambandam and Protor, 2000).

Protein spectra were specified at region between two regions, 1) 3300-3200 cm^{-1} and 2) 1800-1500 cm^{-1}. Bands between 3300-3200 cm^{-1} and 1700-1600 cm^{-1} chiefly characterized amide-I are due to C=O peptide bond (stretching vibrations), these bands illustrate about the protein secondary structure. Absorption peaks from 1600 to 1500 cm^{-1} is due to N-H bending vibrations in amide II complex. Presently, NH was found to be second important group after OH, played vital role in binding of metal from the aqueous solution. After exposure of each biomass to arsenate, either disappearance or down shifting of the stretching and bending absorption bands in protein regions was observed that might be due to conversion of primary amine into secondary amine and chelation of As with NH functionality (Fischer *et al.*, 2006; Souza *et al*., 2008).

The region between 2935 to 2915 cm^{-1} indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids (lipids) (Dumas and Miller, 2003) is found in all the adsorbents. In metal-loaded biomass of different adsorbents the shift in these wavenumbers demonstrated accountability for additional asymmetric C-H stretching vibrations of methylene.

The regions from 1200 to 1050 cm^{-1} are generally occupied by groups like C-O-P, C-C, C-O, and C-O-C having stretching mode of vibrations of polysaccharides. These groups principally found in cellular polysaccharides and carbohydrates of plants. In different treatments shifting in wave number of polysaccharide bands specifically at 1029-1020 cm^{-1} proved their role in coordination with arsenate as stretching vibrations of C–O of alcohol groups and carboxylic acids (Yee *et al*., 2004).

Table II. Comparison of IR spectra of raw and As(V)-loaded biomass of different biosorbents.

	Adsorbents						**Functional group assignment**
	***Moringa oleifera* leaves**	***Triticum aestivum* husk**	***Oryza sativa* husk**	***Pisum sativum* peels**	***Musa acuminate* peels**	***Arachis hypogaea* peels**	
Raw biomass Frequency (cm^{-1})	-	3731.89	3739.41	3739.41	3736.87	3732.73	OH str
	3280.20	3299.94	3287.53	-	3291.98	3283.75	NH str
	2915.81	2917.40	2917.05	2935.80	2916.61	2918.00	CH$_2$
	2847.99	-	-	-	-	-	CH$_2$
	2346.14	2354.55	2346.39	2341.08	-	2354.13	C≡C, C≡N
	-	-	-	2103.35	2118.86	2118.86	C≡C, C≡N
	-	-	-	-	-	1744.28	C=O
	1623.15	1649.24	1648.18	1651.29	-	1645.03	NH def
	-	1527.30	1539.76	1537.32	1557.65-	1529.88	NH def^{-}
	1434.66	1447.23	1442.06	-	-	-	CH$_2$
	-	-	-	-	1392.98	-	OH
	1243.17	-	-	-	-	1245.75	C-O
	1033.94	1033.94	1023.61	1039.11	1032.66	1024.3	R-O str
	670.31	-	-	-	-	680.07	CH def
As(V) laden biomass Frequency (cm^{-1})	3254.34	-	-	-	3239.61	-	NH str
	2915.95	-	-	-	2912.49	-	CH$_2$
	2846.78	-	-	-	-	-	CH$_2$
	2342.11	2346.71	2342.88	2340.68	-	2341.67	C≡C, C≡N
	1620.85	-	-	1615.23	1611.86	1614.32	NH def
	1239.96	-	-	1240.11	-	-	C-O
	1019.97	1021.71	999.71	1021.03	1018.45	1028.78	R-O
	636.63		-	-	-	642.70	CH

It has been speculated that carbohydrates and proteins groups like hydroxyl, amine, amide and carbonyl significantly contribute in arsenate adsorption from the aqueous solution. The findings of current research work could have important implications to reduce the potential risk posed to human health by As entering the food-chain. Biosorption technique could be effective in arsenic remediation through exploring the role of low cost agricultural wastes as adsorbents.

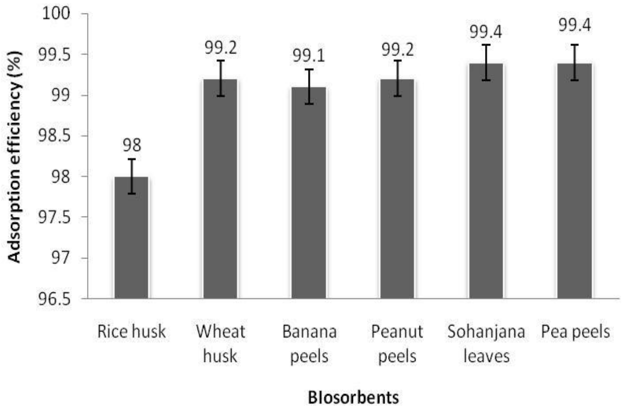
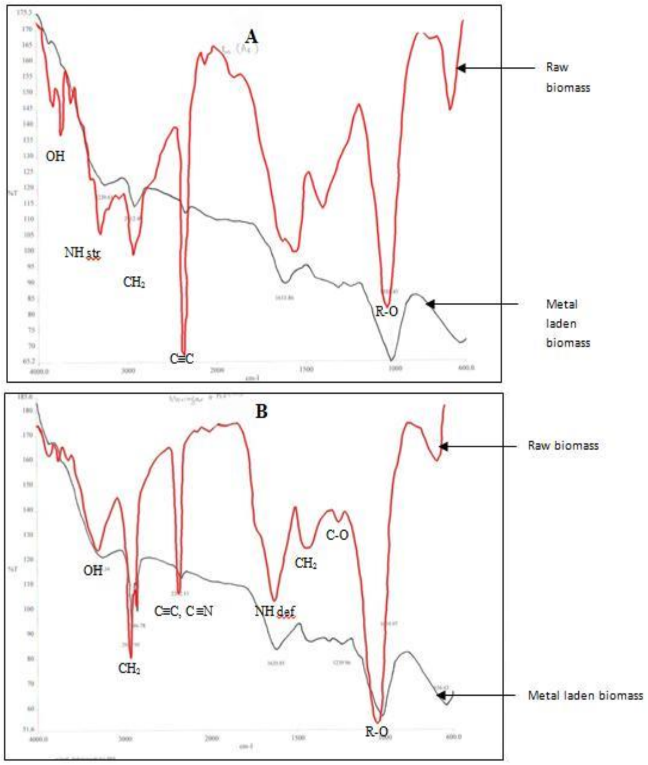


Fig. I: Comparative representation of adsorbents metal uptake efficiency.

Note: Vertical bars show standard error of mean of three replicates



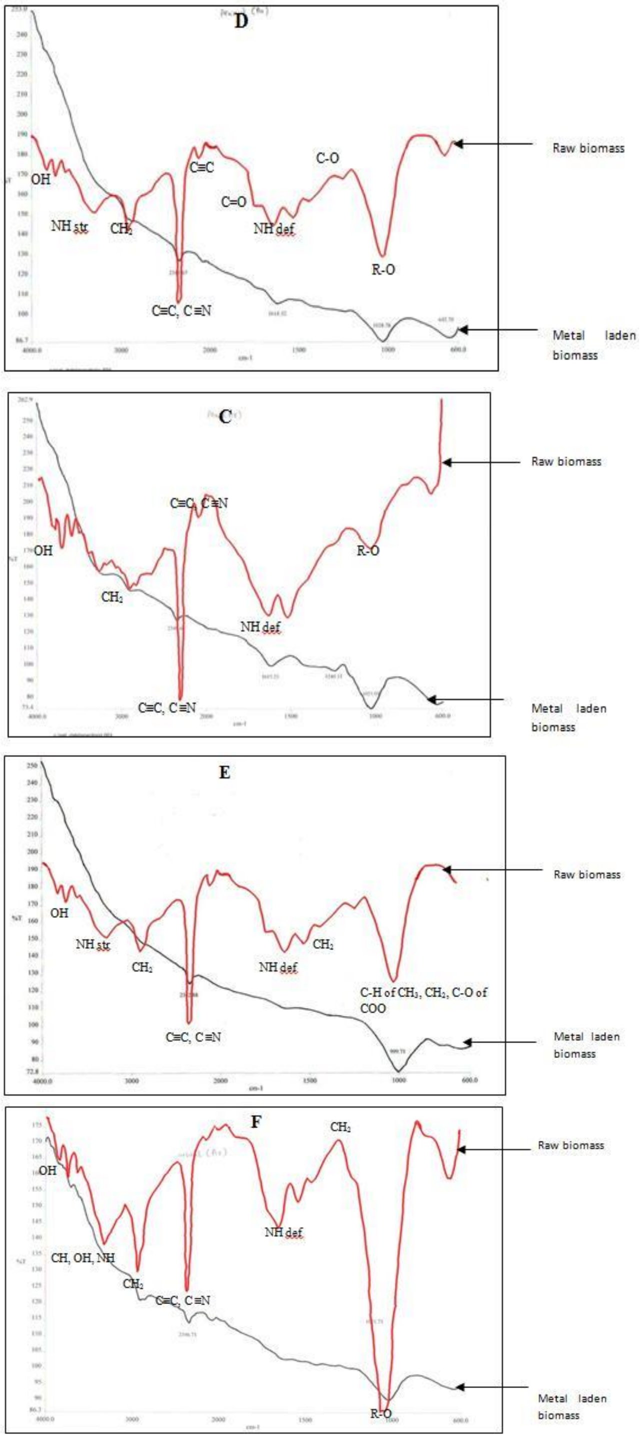


Fig. II A-F: Comparison and characterization of Infra-red spectra of raw and As(V)-loaded biomass of *Musa acuminata* (A), *Moringa oleifera* (B), *Pisum sativum* (C), *Arachis hypogaea* (D), Oryza sativa (E) and *Triticum aestivum* (F).

Acknowledgements: We are very thankful to the Institute of Agricultural Sciences, University of the Punjab for the support to accomplish this research work.

REFERENCES

Ahluwalia, S. S. and D. Goyal (2005). Removal of heavy metals from waste tea leaves from aqueous solution. Eng. Life Sci. 5(2): 158-162.

Al Rmalli, S. W., P. I. Haris, C. F. Harrington and M. Ayub (2005). A survey of arsenic in foodstuffs on sale in the United Kingdom and imported from Bangladesh. Sci. Total Environ. 337, 23-30.

Amin, M. N., T. Kaneco, A. Kitagawa, H. Begum, T. Katsumata, K. Suzuk, and Ohta (2006). Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. Indus. Eng. Chem. Res. 45(24): 8105-8110.

Barros, J., G. R. Maudo, M. M. L. Duarte, E. P. Siliva, and A. K. L. Lobato (2003). Biosorption of cadmium the fungus *Aspergillus niger*. Braz. J. Chem. Eng. 20: 229-239.

Biplob, K. B. (2006). Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product. J. Hazard. Mat. 154:1066-1074.

Blokker, P., S. Schouten, H. Ende, J. W. Leeuw, P. G. Hatcher, and D. J .S. Sinninghe (1998). Chemical structure of algaenans from the fresh water algae *Tetraedron minimum, Scenedesmus communis* and *Pediastrum boryanum*. Org. Geochem. 29(5-7): 1453-1468.

D'Souza, L. D., P. Devi, D. M. P. Shridhar, and C. G. Naik (2008). Use of Fourier Transform Infrared (FTIR) Spectroscopy to Study Cadmium-Induced Changes in *Padina Tetrastromatica* (Hauck). Anal. Chem. Insights, 3: 135-143.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: a review. J. Hazard. Mater. 157: 220 -229.

Dumas, P. and L. Miller (2003). The use of synchrotron infrared micro spectroscopy in biological and biomedical investigations. Vib. Spec. 32(1): 3-21.

Duncan, D. B. (1955). Multiple range and multiple F test. Biometrics, 11: 1-42.

Feist, P. L. (2001). Sampling Technique for Organic Solids in IR Spectroscopy: Thin Solid Films as the Method of Choice in Teaching Laboratories. J. Chem. Educ. 78(3): 351.

Fischer, G., S. Braun, R. Thissen, and W. Dott (2006). FTIR. Spectroscopy as a tool for rapid identification and intra-species characterization of airborne filamentous fungi. J. Microbiol. Meth. 64: 63-77.

Gnanasambandam, R. and A. Protor (2000). Determination of pectin degree of esterification by diffuse reflectance Fourier transform infrared spectroscopy. Food Chem. 68: 327-332.

IARC, International Agency for Research on Cancer (1987). Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs. IARC Monographs of Evolution Carcinogenicity Risk Hum Supply, 7: 1-440.

Israt, J. M., A. M. Lotin, M. Moniuzzaman, and M. A. Sadullah (2008). Arsenic removal from water using activated carbon obtained from chemical activation of jute stick. Indian J. Chem. Technol. 15: 413-416.

Kumari, P., P. Sharma, S. Srivastava, and M. M. Srivastava (2005). Arsenic removal from the aqueous system using plant biomass: a bioremedial approach J. Indus. Microbiol. Biotechnol. 32(11-12): 521-526.

Kratochvil, D. and B. Volesky (1998). Advances in the biosorption of heavy metals. Trends Biotechnol. 16: 291-300

Kundu, S. and A. K. Gupta (2006). Arsenic adsorption onto iron oxide-coated cement (IOCC): Regression analysis of equilibrium data with several isotherm models and their optimization. J. Chem. Engin. 122(1-2): 93-106.

Lin-Fu, J. (1980). Lead poisoning and undue lead exposure in. children: history and current status. In Needleman, H. L. (Ed.), Low Level Lead Exposure: The Clinical Implications of Current Research, Raven Press, New York. 5-16 p.

Mandal, B. K. and K. T. Suzuky (2002). Arsenic round the world: a review. Talanta, 58: 201-235.

Memon, S. Q., M. I. Bhanger and J.-Ur-R. Memon (2008). Evaluation of banana peel for treatment of arsenic contaminated water. Proc. First Tech. Meeting Muslim Water Res. Coope. 104-109.

Naseem, Z. (2010). Arsenic contamination in water and its removal by using different low cost adsorbent. J. Chem. Soci. Pakistan 32: 259-263.

NEQS (2000). National Environmental Quality Standards for municipal and liquid industrial effluents. Compiled and distributed by National Scientific Corporation. Pakistan.

Ofomajaa, A. E. and Y. S. Ho (2007). Effect of pH on cadmium biosorption by coconut copra meal. J. Hazard. Mater. 139(2): 356-362.

Pagnanelli, F. Mainelli, S. Vegliò, F. and L. Toro (2003). Heavy metal removal by olive pomace: biosorbent characterization and equilibrium modeling. Chem. Eng. Sci. 58: 4709-4717.

Ranjana, D., M. Talat, and S. H. Hasana (2008). Biosorption of arsenic from aqueous solution using agricultural residue rice polish. J. Hazard. Mater. 166 (2-3): 1050-1059.

Roychowdhury, T., T. Uchino, H. Tokunaga, and H. Ando (2002). Arsenic and other heavy metals in soils from an arsenic affected area of West Bengal, India. Chemosphere, 49: 605-618.

Shafique, U., A. Ijaz, M. Salman, M. Waheed uz Zuman, N. Jamil, R. Rehman, and A. Javaid (2011). Removal of arsenic from water using pine leaves. J. Taiwan. Inst. Chem. Eng, 43: 256-263.

Sigee, D., A. Dean, E. Levado, and M. J. Tobin (2002). Fourier-transform infrared spectroscopy of Pediastrum duplex: Characterization of a micro-population isolated from a eutrophic lake. Eur. J. Phycol. 37(1) 19-26.

Steel, R. G. D., J. H. Torrie, and D. A. Dickey (1997). Principles and Procedures of Statistics. A biometrical approach. 3rd Ed., McGraw Hill Book Co., New York, USA.

Thomas, S. Y., T. G. Choonga, Y. Chuaha, F. L. Robiaha, G. Koaya, and I. Azni (2007). Arsenic toxicity, health hazards and removal techniques from water: an overview. Desal. 217 (1-3): 139-166.

Volesky, B. (2007). Review Biosorption and me. Water Res. 41(18): 4017-4029.

World Health Organization (WHO) (1971). International standards for drinking water, 3rd Eds. Geneva.

World Health Organization (WHO) (2001). http://www.who.int/inf-fs/en/fact210.html. Geneva.

Yee, N., L. G. Benning, V. R. Phoenix, and F. G. Ferris (2004). Characterization of metal-Cyanobacteria sorption reactions: A combined Macroscopic and infrared spectroscopic investigation. Environ. Sci. Technol. 38(3): 775-82.