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Original Article

Phytoremediation of heavy metals (Cd, Pb and V) in gas refinery wastewater using common reed (*Phragmitis australis*)

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Abstract: Industrial wastewaters are of the major sources of heavy metal pollution in the environment. In the Middle East, gas and oil industry is the major source of heavy metal pollution and releases significant amounts of metals into the terrestrial and aquatic environment. In this research the capability of the common reed (*Phragmitis australis*) in absorbing heavy metals Cd, Pb and V from the wastewater of a gas refinery plant in Iran was investigated. The plant samples were collected from the vicinity of the BidBoland gas refinery plant in Iran and were used for the treatment of wastewaters collected from the outflow of the refinery plant. The metal concentrations were measured in the roots of the plant species before treatment and after 2, 6 and 10 days of treatment procedure. The heavy metal concentrations were measured after acid digestion and using an ICP-OES instrument. After 10 days of treatment, the concentrations of the metals in plant tissues increased by 2.5, 6.9 and 2.7 times for Cd, Pb and V, respectively. The best treatment time was suggested to be 6 days. The common reed was observed to have a very good capability in removing heavy metals from the gas refinery wastewater.

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Introduction

Human beings around the globe release huge amount of wastewater into the environment. In particular, significant concentrations of heavy and hazardous metals, are released in industrial wastewater and these can cause numerous environmental problems (Atashgahi et al., 2011). These adverse effects associated with metals can include the alteration of the structure of crops and functions of organisms and their effects can be observed in food chains. High metal concentrations can be toxic to some organisms and metal imbalance in plant tissues can be critical for different kinds of diseases (Ha et al., 2010).

The capability of some plant species to absorb and accumulate high levels of metals in their organs can be used for the purification of polluted environments; in a process known as phytoremediation. Aquatic macrophytes exhibit a high potential for heavy metal phytoremediation due to their rapid growth and high biomass (Carranza-Alvarez et al., 2008).

Among the different possible methods of wastewater treatment, phytoremediation is an environmental friendly and economic method. One of the plant species which has been widely used for treatment of heavy metals is common reed (*Phragmeties australis*), which can tolerate different environmental conditions, including high concentrations of toxic heavy metals (Ye et al., 1997; Stoltz and Greger 2002; Kropfelova et al., 2006; Sardar Khan, 2009).

In the Middle East, one of the major industries is oil and gas production and the resulting wastewater contains elevated levels of heavy metals such as lead, cadmium and vanadium. In this study, the potential

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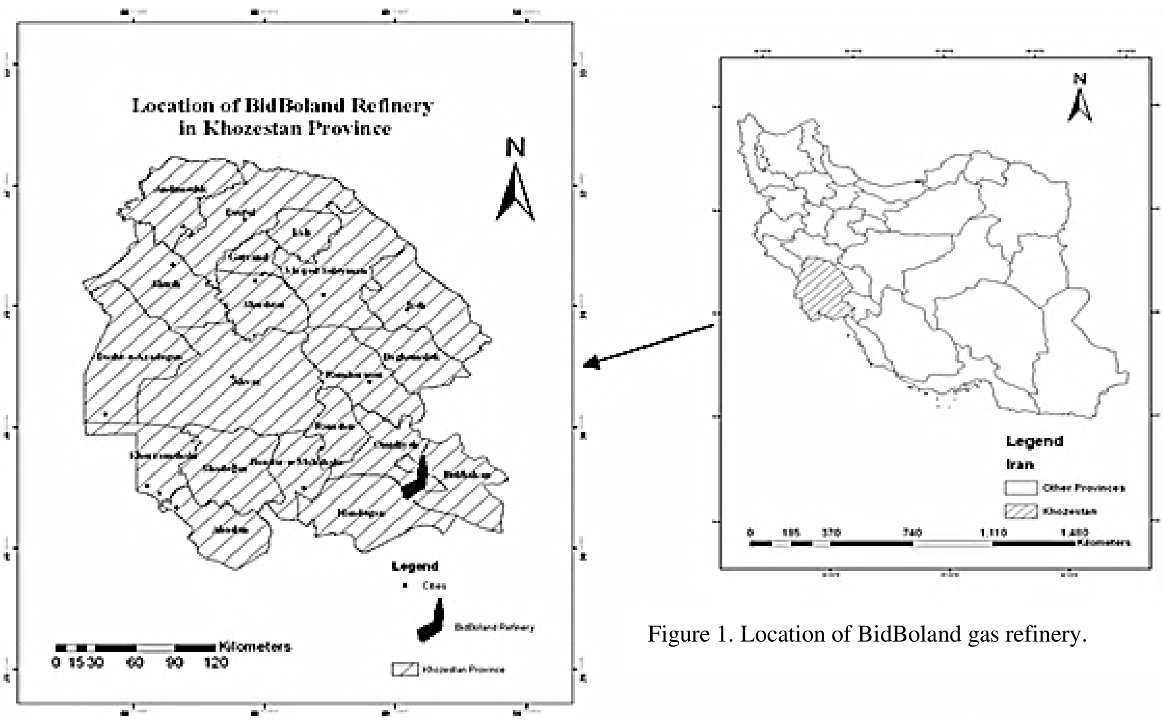

Figure 1. Location of BidBoland gas refinery.

of common reed was investigated for the phytoremediation of Cd, Pb and V in wastewater from the BidBoland gas refinery in Iran.

Material and Methods

Study area: BidBoland gas refinery is located 32 km north east of Behbahan in the province of Khozestan, Iran (Fig.1). Samples of wastewater were collected from the outflow, 300 m south of the refinery. Wastewater discharge was 60 to 70 m^3 per hour. Sixty samples of the common reed (*Phragmeties australis*) were collected from the surrounding area; their roots were placed in plastic bags and immediately transferred to the laboratory. The roots of thirteen of these samples were washed with water, dried and prepared for chemical analysis. Three plastic containers were used in order to plant 30 other plant samples. These 30 plant samples were nourished in these containers within 15 days to reach a height of approximately 40 cm. Wastewater samples were transferred into another plastic container (100×150×40 cm) and the 40 cm plant samples were transferred and planted in this container.

Samples were taken from the roots (using acid washed plastic knives) of the plants during three phases, namely after 2, 6 and 10 days from transferring wastewater into the containers. During each phase, 13 plant samples were selected by random and taken out from the container. The roots of these samples were washed with water, dried in a fume hood and stored in clean plastic bags for chemical analysis.

Preparation of plant samples: All plastic and glassware were washed with soap and hot water, rinsed three times with distilled water and stored in a solution of 10% HNO_3 and HCl for 2 weeks; and rinsed three times with dionized water afterwards. The plant tissues were dried in an oven for 48 to 72 hours in 110°C and ashed in a furnace in 550°C for 48 hours. Wet and dry weights of the samples were recorded. Ashed samples were digested using concentrated Analar grade HNO_3 (Merck, Germany) and diluted by %1 HNO_3. The concentrations of the metals were measured using an ICP-OES instrument. (PerkinElmer, USA). For certifying the analysis method, for each 20 root samples 2 blanks and 2 homogenised and spiked samples were analyzed under the same laboratory conditions.

Statistical analysis: Statistical analyses were performed using SPSS 16. The normalization of data was checked using Kolmogorov Smirnov test.

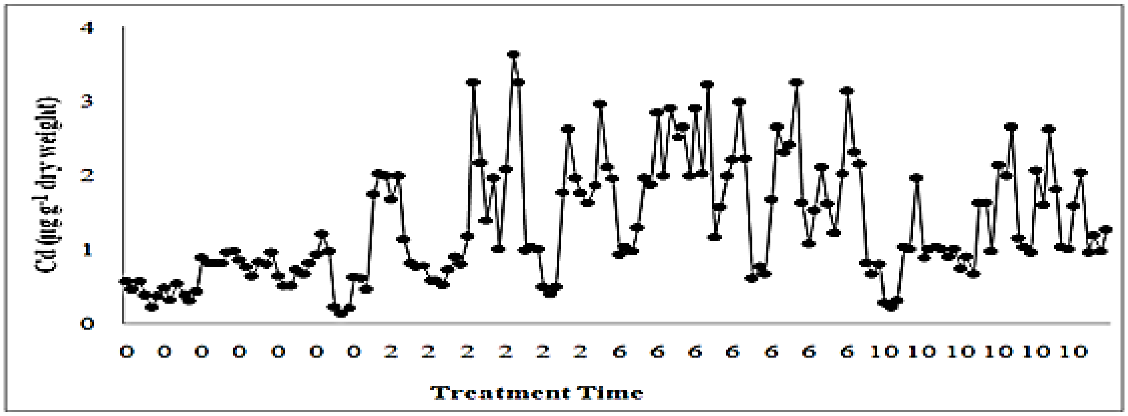

Figure 2. Cd Concentrations in Common reed samples (µg g^{-1} dry weight).

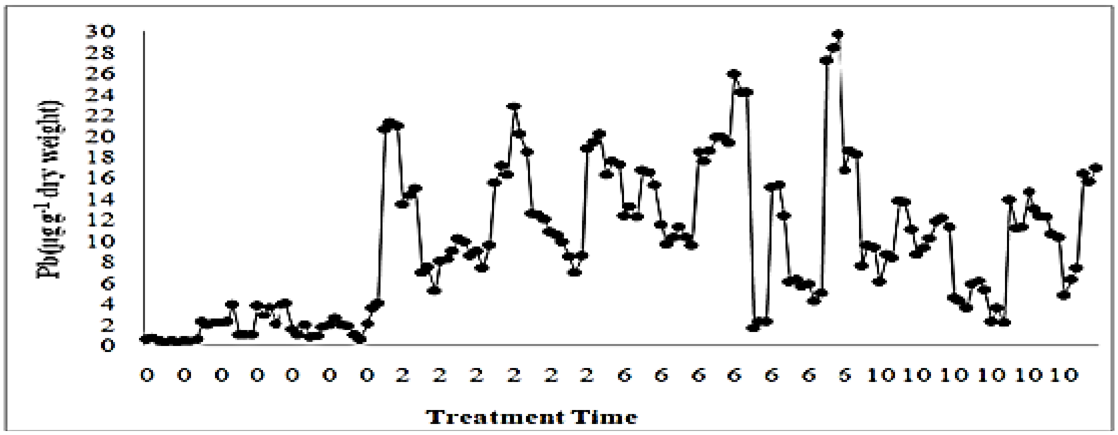

Figure 3. Pb Concentrations in Common reed samples (µg g^{-1} dry weight).

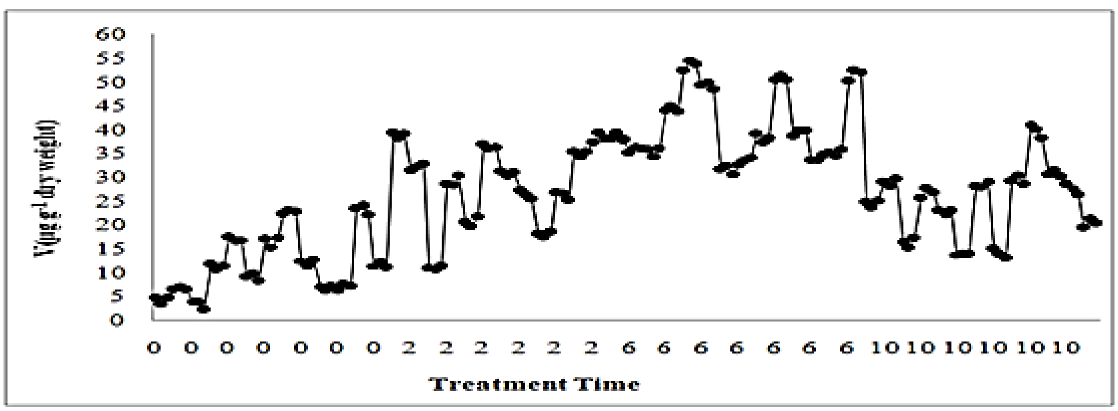

Figure 4. V Concentrations in Common reed samples (µg g^{-1} dry weight)

ANOVA and Duncan tests were used to compare the average concentrations of the metals in different treatment times (0, 2, 6 and 10 days). Pearson correlation coefficients were used for determination of any correlation between concentrations of the metals in the common reed tissues.

Results and Discussion

Heavy metal concentrations in plant tissues: Percentage recoveries were between 90 to 105 percent for all metals measured. The detection limits (equal to 3×SD of blanks) were 2, 10 and 100 ppb for Cd, Pb and V, respectively. The mean and standard deviation of Cd, Pb and V concentrations in plant tissues for different treatment times (0, 2, 6 and 10 days after treatment) are shown in Table 1.

Concentrations of the metals in plant tissues are showed in Figures 2 to 4.

Table 1. Means and standard deviations of Cd, Pb and V concentrations in common reed tissues in different retention times

Treatment time	0		2		6		10	
Metal concentration ($\mu g\ g^{-1}$ dry weight)	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cd	0.61	0.25	1.53	0.84	1.95	0.74	1.21	0.59
Pb	1.78	1.20	13.25	5.03	14.28	7.46	9.38	3.96
V	11.54	6.39	29.24	8.47	40.83	7.65	24.75	7.18

Table 2. The increase in the concentration of Cd, Pb and V by common reed roots

	Cd ($\mu g\ g^{-1}$ dry weight)	Pb ($\mu g\ g^{-1}$ dry weight)	V ($\mu g\ g^{-1}$ dry weight)
Mean in the beginning	0.61	1.78	11.54
Mean after treatment	1.56	12.30	31.61
Increase	2.54 Time	6.87 Time	2.73 Time

The average concentrations of Pb in common reed tissues were 1.78, 13.25, 14.28 and 9.38 ($\mu g\ g^{-1}$ dry weight) for 0, 2, 6 and 10 days of the treatment, respectively. The average concentrations of Cd in plant tissues were 0.61, 1.53, 1.95 and 1.21 ($\mu g\ g^{-1}$ dry weight) for 0, 2, 6 and 10 days after the treatment, respectively. The concentration of V in plant tissues was 11.54 ($\mu g\ g^{-1}$ dry weight); which increased to 29.24, 40.83 and 24.75 ($\mu g\ g^{-1}$ dry weight) after 2, 6 and 10 days of treatment, respectively.

Based on statistical analysis, significant differences ($P<0.05$) were found between the concentrations of heavy metals in common reed tissues; and between the concentrations of each metal in samples taken from different retention times of 0, 2, 6 and 10 days.

The Increase in the concentration of heavy metals in the plant roots: Lead in the roots increased 6.87 times, the highest increase related to the beginning of the treatment, followed by 2.73 times for V and 2.54 times for Cd, as showed in Table 2. The average concentrations of heavy metals in roots of the common reed samples before and after 10 days of treatment followed the order of Cd < Pb < V.

Cadmium: Among the metals, cadmium showed the lowest concentrations in roots of common reed, as was observed before in other studies (Bonanno and Lo Giudice, 2010; Nirmal Kumar et al., 2008). This metal is a non-essential element with high toxic effects on growth and metabolism of the plant species. This metal releases free radicals and reactive oxygen species; which cause oxidative stress and consequently the death of plants with damaging membrane proteins, lipids, nucleic acid and pigments. However, the common reed (*Phragmeties australis*) is one of the species with high tolerance to Cd, as a result of high activity of antioxidant enzymes (Bonanno and Lo Giudice 2010).

Common reed (*Phragmites australis*) accumulates Cd in its roots and hardly transfers it to the shoots. This might be a mechanism to avoid the potential toxic effects on photosynthetic organs (Dhir et al., 2009). The average increase in the concentration of Cd in roots of common reed in this study was 1.56 $\mu g\ g^{-1}$ dry weight, which is comparable with 1.4 μg g-1 dry weight in roots of *Carex rostrata* and 4.6 and 4.3 $\mu g\ g^{-1}$ dry weight in roots of *Phragmites australis* and *Eriophorom ansustifolium*, respectively (Soltoz and Greger, 2002). Sardar Khan (2009) found Cd uptake of 2.9 and 3.6 $\mu g\ g^{-1}$ dry weight in roots of *Phragmites australis* and *Thypha latifolia*, respectively.

Lead: Lead can be naturally found in plant tissues; however it is not recognized as an essential element. Broyer et al. (1972) stated that if Pb is necessary for plants, its concentration at the level of 2–6 μg/kg should be sufficient. Transportation and industrial activities release huge amount of lead into the environment.

Rühling and Tyler (1968) reported an increase of Pb concentration in *Hypnum cuperssiforme* tissues within a 100-year period. Various lead uptake rates have been reported for plant species. This might be because of several environmental factors including geochemical anomalies, type of pollutants, the plant species and seasonal changes (Kabata-Pendias and Pendias, 2010).

In this study, a lead uptake rate of 12.307 μg g^{-1} dry weight was observed, which was higher than the rates Sardar Khan (2009) reported for *Phragmites australis* 2/9 (μg g^{-1} dry weight) and *Typha latifolia* 3/6 (μg g^{-1} dry weight).

Vanadium: Plants can easily uptake vanadium by their roots, especially in acidic soil. A linear relationship between the concentration of V in soil and plant tissues indicates that plant species can uptake VO^{2+} in acidic conditions more rapidly than V^{3-} and $HV4^{2-}$ species, which are dominated in neutral and alkaline solutions. It seems that cationic V might be more available to plant species than anionic V (Welch, 1979).

Vanadium is an essential element for algae and some bacterial species. It is not proved to be an essential metal for higher plant species, however some evidences imply it might be a catalyst in N_2 fixation (Kabata-Pendias and Pendias, 2010). There is no evidence of deterioration effects of V on plants, while Welch and Cray (1975) expressed that V is an essential elements for plant species and a concentration of less than 2 μg/kg is needed for plant growth.

Shacklette and Connor (1973) determined concentration between 50–180 mg/kg V in Spanish moss samples collected from areas affected by crude oil discharges. Gough and Severson (1976), reported V concentrations as high as 700 mg/kg in sagebrush found in vicinity of a plant producing phosphorus fertilizer. In neighborhood of crude oil refinery plant, Pawlak (1976) reported V concentrations of 13 and 8 mg/kg in clover and grass tissues, respectively. In this study a V uptake rate of 31.610 μg g^{-1} dry weight was found for *Phragmites australis*. There is not much information available on the removal of V using *Phragmites australis*, therefore, it is not possible to make comparisons.

Proper treatment time for metal removal using phytoremediation: This study showed that a treatment time of 6 days is the best for the removal of Cd, Pb and V from wastewater using common reed. This is in agreement with a treatment time of 7 days that Hadad et al. (2006) found for *Typha domingensis*. He suggested this treatment time for treatment of wastewater with high EC, pH and heavy metal content. After 10 days of treatment, the concentrations of metal, in plant tissues were decreased, which might be due to metal release and that uptake rate, might have gone higher that tolerant threshold of the plant. Ye et al. (2003) suggested a retention time of 12 days as the proper time for the removed of nutrient and metals.

Correlation between Cd, P and V concentrations in plants roots: Balancing heavy metals in plant organs is very important and necessary; and affect their physiology and consequently their growth. In this study, significant correlations (P<0.01) were found between the concentrations of Pb and Cd; Pb and V; and Cd and V in plant tissues with correlation coefficients of 0.40, 0.51 and 0.41, respectively. The interaction between metals is one of the major causes of their toxicity. For example, Hernandez et al. (1998) reported that uptake of Mn by plant can be reduced in presence of Cd. When plants uptake metals to the concentrations higher than their tolerance or toxic threshold, there might be interactions between the metals and their metabolic functions might be interfered. For instance, excessive uptake of Zn by plant might affect Fe metabolic function, and even in normal concentrations of Fe, the plant might suffer from chlorosis (Market, 1987).

Conclusions

Phytoremediation is a natural method for wastewater treatment with numerous benefits such as its easy processing, energy saving, environmental conservation; e.g. improving local biodiversity, enhancing the quality of local weather, less emission of CO_2, using natural resources of energy (such as solar radiation and wind) and soil, plants and animals in wastewater treatment, control of soil erosion and increasing available water supply (Schröder et al., 2007). Due to our observed uptake rates of Pb, V and Cd by common reed plant during wastewater treatment (compared to other studies) and because it is a native plant species in Khozestan Province (due to appropriate climate conditions), and because this plant species has a very high growth rate in this area, it is suggested to use common reed for the removal of heavy metals from this specific wastewater. However, in similar situations when common reed is regarded to be used for the treatment of wastewater, the source and type of pollutants should be investigated and a pilot study is needed before any further investment.

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References
Agunbiade F.O., Olu-Owolabi B.I. Adebowale K.O. (2009). Phytoremediation potential of *Eichornia crassipes* in metal-contaminated coastal water. Bioresource Technology, 100: 4521-4526.

Atashgahi M., Hamidian A.H., Parvizi Mosaed H. (2011). Phytoremediation of heavy metals a method towards sustainable development [abstract]. In: University of Tehran 5th national conference on world environment day. University of Tehran, June 2011.

Bonanno G., Giudice R.L.O. (2010). Heavy metal bioaccumulation by the organs of Phragmites australis (Common reed) and their potential use as contamination indicators. Ecological Indicators, 10: 639-645.

Broyer T.C., Johnson C.N., Paull R.E. (1972). Some aspects of lead in plant nutrition. Plant and Soil, 36(1-3): 301-313.

Carranza-Alvarez C., Alonso-Castro A.J., Alfaro-De La Torre M.C., Garcia-De La Cruz R.F. (2007). Accumulation and Distribution of Heavy Metals in Scirpus americanus and Typha latifolia from an Artificial Lagoon in San Luis Potosí, México. Water Air Soil Pollution, 188: 297-309.

Dhir B., Sharmila P., Saradhi P., Pardha. (2009). Potential of Aquatic Macrophytes for Removing Contaminants from the Environment. Critical Reviews in Environmental Science and Technology, 39(9): 754-781.

Gough L.P., Severson R.C. (1976). Impact of point source emission from phosphate processing on the element content of plants and soils, Soda Spring, Idaho, in Trace Substances in Environmental Health, Vol. 10, Hemphill, D.D., ed., University of Missouri, Columbia, MO, 225.

Ha N.T.H., Sakakibara M., Sano S. (2010). Accumulation of Indium and other heavy metals by *Eleocharis acicularis*: an option for phytoremediation and phytomining, Bioresource Technology, 102(3): 2228-2234.

Hadad H.R., Maine M.A., Bonetto C.A. (2006). Macrophyte growth in a pilot-scale constructed wetland for industrial wastewater treatment. Chemosphere, 63: 1744-1753.

Hernandez L.E., Lozano E., Garate A., Carpena R. (1998). Influence of cadmium on the uptake, tissue accumulation and subcellular distribution of manganese in pea seedlings. Plant Sciences, 132: 139-151.

Kabata-Pendias A., Pendias H. (2000). Trace elements in soils and plants. In: CRC press, Florida. 505 p.

Kropfelova L., Vymazal J., Svehla J., Stıchova J. (2009). Removal of trace elements in three horizontal sub-surface flow constructed wetlands in the Czech Republic. Environmental Pollution, 157: 1186-1194.

Market B. (1987). Interelement correlations in plants. Fresenius' Zeitschrift für Analytische Chemie, 329: 462-465.

Nirmal Kumar J.I., Soni H., Kumar R.N, Bhatt I. (2008). Macrophytes in phytoremediation of heavy metal contaminated water and sediments in Pariyej community reserve, Gujarat, India. Turkish Journal of Fisheries and Aquatic Sciences, 8: 193-200.

Obarska-Pempkowiak H., Haustein E., Wojciechowska E. (2005). Distribution of heavy metals in vegetation of constructed wetlands in agricultural catchment. In: Vymazal J. (Ed.), Natural and Constructed Wetlands:

Nutrients, Metals and Management. Backhuys Publishers, Leiden, pp. 125–134.

Perkin Elmer. (1994). Analytical Methods for Atomic Absorption Spectrometry. USA.

Pawlak L. (1980). Trace Element Pollution of Soils and Plants in the Vicinity of the Oil Refinery Plant near Plock [Doctoral thesis]. Agricultural University, Warsaw. p. 165.

Ruhiling A., Tyler G. (1968). An ecological approach to the lead problem, Botanical Notiser, 121: 321-342.

Shacklette H.T., Connor J.J. (1973). Airborne chemical elements in Spanish moss, U.S. Geological Survey Professional paper, 574e, 46.

Khan S., Irshad Ahmad, M., Shah T., Rehman S., Khaliq A. (2009). Use of constructed wetland for the removal of heavy metals from industrial wastewater. Journal of Environmental Management, 90: 3451-3457.

Schröder P., Navarro J. (2007). Using phytoremediation technologies to upgrade waste water treatment in Europe. Environmental Science and Pollution Research, 14 (7): 490-497.

Stoltz E., Greger M. (2002). Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings. Environmental and Experimental Botany, 47: 271-280.

Terzakis S., Fountoulakis M.S., Georgaki I., Albantakis D., Sabathianakis I., Karathanasis A.D., Kalogerakis N., Manios T. (2008). Constructed wetlands treating highway runoff in the central Mediterranean region. Chemosphere, 72: 141-149.

Welch R.M. (1979). The biological significance of nickel. In: International Symposium on Trace Element Stress in Plants, Los Angeles, November 6: 36.

Welch R.M., Cary E.E. (1975). Concentration of chromium, nickel, and vanadium in plant materials. Journal of Agricultural and Food Chemistry, 23 (3):479-482.

Ye Z.H., Baker A.J.M., Wong M.H., Willis A.J. (1997). Zinc, lead and cadmium tolerance, uptake and accumulation by the common reed, *Phragmites australis* (Cav.) Trin. ex Steudel. Annals of Botany, 80: 363-370.