

Effect of *Eh* and pH on As Removal from Water in Constructed Wetland Mesocosms

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ABSTRACT: Arsenic (As) retention in constructed wetlands (CW) is highly influenced by the physicochemical conditions of the environment, which usually manifests as a redox potential (*Eh*) variation in the system which also depends on the pH and water temperature. This study analyzes the influence of *Eh* and pH on As removal in a CW mesocosms. The study was conducted with three CW prototypes. Two prototypes were planted with *Eleocharis macrostachya* and *Schoenoplectus americanus* (CWA and CWB respectively), while another one remained unplanted as a control (CWC). The CW prototype system operated in parallel for 338 days. It was nourished using synthetic water prepared with ground water and NaAsO₂ at a concentration of 90.66 ± 14.95 µg/L. The theoretical retention time was two days. The parameters monitored during the experiment were: *Eh*, pH, CW temperature and room temperature, and As inflow and outflow.

In the warmer months the CW presented oxidizing conditions (0 to 508 mV) most of time, but often had reducing conditions (0 to -539 mV). In the coldest months, CW showed only oxidizing conditions. The pH of CWA and CWB (planted) remained within the same range (7.0 to 8.0), showing similar behavior throughout all the experiment, unlike CWC (unplanted), which remained a higher pH values (8.0 to 8.5). The removal of As from the beginning of the experiment was higher in CWA and CWB than in CWC. The first two weeks, the three CW had a retention of 60 to 70%; the CWA and CWB improved their retention (80 to 100%) during the first 150 days. After that, removal decreased to 40 and 60%. The CWC had a good removal percentage close to 80% only the third week, after that, it began to decrease down to 5% of retention.

The sulphate reduction rate decreases with temperature, whereas the oxygen solubility increases as temperature decreases. The organic substrate of the plants is easily decomposed, which accelerates the microbial process and oxygen consumption, thereby decreasing the *Eh*. When the root exudation is not intense and carries oxygen from the roots to the soil, *Eh* increases. But if the plant growth is strong and the roots exudation as well, then *Eh* decreases because of the oxygen decrease.

In an oxygenated environment As can be removed by coprecipitation/absorption on Fe(III) oxyhydroxides, which are the Fe dominant forms (at pH ≥ 6.5 and *Eh* > 0). Given the reducing conditions presented in warmer months and the favorable temperature range for the microorganism activity (16-31°C), in addition to bacteria preferring neutral environments, it is assumed that a possible As removal mechanism at reduced conditions was the accomplishment of sulphate-reducing bacteria in CWA and CWB.

As immobilization was more stable and higher in planted prototypes (CWA, CWB) than in the unplanted prototype (CWC), which is attributed to the fact that wetland rhizosphere provides the specific redox gradient that allows the development of a diverse microbial consortium capable of enabling different beneficial redox reactions. Despite the probable sulfur re-oxidation and the As release, the root activity of plants (providing O₂ to the rhizosphere), probably contributes to a potentially strong As immobilization in

CW; therefore, plants play an important role in a better stabilization for As immobilization despite a probable re-oxidation of reduced compounds.