

TREATMENT OF Cr(VI)-CONTAMINATED WATER DISCHARGED TO ASOPOS RIVER USING LOW-COST NATURAL MATERIALS

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ABSTRACT

Batch experiments were carried out using three (3) low-cost natural materials in order to examine their Cr(VI)-removal ability from contaminated water. These materials were reeds, in ground (R_g) and non-ground form (R), plant-derived compost (C) and stabilized wastewater sludge (S). Experiments were conducted with initial Cr(VI) concentration of 3 mg/L and pH value equal to 8.5 ± 0.5 . The concentration of the organic material used was 100 g/L. Initial Cr(VI) concentration and pH value simulated the physicochemical conditions prevailing in a stormwater outfall flowing into the Asopos river in Inofyta, Central Greece. The discharge contained mainly draining stormwater, but also contaminated groundwater from nearby industries.

Experimental results revealed that initial Cr(VI) concentration of 3 mg/L could be completely removed by all materials, given sufficient time. Cr(VI) removal followed a first order reaction kinetic model. The half-life time ($t_{1/2}$) for the tested initial Cr(VI) concentration was 2.21 h for R_g , 3.68 h for C, 4.78 h for R and 24.24 h for S. A major Cr(VI) decrease was observed in the first 5 minutes at all samples, which was the greatest (40.8%) for R_g sample and was attributed to Cr(VI) adsorption. Soluble organic matter from reed, measured as chemical oxygen demand (COD), showed a continuous increase, with maximum values of 1305 mg/L (R) and 3455 mg/L (R_g). Given that these were positively correlated to Cr(VI) removal, the latter is concluded to occur through a chemical reduction mechanism. Significantly lower COD values for compost (max 437 mg/L) and sludge (max 417 mg/L) were observed and these were quickly stabilized. It was concluded that compost and sludge removed Cr(VI) through a microbially-mediated reduction, as evidenced by the constant COD and decreasing dissolved oxygen and redox potential, which also caused a rise in pH value.

Keywords: Hexavalent chromium, low-cost materials, natural materials, biosorbents, batch experiments

1. Introduction

The main oxidation states of chromium in the geoenvironment are the trivalent [Cr(III)] and hexavalent [Cr(VI)] forms (Fendorf, 1995). Cr(III) is, in small quantities, an essential trace element for the human body, but Cr(VI) compounds have been proven to be carcinogenic and irritants (WHO, 2003). High-level concentration of Cr(VI) in the geoenvironment is commonly attributed to anthropogenic activities (Boni and Scaffoni, 2009).

Among chemical, physicochemical and biological methods for treatment of industrial wastewater and groundwater contaminated with Cr(VI), adsorption has been widely used for Cr(VI) removal (Mohan and Pittman, 2006). In search of low-cost adsorbents, natural materials, such as agricultural and

industrial biowaste, have been studied (Bailey *et al.*, 1999, Fu and Wang, 2011). Organic materials are also an example of natural materials, characterized as biosorbents. Cr(VI) removal using biosorbents takes place through the combination of adsorption and reduction mechanisms (Park *et al.*, 2007).

Surface and groundwater contamination with Cr(VI) is one of the major problems that the area of Inofyta currently faces. Located in Boeotia, Central Greece, Inofyta is an unplanned industrialized region in which several Cr-using industries were established back in the 1980s. This has resulted to substantial groundwater contamination of the Asopos river basin, where, in some cases, Cr(VI) concentrations exceed 100 µg/L. Despite the increased public concern, there are still Cr(VI) sources discharging high amounts of Cr(VI) into environment. One of them is a stormwater outfall in the south region of Inofyta, which is currently discharging contaminated water into the Asopos river. The discharge has Cr(VI) concentration ranging from 3.3 to 4.8 mg/L. The route of the stormwater pipe is not precisely known, but it includes an industrial cluster, so that it is speculated that probably contaminated groundwater is entering the drainage through cracks in the piping. In order to protect the local ecosystem from this discharge, a treatment system using biomaterials that removes Cr from the discharge is considered as an option.

The study presented herein aims at investigating the Cr(VI) removal ability of three (3) low budget natural organics that are locally available and might be used for the treatment of Cr(VI)-contaminated water.

2. Materials and methods

2.1. Natural materials preparation

The materials investigated herein can be classified as natural organics and have been studied for their Cr(VI) removal ability (Rawajfih and Nsour, 2008, Vargas *et al.*, 2012, Wu *et al.*, 2010). Material selection was based on their low cost and their availability at the investigated site. These materials are: a) reeds (plants of *Phragmites* spp.) that naturally grow in the riverbed of Asopos river, b) plant-derived compost of standard quality that is produced in a local industry and, c) stabilized wastewater sludge from the nearby "Schimatari-Inofyta" wastewater treatment plant, after being thickened and dewatered. After their collection, materials were dried at room temperature, were ground and sieved to obtain grain size ≤ 2 mm. Treated materials were stored in airtight plastic bags. From the above-mentioned preparation samples of ground reed (R_g), non-ground reed (R) composed of 5-7 cm size particles, sludge (S) and compost (C) were obtained and used in the batch experiments.

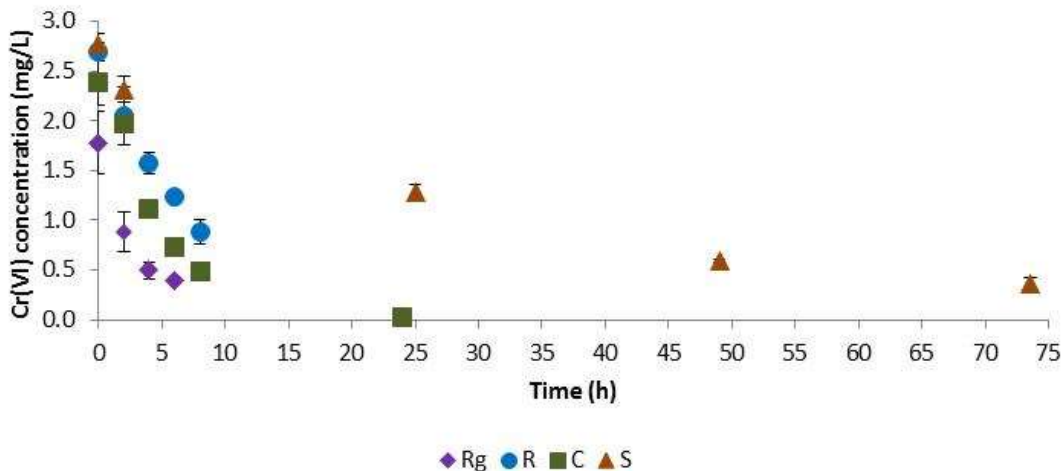
2.2. Batch experiments

Batch experiments were conducted in triplicate reactors so as to assess the material behavior related to Cr(VI) removal ability. The liquid to solid (L:S) ratio used was 10:1, using 45 g of dry solid material. Cr(VI) stock solution was prepared with 3 mg/L Cr(VI) concentration and pH value 8.5 ± 0.5 . All experiments were performed in 1 L reactors under aerobic conditions, without mechanical stirring. Samples of the supernatant were periodically removed, filtered and analyzed for Cr(VI) according to method 7196A (U.S. EPA, 1992). Except Cr(VI) concentration, at each sampling point soluble COD was also determined by Standard Method 5220D (APHA *et al.*, 2005). Total sampling volume in each experimental set did not exceed 10% of the solution volume.

3. Results and discussion

3.1. Cr(VI) removal

Triplicate batch experiments revealed that all samples can completely remove 3 mg/L of Cr(VI), however, at different time. Materials classification according to Cr(VI) removal rate was $R_g > C > R > S$ (see Figure 1). In particular, 70% removal of Cr(VI) occurred in 2 h for R_g , 6 h for C, 8 h for R and 38 h for S, indicating that ground reed is the most efficient material, non-ground reed and compost is similarly efficient but less than the ground reed and sludge is by far the less efficient material.



Note: Error bars depict standard deviation values based on triplicate experiments.

Figure 1. Cr(VI) concentration profile.

A major decrease of initial Cr(VI) concentration was detected for all samples at the first sampling point of 5 minutes, which did not fit the first-order kinetic model that followed the remaining points. At this time, 7.7 - 40.8% of initial Cr(VI) concentration was removed. The maximum value (40.8%) was identified for R_g sample, while C, R and S samples demonstrated 20.6%, 10.2% and 7.7% Cr(VI) removal, respectively. While the longer-term removal mechanism was determined to be primarily reduction (as will be discussed later), this initial removal was thought to be either absorption (removal by the bulk material) or adsorption (removal by the surface). Absorption could occur initially, as the materials absorbed water into their structure.

In order to differentiate between the two processes, an experiment was conducted by comparing the initial removal by R_g sample using pre-wetted and dry material. The Cr(VI) measurement of the pre-wetted sample at 5 min was 1.76 mg/L, which is almost the same with the 1.78 mg/L measured in the dry sample experiment. The microporous reed structure has been shown to have high Cr(VI) uptake through adsorption mechanism (Rawajfih and Nsour, 2008), a phenomenon that is enhanced in the ground reed sample.

3.2. Chemical kinetics

Kinetic models based on first and second order reactions were used for interpretation of Cr(VI) concentration decrease over time. Through kinetic models equations constant reaction rates (k) and linear correlation coefficients (R^2) were calculated. Comparing R^2 coefficients, it was obvious that the Cr(VI) decrease was best described by a first order rather than second order reaction, except the R_g sample (see Table 2).

Table 2. Values calculated for k rates and R^2 coefficients for first and second order kinetic models and $t_{1/2}$ for first order kinetic model, in triplicate experiments.

| Samples | 1st order | | 2nd order | | 1st order |
|----------------|--------------------------|-------|--|-------|---------------|
| | k_1 (h ⁻¹) | R^2 | k_2 (Lmg ⁻¹ h ⁻¹) | R^2 | $t_{1/2}$ (h) |
| R _g | -0.313 | 0.902 | 0.363 | 0.988 | 2.21 |
| R | -0.145 | 0.993 | 0.093 | 0.966 | 4.78 |
| C | -0.188 | 0.994 | 1.397 | 0.905 | 3.68 |
| S | -0.029 | 0.990 | 0.032 | 0.967 | 24.24 |

This occurs as R^2 and k calculation is based on 4 sampling points. Thus for R_g sample, first order kinetics is taken into consideration. Using k_1 reaction rates, half-life time was calculated ($t_{1/2}$) (see Table 2). The R_g sample had the shortest half-life time of 2.21 h, followed by the C sample with 3.68 h and the R sample with 4.78 h. S had the greatest half-life of 24.24 h. In terms of reed, the R_g sample removed Cr(VI) 2.2 times faster than R.

3.3. Soluble COD

Figure 2 demonstrates an increase in soluble COD values over time for all materials. The COD values of reed samples were much higher compared to the other materials, especially for the ground sample (see Figure 2a).

In both reed samples (R_g and R), the continuous COD increase is most likely attributed to the released organic material, which has been proven to have a significant role in Cr(VI) reduction (Elangovan *et al.*, 2008). COD values were significantly higher for R_g (1756-3455 mg/L) compared to R (263-1305 mg/L). A strong linear correlation between Cr(VI) removal and soluble COD was observed in both reed samples ($R^2 = 0.95-0.97$) (see Figure 2b). This correlation leads to the conclusion that Cr(VI) removal by reed is through a chemical reduction mechanism, facilitated through the release of dissolved organic material from the solid.

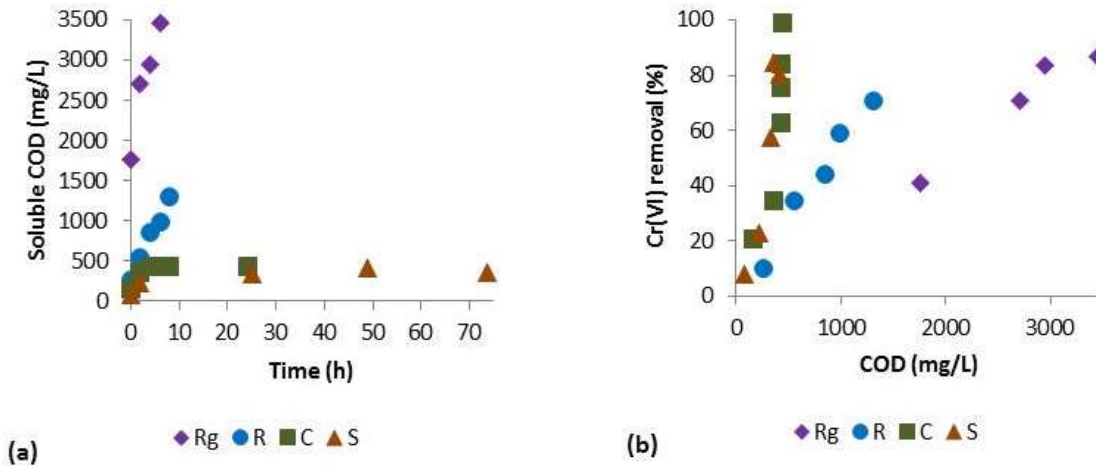


Figure 2. Soluble COD values over time **(a)** and Cr(VI) percentage removal and soluble COD correlation **(b)** in triplicate batch experiments.

In the compost and sludge samples, a smaller initial COD increase was observed, followed by value stabilization at 400-450 mg/L, implying that the organic substance leached from S and C samples did not have resemblance to that of reed samples. Despite the COD stabilization, Cr(VI) removal continued in both C and S, which indicated that chemical reduction was not the main removal mechanism. Instead, the decreasing redox potential and dissolved oxygen measurements indicated that microbial activity was substantial, consuming the available oxygen faster than it could be replenished (the bottles were open to the atmosphere). Thus, it is concluded that microbially mediated reduction, which is a redox-sensitive process under both aerobic and anaerobic conditions (Chen and Hao, 1996), was the active removal mechanism in C and S samples. PH values (6.0-7.5) revealed the prevailing buffering capacity of all samples that altered initial pH of Cr(VI) solution. Cr(VI) removal through reduction mechanism is proven to rise pH values because of H^+ consumption (Park *et al.*, 2004), a fact that is verified for C and S samples.

4. Conclusions

Batch experiments revealed that reed, compost and stabilized sludge could remove Cr(VI) from the stormwater with varying efficiency. The most efficient materials were reed and compost, while

stabilized sludge was much slower to reduce the initial Cr(VI) concentration of 3 mg/L. Following first-order reaction kinetics, ground reed (R_g) demonstrates the shortest half-life time (2.21 h), followed by compost (3.68 h) and non-ground reed (4.78 h). Sludge yielded the highest half-life time (24.24 h). However, all materials (reed, compost, sludge), completely removed the initial Cr(VI) concentration of 3 mg/L, given enough time. Cr(VI) removal took place both through reduction and adsorption mechanisms; a major Cr(VI) decrease in the first 5 minutes was attributed to Cr(VI) adsorption, especially for R_g sample, which removed 40.8% of Cr(VI). The concentration of soluble organic matter released from reed (maximum values of 1305 mg/L for non-ground and 3455 mg/L for ground) was significantly higher, than that released from compost (437 mg/L) and sludge (417 mg/L). In addition, released soluble organic substances by reed were found to facilitate Cr(VI) removal through a chemical reduction mechanism. In contrast, compost and sludge removed Cr(VI) through a microbially-mediated reduction, as evidenced by the constant COD and decreasing dissolved oxygen and redox potential. These observations support the idea that, in practice, a smaller treatment plant using ground reed or a mix of compost and non-ground reed would be more efficient for the stormwater treatment in Inofita. However, material selection should also consider other criteria such as availability, capital and O&M cost and environmental impacts.

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