

## REED MATERIAL – A POTENTIAL BIOSORBENT FOR THE TREATMENT OF Cr(VI)-CONTAMINATED WATER DISCHARGED INTO ASOPOS RIVER

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### ABSTRACT

The aim of the present study is the preliminary investigation of reed material to treat Cr(VI)-contaminated water discharged into Asopos River at Inofyta, Central Greece. Batch and up-flow column experiments were conducted with reed material, initial Cr(VI) concentration of 5 mg/L and different values of pH, liquid:solid ratio and contact time in order to investigate the Cr(VI) removal efficiency of reed material under different conditions. Experimental results indicated that although reed material demonstrates significant Cr(VI)-removal performance, the high amount of reed required render this method unsuitable to be used as a single-stage treatment process for heavily Cr(VI)-contaminated water, such as the stormwater discharged into Asopos River. This is still, however, a promising alternative that might be used as a potential water pretreatment scheme.

**Keywords:** Hexavalent chromium, Reed biomaterial, Chromium reduction, Up-flow percolation experiments

### 1. Introduction

Chromium (Cr) is a heavy metal and Cr(III) and Cr(VI) are the most common species. Cr(VI) is more toxic than Cr(III) because of its high water solubility and mobility (Gomez et. al., 2006). Inofyta (Central Greece) is a heavily industrialized area where high Cr(VI) concentrations in groundwater have been recorded systematically. At the nearby area a stormwater outfall discharges heavily contaminated water into Asopos river, with Cr(VI) concentration as high as 5.0 mg/L and flow rate approximately 5 m<sup>3</sup>/h. Although the discharge of industrial wastewater cannot be excluded, it is believed that contaminated groundwater enters the drainage, through cracks in piping at several hundred meters upstream (Panagiotakis et al. 2014).

Several studies have reported the utilization of locally available adsorbents like fly ash, peat, microbial biomass and agricultural byproducts for Cr(VI) removal from contaminated water or wastewater (Nourbakhsh et. al., 1994, Aksu et al., 2002, Bai et al., 2003, Park et al., 2005). The majority of these studies have investigated the mechanism of Cr(VI) removal from contaminated water and the effects of contact time, pH, Cr(VI) concentration, biomass concentration and temperature on Cr(VI) removal, mainly by using batch experiments and under very acidic conditions (pH<3). A previous study investigated the Cr(VI) removal efficiency of reed, compost and treated wastewater sludge and proved that reed, which is locally available, demonstrates satisfactory Cr(VI) removal behavior (Lagiopoulos, 2014).

The aim of the present study is the preliminary investigation of the ongoing natural Cr(VI) removal performance of reed (*Phragmites* spp.) that takes place in the Asopos River bed, as well as the potential efficiency of reed material as biosorbent in engineered treatment schemes, such as

constructed wetland for wastewater treatment or permeable reactive barriers for contaminated groundwater.

## **2. Materials and methods**

### **2.1. Preparation and characterization of reed**

Reed (*Phragmites* spp.) used in the experiments was harvested from the river bed of Asopos River and particularly from the area of Inofyta, where the heavily contaminated stormwater is discharged into the river. As soon as reeds were harvested, they were air dried for 48 h and chopped into small pieces obtaining particle size of 1-2 cm. Elemental analysis was carried out using X-ray fluorescence spectrometry (XRF) (Spectro Xepos). Sample preparation involved drying at 103 °C for 24 hours and crushing to -100 µm. Cr(VI) was measured colorimetrically applying the diphenylcarbazide method (US EPA method 7196A). Soluble COD was determined by the sealed tube method (ISO 15705). The concentration of adsorbed Cr(VI) in the reed was determined by desorption, by elevating the pH of the reed solution at 11.

### **2.2. Up-flow percolation column experiments**

The removal capacity of reed material was investigated using up-flow percolation column experiments. In order to simulate the conditions of the stormwater, a 5 mg/L Cr(VI) solution with pH equal to 8.5 was prepared. Plexiglas columns of 7 L (height=1 m, diameter=9.44 cm) were filled with chopped reed and a peristaltic pump was used in order to achieve contact time equal to 8 h (constant at all column experiments). The first two (2) column experiments conducted with different L:S values (4.5:1, 3.5:1) in order to investigate the influence of L:S on Cr(VI) removal and lasted 8 h. The third column experiment lasted 290 h, the column was fed continuously with 5 mg/L solution and the L:S ratio was 4.5:1. The water velocity in all experiments was estimated equal to 10 cm/h.

### **2.3. Batch experiments**

The influence of pH, L:S ratio and contact time on Cr(VI) removal of reed material was investigated using batch experiments. 20 g of chopped reed was added in Erlenmeyer flasks containing water with 5 mg/L Cr(VI) initial concentration. The flasks were placed at an orbital shaker at 200 rpm, under aerobic conditions and at room temperature.

Firstly, the influence of contact time on Cr(VI) removal, was tested for several values of contact time ranged between 8 to 28 h (15 different values), while pH and L:S ratio values were constant and equal to 8.5 and 4.5:1, respectively. Afterwards, the effect of L:S was tested for seven (7) different values (2.5-8.5), keeping constant the pH (8.5) and contact time values (8 h). Finally, the effect of pH was tested conducting twelve (12) different batch tests with four (4) pH values (5.5, 6.5, 7.5, 8.5) at three (3) different cases of contact time (8, 20, 26 h). In all cases, the L:S ratio was kept constant (4.5:1).

### **2.4. Cr(VI) removal mechanism**

In order to determine the Cr(VI) removal mechanism, desorption experiments carried out after each column experiment. An amount of 50 g of used reed material and 450 ml of deionized water were placed in Erlenmeyer flasks, while pH was adjusted at 11, using 1 M NaOH solution. The desorbed Cr(VI) was measured after 24 h. By the end of the experiments, reed material was dried and elemental analysis was carried out. XRF was used to measure Cr concentration before and after the adsorption experiment .

## **3. Results and discussion**

### **3.1. Reed characterization**

Elemental analysis of reed showed that 43.4 mg of Cr(total) per kg of reed material existed in the reed as collected from the field. However, the desorption experiment that followed indicated, that

Cr(VI) in the reed material was not detectable, demonstrating that the entire mass of Cr existed most likely as Cr(III). The soluble COD measured equal to 1 mg/L after 24 h when 100 g of reed material were placed in 450 ml deionized water.

### **3.2. Results of column experiments**

Column experiments aimed at investigating the Cr(VI) removal capacity of reed material. Firstly, two (2) column experiments with different L:S ratios (4.5:1 and 3.3:1) but with similar pH (8.5), contact time (8 h) and initial Cr(VI) concentration (5 mg/L) were conducted. No difference on Cr(VI) removal was observed by the results of the experiments, since the achieved removal was 75% and 73%, respectively. The effect of L:S ratio on Cr(VI) removal capacity was further investigated carrying out batch experiments (see Section 3.3).

Furthermore, another percolation experiment conducted in order to define the effect of operation time (column was fed continuously with 5 mg/L solution for 290 h while the contact time was constant at 8 h) on Cr(VI) removal. The maximum Cr(VI) removal was achieved at the first 8 hours and was estimated at 75%. For higher values of operation time Cr(VI) removal was gradually decreased, reaching 20% after 290 h of column operation, indicating that the material was saturated regarding its Cr(VI) removal capacity (see Figure 1a). The decrease of Cr(VI) removal was followed by decrease of soluble COD values, from 740 mg/L to 34 mg/L during 290 h, showing that Cr(VI) reduction took place and removal efficiency is proportional to the COD of the system. These results are in accordance with another study (Elangovan et. al., 2007). The total volume of Cr(VI) solution passed through the column was 100 L and the maximum Cr(VI) removal capacity of reed was estimated at 380 mg of Cr(VI) per kg of reed. Based on the figure presented below (see Figure 1a), it is obvious that reed is a potential biosorbent that currently, at least partially, treat the heavily Cr(VI)-contaminated stormwater discharge that flows into the Asopos River. However, it is also obvious that Cr(VI) removal by reed cannot be used as the main treatment scheme, at least for this particular case, since almost 600 t per year of reed material would be required to treat the stormwater discharge (approximately 5 mg/L; 5 m<sup>3</sup>/h). However, this treatment scheme is still an alternative pretreatment solution to reduce the required capacity and subsequently the cost of the following main treatment scheme.

### **3.3. Results of batch experiments**

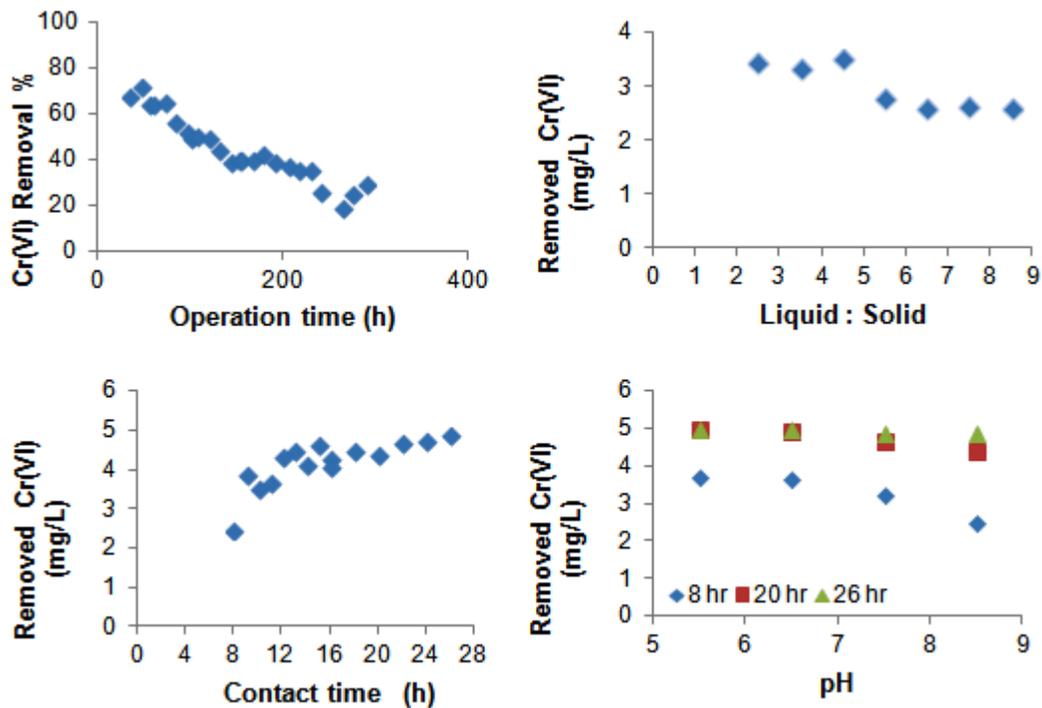
In order to further investigate the effect of L:S ratio on Cr(VI) removal, a series of batch experiments were conducted. The results showed that increasing the amount of reed in the system (increasing the S factor), Cr(VI) removal was not affected significantly, since by decreasing the L:S ratio four (4) times, Cr(VI) removal was increased almost 14%. Keeping constant the contact time (8 h), for ratios between 2.5:1 and 4.5:1, Cr(VI) removal was 3.5 mg/L, while for ratios between 5.5:1 and 8.5:1, Cr(VI) removal decreased at 2.5 mg/L (see Figure 1b).

A second series of fifteen (15) batch experiments investigated the influence of contact time on Cr(VI) removal. The results showed that the minimum contact time required for total removal of Cr(VI) (5 mg/L) was 26 h (see Figure 1c).

The last series of twelve (12) batch experiments aimed at testing the pH influence on Cr(VI) removal. The results showed that 20 h were sufficient for total Cr(VI) removal under acidic conditions (pH<6.5). However, for the pH values prevailing in the contaminated site (pH≈8.5), more than 26 h are demanded (see Figure 1d). These results are in accordance with those of other studies (Carg et. al., 2004, Park et. al., 2005, Elangovan et. al., 2008), which showed that Cr(VI) removal increases with decreasing pH values. Therefore, both water pH values and contact time are two crucial factors affecting Cr(VI) removal.

### 3.4. Cr(VI) removal mechanism

After the column experiment during which 73% of Cr(VI) was removed (Section 3.2), XRF analysis carried out at the used reed material, showing an increase of Cr(total) from 43.4 mg/kg (Section 3.1) to 129 mg/Kg. Afterwards, a desorption experiment at the used reed material was carried out in order to determine the concentration of Cr(VI). No Cr(VI) was detected, though. However, a second XRF analysis at the reed material sample after desorption showed a significant decrease of Cr(total) concentration at 56 mg/Kg. This decrease most likely is possibly attributed to the loss of Cr(III), which is soluble in alkaline environment (pH>10) (Remoudaki *et al.*, 2003). These results indicate that the Cr(VI) removal mechanism is probably the reduction of Cr(VI) to Cr(III), by the biomaterial. Park *et. al.* (2005), showed that Cr(VI) can be removed from an aqueous system by natural biomaterials through both direct and indirect reduction mechanisms. According to this mechanism, Cr(VI) is reduced to Cr(III) by biomaterial and then part of Cr(III) is adsorbed to biomaterial. The amount of adsorption strongly depends on the nature of the biomaterial.



**Figure 1:** a) Cr(VI) removal capacity over operation time during the column experiment. b) Cr(VI) removal vs. L:S ratio in batch experiments. c) Cr(VI) removal over contact time in batch experiments. d) Cr(VI) removal vs. pH values in batch experiments.

### 4. Conclusions

The present study investigated the Cr(VI) removal efficiency of reed that naturally exists in the Asopos river bed. The main conclusions drawn from this study are listed below:

- Reed material can treat heavily Cr(VI) contaminated water, if sufficient contact time is provided.
- pH values severely affect Cr(VI) removal. However, in cases where pH values adjustment is not possible, sufficient contact time with reed material should be provided.
- L:S ratio do not significantly affect the Cr(VI) removal in the range of 2.5:1 and 8.5:1, however further investigation is required to conclude the ideal L:S ratio that can achieve satisfactory performance at low cost.

- The time required for reed saturation, after which no Cr(VI) removal is possible, is an important parameter that should be taken into account during the design of a potential treatment system.
- For the Cr(VI) contaminated water discharged to Asopos River at Inofyta a contact time of 26 h is required for total Cr(VI) removal at 8.5 pH, if L:S ratio is equal to 4.5:1.
- Cr(VI) removal by reed material is most likely a two-step mechanism, where Cr(VI) is initially reduced to Cr(III) and then part of Cr(III) is adsorbed to the reed material.

Although reed material demonstrates significant Cr(VI)-removal performance, the high amount of reed required render this method unsuitable for heavily contaminated water flows. However, reed material is still a promising biosorbent alternative that might be used for pretreatment purposes.

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