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Removal and fate of arsenic in the rhizosphere of *Juncus effusus* treating artificial wastewater in laboratory-scale constructed wetlands

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ABSTRACT

The deposition, fate and distribution of arsenic (As) under dynamic redox conditions within the rhizosphere of helophytes in treatment wetlands are still poorly understood. For this purpose, long-term experiments were carried out in specially designed laboratory-scale constructed wetland reactors treating artificial domestic wastewater containing As (200 μg As l^{-1}) in order to investigate the key aspects of As immobilization, to identify the main As removal pathway by using a mass balance approach and to assess the role of different sulfate (SO_4^{2-}) concentrations on As mass retention. The results with a highly efficient As mass retention (>92%) indicated a better performance under C-deficient and oxidized conditions (E_h ~324–795 mV) regardless to the SO_4^{2-} concentration in the inflow wastewater. An elevated SO_4^{2-} concentration (25 mg S l^{-1} in the inflow) facilitated high As-retention (>90%) under C-surplus and microbial dissimilatory SO_4^{2-} reducing condition (E_h ~−225–−149 mV) within the root-near environment of the rhizosphere in constructed wetlands. Mean pH in a range of 6.6–7.7 might be favoring the immobilization of As but a comparatively low pH (3.9–5.9) within the root vicinity might enhance plant uptake. In general, higher As concentrations were exhibited by the plant roots (90–315 mg As kg^{-1} dry wt) as compared to the shoots (3.5–3.8 mg As kg^{-1} dry wt). Nearly 3.5-fold higher As concentrations within the roots from the experimental reactor as compared to the roots collected from control reactor clearly indicated that a higher amount of As was retained, accumulated, adsorbed, metabolized to other forms on root surface and/or translocated into the roots of *Juncus effusus*, where organic C and SO_4^{2-} were abundant. Based on As mass balance calculation, the reactor with the highest SO_4^{2-} loading was found to be retained nearly 85% of the total As mass input. Out of which only <1% of the total inflow As mass was sequestered or translocated into the plant shoots, 42.2% was accumulated/recovered within the plant roots, 17.2% was entrapped or deposited within the sediments of the gravel bed, 16.2% was recovered in the pore water and 15.3% was flushed out as outflow. The remaining 9% was considered as unaccountable, which might be released due to volatilizations or lost due to various unknown reasons. A 5-fold higher SO_4^{2-} concentration within the reactor might facilitate lower pH (3.9–5.9) and consequent remobilization caused a higher amount of free or exchangeable As in the pore water (16.2%), that probably resulted in a higher As uptake (42.2%) by the plant roots as compared to the roots from the control reactor (only 13%). The findings demonstrate the deposition and fate of As within the rhizosphere, which are of high importance for an efficient treatment of wastewater containing As under constructed wetland conditions.

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1. Introduction

Arsenic (As) is a toxic metalloid which can pollute water, soil, crops and the environment at large, ultimately affecting human health (Zhao et al., 2010). More than 245 minerals contain As, and the principal source of As is geological. However, human activities such as mining, pesticide application, and burning of fossil fuels also cause As pollution (Sharma and Sohn, 2009). In recent years, there has been an increasing contamination of water, soil and crops by this metalloid in many regions of the world (Tripathi et al., 2007), particularly in some countries of southern Asia (Meharg, 2004). It is therefore very important to choose appropriate methods to control As in the environment. Several treatment technologies have been applied for the removal of As from contaminated waters, such as coagulation/filtration, ion exchange, lime softening, adsorption on iron oxides or activated alumina, reverse osmosis etc. (Zouboulis and Katsoyiannis, 2002).

Constructed wetlands are low-energy based 'green' technologies that have been increasingly applied in wastewater treatment since the mid-1980s (Sun and Saeed, 2009) and have considerable potential to remove metals and metalloids, including As (Buddhawong et al., 2005; Rahman et al., 2008a; Ye et al., 2003). Wetland plants have been shown to play important roles in constructed wetlands to remove As from wastewater (Rahman et al., 2008a, 2011; Singhakant et al., 2009). Complex interactions of As under redox gradient (both micro- and macro) conditions have already been investigated in different laboratory-scale horizontal subsurface-flow constructed wetlands treating an artificial wastewater (Rahman et al., 2008a).

The rhizosphere of constructed wetlands offers specific macro- and micro gradients of redox conditions enabling the development of highly diverse microbial consortia capable of different beneficial redox reactions (Bezbaruah and Zhang, 2004; Liesack et al., 2000; Wiessner et al., 2005b). Particularly due to the release of oxygen and organic carbon at the same time by the roots of helophytes into the rhizosphere, spatial and temporal micro-scale gradients of oxygen concentrations and redox states are established close to the root surfaces. These conditions enable the development of microbial mats and layers of functionally different microorganisms which simultaneously realize multiple interactive processes like nitrification, denitrification, mineralization of organic carbon, methanogenesis, reduction and oxidation of several sulfur and As compounds on a small spatial scale (Bezbaruah and Zhang, 2004; Darrah et al., 2006; Rahman et al., 2008b; Wiessner et al., 2005b). Recently, the application of a specially designed laboratory-scale constructed wetland (Kappelmeyer et al., 2002) in order to evaluate micro-gradient processes within the near-root environment of the rhizosphere was shown to be useful (Wiessner et al., 2005a,b).

The behavior of metals in aquatic systems is complex and may include interactions among or between the major wetland compartments, above-ground plant parts, roots, litter, biofilms, soil, and water (Kadlec and Knight, 1996). Volatilization of metals into a gaseous phase occurs with mercury, selenium, and arsenic to a lesser degree. Dissolved metals can adsorb onto particles, or exist complexes to inorganic and organic ligands, or be present in solution in the free-ion state. The adsorption and co-precipitation of As on hydrous oxides of Fe, Mn or Al oxides and Fe sulfides is an important sink for As immobilization (Jacks et al., 2002). Moreover, dissimilatory reduction caused by iron- and sulfate-reducing bacteria is widely considered the primary mechanism responsible for the rapid As reduction and release observed in anaerobic environments (Islam et al., 2004; Kirk et al., 2004).

Based on the characteristic of metal hyperaccumulation in plants, suitable and sustainable remediation strategies could be developed (Rai et al., 1995). Fitz and Wenzel (2002) proposed that hyperaccumulators may enhance metal solubility in the rhizosphere via root exudation, consequently increasing plant metal uptake. Larios et al. (2012) showed that the plants accumulated extremely high amounts of total As in their tissues which varied depending on the part of the plant, with roots accumulating the most As in all the studied plants (up to 1400 mg kg^{-1} dry wt). In the context of constructed wetlands, García et al. (2010) reported that the direct uptake and accumulation of As in plants appears to play a very minor role in As removal. The same conclusion was drawn by Singhakant et al. (2009), who reported that only 0.5–1% of the total As input was accumulated in plant tissues. However, there are also studies indicating that wetland plants have a remarkable effect on As retention (Rahman et al., 2011; Sasmaza and Obek, 2009).

First results of laboratory-scale investigations showed the transformation processes and redox dynamics of As-species particularly in the near-root environment of the *Juncus effusus* in model constructed wetlands. Changes in dynamic redox conditions and re-oxidation of reduced sulfur into other S species (e.g. S^0, SO_4^{2-}) caused a total sulfur enrichment and a consequent As remobilization within the rhizosphere in this study (Rahman et al., 2008b). But it is necessary to investigate the role of organic C, S and pH on As retention within the root vicinity and enhanced plant uptake under different redox conditions. Differences between corresponding inflow and outflow data of total As indicated remarkable amounts of As immobilization within the rhizosphere. Therefore, in addition to the investigations of As-removal efficiency and dynamics of As-species (Rahman et al., 2008b), it is necessary to deepen the understanding of the deposition, fate and mass balance of As within the micro-scale root zone environment of the rhizosphere in treatment wetlands. However, Rahman et al. (2011) in another study showed the fate and distribution of As along the flow path of a laboratory-scale horizontal subsurface-flow constructed wetland. But the knowledge regarding the accumulation and mass balance of As under the micro-scale gradient of redox conditions and the role of C, S and pH within the rhizosphere of helophytes is still insufficient. In the past, little attention has been paid and virtually no information is available until now that directly addresses the removal, fate and plant uptake of As under dynamic redox conditions within the rhizosphere of constructed wetland.

In the context of our research work in this field, several investigations like fundamental aspects and mechanisms of As fixation, influences of dynamic redox conditions on As biotransformation processes, stability of As within the planted and unplanted wetlands, bioaccumulation and uptake of As in plant biomass, sludge sediment analysis, mass balance of As and S, etc., were carried out in different laboratory-scale constructed wetlands (Rahman et al., 2008a,b; Rahman et al., 2011). In principle, the major objectives of this study were i) to investigate the fate, accumulation and distribution of As under redox dynamic conditions on a micro-scale gradient within the rhizosphere; ii) to use a mass balance approach to identify the main As removal pathway under "ideal flow" conditions; and iii) to assess the role of organic C, pH and different SO_4^{2-} concentrations on As mass retention within the rhizosphere of helophytes in treatment wetlands. By using *Juncus effusus*, long-term experiments in a specially designed laboratory-scale constructed wetland treating an artificial wastewater containing As (200 $\mu g\,l^{-1}$) were performed to evaluate all these processes. The results of this study may help to better understand the key aspects of As immobilization within the plant root-zone of the rhizosphere under constructed wetland conditions and to optimize management practices for maximum As retention in different wetland compartments (shoots, roots, sediments etc.) through a complete mass balance analysis.