

A microcosm study of permeable reactive barriers filled with granite powder and compost for the treatment of water contaminated with Cr (VI)

AUTHORS

Cancelo-González J.^{@,1}
javier.cancelo@usc.es

Prieto D.M.¹

Paradelo R.²

Barral M.T.¹

© Corresponding Author

¹ Departamento de Edafología e Química Agrícola, Facultade de Farmacia, Universidade de Santiago de Compostela. Campus Vida. 15782 Santiago de Compostela (A Coruña), Spain.

² Departamento de Bioloxía Vexetal e Ciencia do Solo, Área de Edafología e Química Agrícola, Facultade de Ciencias, Universidade de Vigo. As Lagoas s/n. 32004 Ourense (Ourense), Spain.

Estudio a escala de microcosmos de barreras permeables reactivas con serrines graníticos y compost para el tratamiento de aguas contaminadas con Cr (VI)

Estudo a escala de microcosmos de barreiras reativas permeáveis com serragem de granito e composto para o tratamento de água contaminadas com Cr (VI)

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ABSTRACT

The permeable reactive barrier (PRB) is a technology developed for the removal of contaminants in groundwater. It consists of a screen perpendicular to the flow of contaminated groundwater filled with a material capable of adsorbing, precipitating or degrading pollutants. Several materials have been tested for their use as reactive substrates for the construction of PRBs. Waste materials are of particular interest for this purpose due to the possibility of their reuse and their generally lower cost. With this aim, the Cr (VI) retention capacity of a filler material consisting either of pine bark compost (PB) or a 50% mixture of compost and granite powder (PB50) was evaluated using an experimental device specifically designed for this study, which reproduces a permeable reactive barrier at the laboratory scale. Percolation experiments were carried out with a solution of 100 mg L⁻¹ Cr (VI) in 0.01M KNO₃, followed by a leaching step with the saline background. The results show that compost is a highly efficient filler for permeable reactive barriers with almost 100% retention of Cr, whereas the retention efficiency of the mixture of PB50 oscillated between 18 and 46% during the experiment. The Cr retained by the filling material is strongly fixed, since no desorption was detected by leaching with the saline background, and concentrations in the standard Toxic Characteristic Leaching Procedure (TCLP) extracts were lower than 1 mg L⁻¹. This behaviour minimizes the risk of release of the Cr retained by the material of the barrier in the event of it being traversed by water not contaminated with Cr. Modelling with Visual Minteq indicates that in the experiments with PB, the reduction of Cr (VI) to Cr (III) occurs and that Cr (III) is associated with dissolved organic matter, which is a form of lower toxicity than the initial Cr (VI) species. In turn, in the experiments with PB50, Cr (III) and Cr (VI) coexist and the oxidised form is not associated with dissolved organic matter, which suggests greater toxicity. The results indicate that pine bark compost is a potential candidate for use as filler material permeable reactive barriers.

RESUMEN

Las barreras permeables reactivas (BPRs) son tecnologías de eliminación de contaminantes en aguas subterráneas, que consisten en una pantalla perpendicular al flujo de agua subterránea contaminada, rellena de un material con capacidad de adsorber, precipitar o degradar los contaminantes. Se han evaluado diversos materiales reactivos como material de relleno de BPRs, siendo de especial interés la utilización de materiales residuales, por la posibilidad de su reutilización y, frecuentemente, menor coste. Con este fin se estudió la capacidad de retención de Cr (VI) de compost de corteza de pino (PB) y de una mezcla al 50% de compost y serrines graníticos (PB50), utilizando un dispositivo diseñado específicamente para este estudio, que reproduce una barrera permeable reactiva a escala de laboratorio. Para evaluar la retención se llevó a cabo un experimento de percolación con una disolución de 100 mg L⁻¹ de Cr (VI) en KNO₃ 0,01M, seguido de una etapa de lavado con el fondo salino, para evaluar la liberación del Cr previamente retenido. Los resultados mostraron una gran eficacia del compost como material de relleno de

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BPRs, consiguiendo una retención de Cr cercana al 100%. La mezcla de serrín granítico y compost presentó una capacidad de retención que osciló entre el 18 y el 46% a lo largo del experimento. El Cr retenido por el material de relleno se encuentra fuertemente fijado, pues no se desorbe por lixiviación con la solución salina y las concentraciones en los extractos obtenidos mediante la aplicación del procedimiento estándar de lixiviación Toxic Characteristic Leaching Procedure (TCLP) fueron inferiores 1 mg L^{-1} . Este comportamiento minimiza el riesgo de liberación del Cr retenido por el material de la barrera, en el supuesto de que fuera atravesada por un agua no contaminada con Cr. La modelización con Visual Minteq indica que, en los eluatos de los experimento con PB, se ha producido reducción de Cr (VI) a Cr (III), y éste se encuentra asociado con la materia orgánica disuelta, lo que sugiere una reducción de la toxicidad en comparación con la que presenta el Cr (VI) introducido en la solución de percolación. En los eluatos del experimento con PB50 se encuentran tanto Cr (III) como Cr (VI), y la forma oxidada no se encuentra asociada con la materia orgánica disuelta. Los resultados de este estudio indican que el compost de corteza de pino tiene un gran potencial para ser usado como material de relleno de barreras permeables reactivas.

RESUMO

Entre as tecnologias desenvolvidas para a remoção de contaminantes em águas subterrâneas são as barreiras permeáveis reativas (BPRs), as quais consistem de uma trincheira perpendicular ao fluxo das águas subterrâneas contaminadas, cheia com um material capaz de adsorver, precipitar ou degradar poluentes. Diversos materiais foram ensaiados como substratos reativos na construção de BPRs, sendo de interesse a utilização de materiais residuais, pela possibilidade de reutilização e, geralmente, menor custo. Para este fim foi avaliada a capacidade de retenção de Cr (VI) de um composto de casca de pinheiro (PB) ou uma mistura de 50% de composto e pó de serragem de granito (PB50), usando um dispositivo experimental que simula uma barreira permeável reativa a escala de laboratório. Experiências de percolação foram levadas a cabo com uma solução de 100 mg L^{-1} de Cr (VI) em $0,01 \text{ M KNO}_3$, seguida por um passo de lavagem com a solução salina. Os resultados obtidos mostram uma alta eficácia do composto, com uma retenção de 100% de Cr. A eficiência de retenção da mistura de serradura de granito e de composto oscilou entre 18–46% ao longo do experimento. O Cr é fortemente retido pelo material de enchimento, não desorvido por lixiviação com a solução salina, enquanto que as concentrações dos extractos obtidos pela aplicação do procedimento de lixiviação standar Toxic Characteristic Leaching Procedure (TCLP) eram inferiores a 1 mg L^{-1} . Este comportamento reduz o risco de a liberação da carga de Cr retida pelo BPR o que poderia acontecer se águas limpas passan através da barreira. O modelado com Visual Minteq indica que nas experiências com PB ocorre redução de Cr (VI) a Cr (III), e que o Cr (III) está associado com a matéria orgânica dissolvida, que é uma forma de toxicidade mais baixa do que as espécies de Cr (VI) iniciais, enquanto nas experiências com PB50, Cr (III) e Cr (VI) coexistem, e o Cr (VI) não está associado com a matéria orgânica dissolvida, o que sugere uma maior toxicidade. Os resultados indicam que o composto de casca de pinheiro é um candidato potencial para utilização como material de enchimento de barreiras permeáveis reativas.

KEY WORDS

Chromium, bioremediation, sorption, decontamination, waste, reuse

PALABRAS

CLAVE

Cromo, adsorción, descontaminación, biocorrección, residuos, reutilización

PALAVRAS-

CHAVE

Crómio, adsorção, desorção, descontaminação, biorremediação, resíduos

1. Introduction

Water pollution by chromium is an environmental hazard that poses serious risks to human health. Cr exists in nature in two stable oxidation states: Cr (III) and Cr (VI), which differ in terms of mobility, bioavailability and toxicity. Cr (VI) is toxic, mutagenic and potentially carcinogenic, and has great mobility. In contrast, Cr (III) is considered as an essential nutrient, less toxic and less mobile than Cr (VI).

The most common Cr form in nature is Cr (III); however, under strongly oxidizing conditions, Cr is found as Cr (VI), mostly as a chromate anion (CrO_4^{2-}). In turn, Cr (VI) can be reduced to Cr (III) in environments where a ready source of electrons is available: dissolved Fe (II), reduced Mn

oxides or reduced S compounds. Organic matter can also act as an electron donor, the reduction being more favourable in acid than in alkaline environments (Bartlett and Kimble 1976; Cary et al. 1977). It has been found that the addition of a C source and protons can stimulate microbial activity, thus favouring the reduction of Cr (VI) to Cr (III) (Losi et al. 1994; Bolan et al. 2003).

Chromium pollution is mainly derived from mining and industrial activities. Cr is used in many products and industrial processes such as leather tanning, wood treatments and chrome plating (USEPA 1997). Many of these industrial applications use Cr in the VI oxidation state. Occasionally, Cr reaches the soil through spillages and disposal. As rainwater infiltrates into the soil, Cr may dissolve and Cr-rich lixiviates can reach the water table, causing contamination of groundwater and leading to potential problems for drinking water quality.

Among the technologies for groundwater remediation, permeable reactive barriers (PRBs) are considered suitable systems for the treatment of contamination plumes. This technique is based on the *in situ* installation of a trench perpendicular to the direction of the flow of the polluted plume. The walls of the barrier are permeable and allow the passage of water, contacting the filler material (reactive material) which can adsorb, precipitate or degrade the contaminants. As the contaminated water passes through the reactive zone of the barrier, the harmful chemicals are retained or transformed into harmless substances (USEPA 1997). Selection of the reactive material used to construct PRBs will depend on the substances that have to be removed and on the mechanism used for this purpose (adsorption, precipitation or degradation). One of the most commonly used materials is granulated metallic Fe⁰, which has been used to degrade organic compounds and to precipitate organic and inorganic substances (USEPA 1997), but other materials such as compost have also been tested (Boni and Sbaiffoni 2009).

Traditionally, Cr treatment technologies include ion exchange and chemical reduction followed by precipitation (Benefield et al. 1982). PRBs filled

with Fe⁰ have been used to treat groundwater contaminated with Cr (VI), reducing Cr (VI) to Cr (III) and giving rise to the coprecipitate Cr_xFe_{1-x}(OH)₃ (James and Barlett 1983; Palmer and Wittbrodt 1991). Other Fe compounds, such as Fe sulphides and Fe oxyhydroxides, also promote the reduction and precipitation of the chromate anion (Blowes et al. 2000). The use of biological materials has been proved as an alternative to the mentioned methods due to their removal efficiency and low cost (Battacharayya et al. 2008; Jain et al. 2009; Miretzky and Cirell 2010). Particularly, diverse biosorbents have been used to remove Cr (VI) from contaminated waters (Boddu et al. 2003; Koby 2009).

The use of readily available, safe and inexpensive waste materials as filler materials for PRBs represents an interesting opportunity from an economic and environmental perspective. In a previous study, Barral et al. (2014) conducted batch type experiments addressed to evaluate the Cr (VI) adsorption capacity of granite powder (GP), pine bark compost (PB), composted municipal solid waste (M) and mixtures containing different proportions of GP and compost. Individually, GP was not suitable for use as a PRB filler because of its moderate permeability and Cr (VI) adsorption capacity. The addition of compost M decreased the hydraulic conductivity of the mixtures and only slightly improved the adsorption capacity. In turn, the addition of compost PB increased the hydraulic conductivity and improved the Cr (VI) adsorption capacity of the material, while decreasing Cr desorption. Adsorption data for compost PB were well fitted by the Langmuir model and the maximum adsorption capacity (X_m) determined was 21 mg g⁻¹. This value was in accordance with that found by Wei et al. (2005) for the adsorption of Cr (VI) on compost (36 mg g⁻¹) and higher than the value reported by Jain et al. (2009) for sunflower waste biomass (8 mg m⁻¹). Barral et al. (2014) recommended mixtures containing 50 or 25% granite powder and 50 or 75% pine bark compost (v/v), respectively, as the best materials for use as PRBs in relation to cost/effectiveness.

In this work the use of pine bark compost and its mixture with granite powder as PRB filler is tested at a microcosm scale. To this end, an experimental device that was called “reactive box” was specifically designed to evaluate Cr (VI) retention capacity in conditions that resemble those of the barrier. The reactive box simulates the arrangement of the filler materials in PRBs at a laboratory scale and allows the permeation of Cr solutions and the collection of eluates. Adsorption capacity was evaluated by percolating Cr solutions and determining Cr concentrations in the eluates. Because leachability of the previously retained Cr is a critical aspect of the performance of a PRB, desorption of previously adsorbed Cr was subsequently evaluated by means of percolation experiments with unpolluted solutions and by chemical extraction of the filling materials. Finally, modelling with Visual Minteq was applied to estimate the Cr forms in the eluates, since this is a critical aspect in terms of mobility and potential toxicity.

in windrows and was supplied by Costiña Orgánica (A Coruña, Spain). Granite powder (GP) is a waste product generated during the cutting, polishing and finishing of the blocks extracted from quarries, and was supplied by granite transformation plants located in Porriño (Pontevedra). The industries in this area mainly use local adamellitic granites, with quartz, abundant biotite and equivalent proportions of potassium feldspar and plagioclase, as well as granodiorites and biotite-amphibole granites, with less potassium feldspar than plagioclase and biotite as the principal mica (IGME 1981). GP composition is coincident with that typical of the rocks from which it is originated, except for the concentrations of Ca, Fe and some trace elements which are higher in the granite powder, due to the use of metal filings as abrasive products during the cutting process and the addition of calcium hydroxide to avoid the appearance of iron oxide stains on the stone. More details on GP composition can be found in Barral et al. (2005) and Silva et al. (2013). GP samples were air-dried and gently crushed to <2 mm and then combined into a single representative sample which was employed for PB50 preparation.

2. Materials and Methods

2.1. Reactive materials

The reactive materials tested were: 100% pine bark compost (PB) and a 50% (v/v) mixture of PB and granite powder (PB50). PB was obtained through an aerobic transformation

The tested materials were characterized in a previous study (Barral et al. 2014) and their main properties are shown in **Table 1**. GP shows alkaline pH, and low EC and water content; it is practically devoid of organic matter and has a moderately low permeability. In turn, PB has an acidic pH, slightly higher EC and permeability, and is mostly constituted by organic matter.

Table 1. General properties of the tested materials. EC: electrical conductivity; CBD: compacted bulk density; OM: organic matter; NTK: Total Kjeldahl N; k_s : saturated hydraulic conductivity; nd: not detected, - not determined; GP: granite powder; PB: composted pine bark; PB50: 50% mixture (v:v) of pine bark and granite powder.

| | pH | EC (dS m ⁻¹) | CBD (g L ⁻¹) | Water content (%) | Ashes (%) | NTK (g kg ⁻¹) | C (g kg ⁻¹) | ks (m s ⁻¹) |
|-------------|-----|--------------------------|--------------------------|-------------------|-----------|---------------------------|-------------------------|-------------------------|
| GP | 9.2 | 0.23 | 1035 | 1.7 | 99.9 | nd | 0.7 | 5.3·10 ⁻⁰⁷ |
| PB | 5.3 | 0.37 | 455 | 62.9 | 8.62 | 2.8 | 531.0 | - |
| PB50 | 8.4 | 0.22 | 682 | 16.9 | 88.2 | 0.3 | 69.0 | 11.0·10 ⁻⁰⁷ |

2.2. Experimental Device ("Reactive Box")

For this study an experimental device called "reactive box" was specifically designed to simulate, at a microcosm level, a reactive barrier disposed vertically through which the contaminant plume passes. The "reactive box" consists of a prismatic container (25 x 15 x 12 cm), which can be divided into two compartments by a sheet of multiperforated methacrylate (Figure 1). The first compartment, which occupies a third of the volume of the device, is filled by washed quartz sand, aimed at achieving a homogeneous distribution

of the percolating liquid, and the rest is filled by the reactive material. A 0.5-cm diameter hole at the bottom end of the first compartment allows the entry of the solutions. The pollutant output is produced by another hole located at the top of the opposite face of the box, to ensure that the fluid path includes all the material under test. The device includes a reservoir for the solutions to be percolated, which move through a flexible tube, driven by a Gilson peristaltic pump operating at 2 rpm. It was previously demonstrated that the material is homogeneously wetted, and no apparent preferential flow areas were observed.

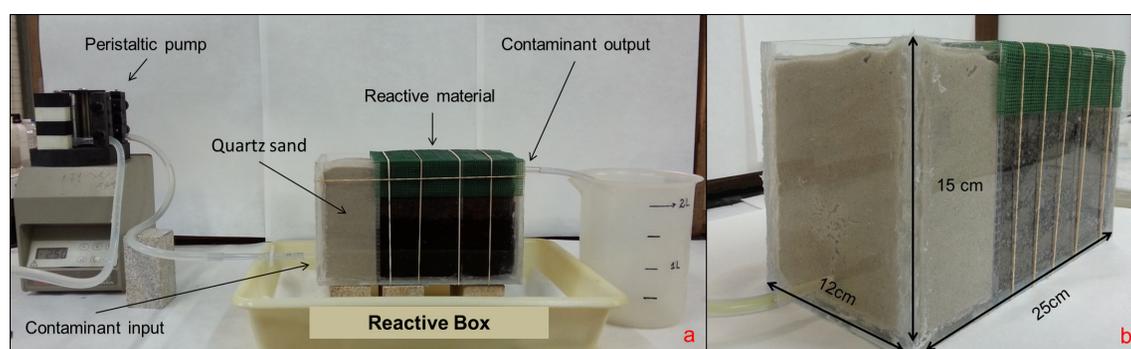


Figure 1. Reactive box for percolation experiments: a) Experimental setup, and b) Detail of the Reactive Box.

2.3. Experimental procedure

The device was initially saturated with a 0.01M KNO_3 solution. Subsequently, a solution of 100 mg L^{-1} of Cr (VI) (as $\text{K}_2\text{Cr}_2\text{O}_7$) in a 0.01M KNO_3 saline background was percolated, in a volume approximately equivalent to four pore volumes (8 L). To evaluate the desorption of the Cr retained by the reactive material, a leaching experiment was subsequently performed with 0.01M KNO_3 solution, in a volume equivalent to four pore volumes (8 L). The total duration of the experiment was about 30 h. Consecutive aliquots of 0.5 L of effluent were collected during the adsorption and desorption steps (approximately every hour) and submitted to analysis of Eh, pH, total Cr, inorganic carbon (IC) and total organic carbon (TOC) as described below.

2.4. Chemical analysis of leachates

The pH and Eh of the eluates were measured using a portable electrode (HANNA HI 9025C). Then the eluates were filtered by $0.45 \mu\text{m}$ and total Cr concentration was determined by flame atomic absorption spectroscopy (SPECTRAA220 FS from VARIAN) (detection limit 1 mg L^{-1}). Total carbon (TC) was determined by catalytic oxidation at 680°C and determination of the CO_2 evolved by IR detection (TOC-5000 from SHIMADZU). Inorganic carbon (IC) is determined by measuring the CO_2 released following sample acidification in the same apparatus. Total organic carbon (TOC) was obtained from the difference between TC and IC. All measurements were performed in duplicate.

3. Results and Discussion

2.5. Chemical speciation of the leachates

To estimate the composition of the leachates, the chemical equilibrium model for the calculation of metal speciation Visual MINTEQ version 3.0 (Gustafsson 2010) was applied to eluates from the retention step. For the modelling of the interactions between metallic ions and humic substances, the NICA-Donnan model was used, a combination of the non-ideal competitive adsorption (NICA) isotherm description of binding to a heterogeneous material, coupled with a Donnan electrostatic sub-model describing the electrostatic interactions between ions and the humic material. In the NICA-Donnan model, the specific bond between the cations and the negatively-charged functional groups is described using the NICA isotherm, whereas the non-specific electrostatic bond with any negative charge is described using the Donnan model (Kinniburgh et al. 1996). The model assumes that the humic substances present two binding sites, mainly attributed to the carboxylic and phenolic functional groups (Milne et al. 2001). Additionally, the model considers that the humic substances are formed by a mixture of 90% fulvic acid (FA) and 10% humic acid (HA), which are representative values of humic substances in natural water (Tipping 2002).

2.6. TCLP extractions

To evaluate the potential desorption of the retained Cr, the standard Toxicity Characteristic Leaching Procedure (TCLP), according to EPA Method 1311 (USEPA 1992), was applied to the filler materials removed from the reactive box after the desorption step. An extraction with aqueous acetic acid (a solution made with 5.7 mL glacial acetic acid in 1000 mL distilled water buffered to pH 4.93 with 0.1N NaOH) was performed using a 1:20 solid: solution ratio. The suspensions were shaken on an end-over-end shaker at 30 rpm during 18 h at 23 °C. After the extraction step, samples were centrifuged at 2000 rpm during 15 min and filtered by 0.45 µm. Total Cr was determined in the extracts as explained above.

The percentages of Cr retention and release are presented in **Figure 2**. The first 2 L of the eluate in the sorption step (roughly corresponding to one pore volume) are not represented because in this volume substitution of the saturating saline solution by the Cr solution occurs and Cr concentrations in the eluates are affected by dilution, thus overestimating retention. Similarly, Cr data corresponding to the first 2 L of the eluates in the desorption step are not represented because in this volume substitution of Cr solution by the saline leaching solution occurs and Cr concentrations in the eluates mostly represent Cr remaining in the percolating solution, thus overestimating desorption.

PB compost showed high efficiency as a potential PRB filler, as almost 100% of Cr in the percolating solution was retained by the material throughout the experiment, whereas the mixture of PB and GP only retained between 18 and 46%. Taking into account the percolated volume, the initial Cr concentration and the mass of reactive material, 0.11 mg of Cr per gram of reactive material was retained by PB50 at the end of the sorption experiment, whereas PB retained 1.05 mg g⁻¹. The latter value was notably lower than the maximum adsorption capacity (36 mg g⁻¹) for PB determined by Langmuir model in Barral et al. (2014). Although the compost is more effective for Cr retention, its mixture with GP would improve the constructive properties of the PRB and allow adjusting the hydraulic properties of the mixture to achieve the retention times that would allow the attenuation of the contaminant (Barral et al. 2014).

No desorption was observed in the subsequent percolation with KNO₃ 0.01M, and no significant Cr was extracted by the TCLP procedure (concentrations were under the detection limit 1 mg L⁻¹). This fact confirmed the strong retention of Cr (VI) by the tested material, which is a relevant feature for potential PRB fillers, as Cr would not be remobilised when unpolluted water passes through the barrier.

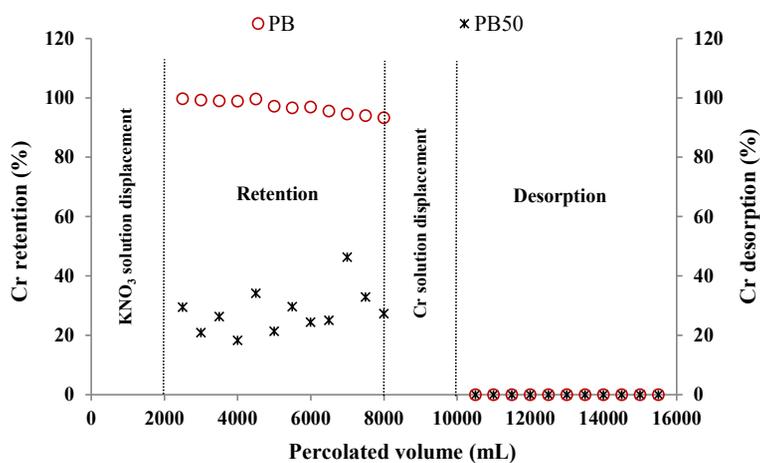


Figure 2. Retention and desorption of Cr by the tested materials.

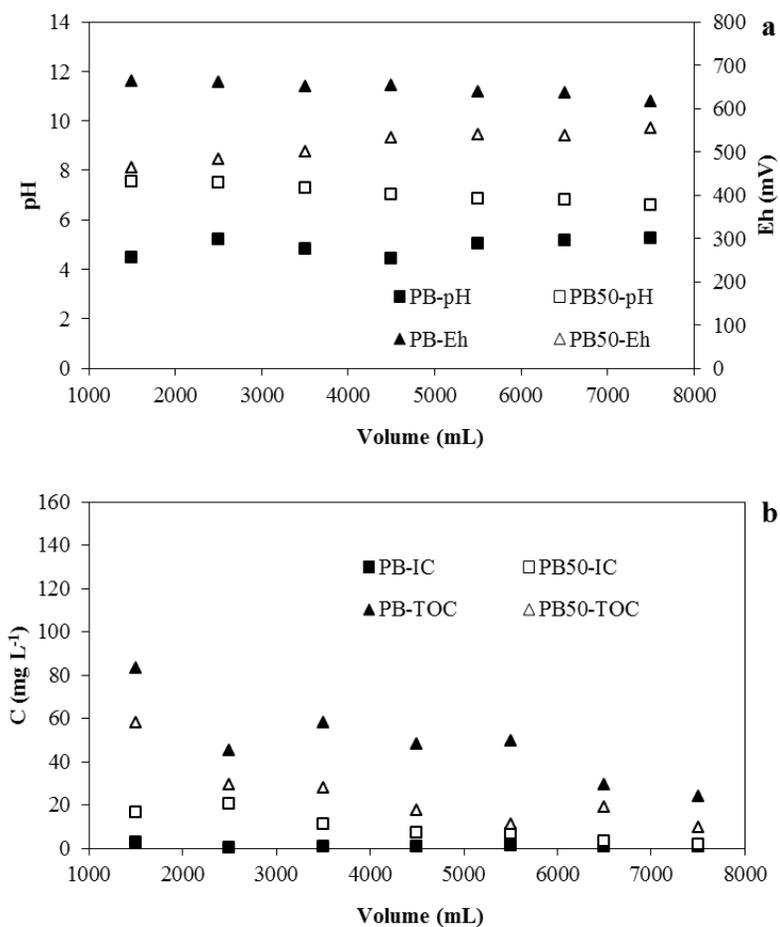


Figure 3. (a) pH and Eh conditions in the eluates of the retention step, (b) Total organic carbon (TOC) and inorganic carbon (IC) in the eluates.

The eluates of PB presented higher Eh and were more acidic than the eluates of PB50, and showed constant values for these parameters throughout the sorption experiment (Figure 3a). IC was scarce in the eluates, mostly for the more acidic PB. TOC decreased for both filling materials along the experiments and was almost exhausted after the passage of 4.5 L of percolating solution for PB50 (Figure 3b).

Modelling with Visual Minteq was applied to the eluates obtained in the sorption step. pH and Eh, and concentrations of dissolved Cr and TOC were introduced as inputs in the model.

To determine the proportion between TOC and total dissolved organic matter (DOM), a default factor of 1.65 was used in the model, which is an average of the results obtained for lakes and streams in Sweden (Sjöstedt et al. 2010). The model indicates that Cr (VI) was completely reduced to Cr (III) in the eluates of PB and that Cr (III) is completely associated with DOM (Figure 4). On the contrary, in the experiments with PB50, Cr (VI) was the predominant form in the sorption step. Moreover, Cr (VI) is not associated with DOM in the eluates, whereas this fraction represents between 8 and 55% (mean 33%) of Cr (III) in the sorption step.

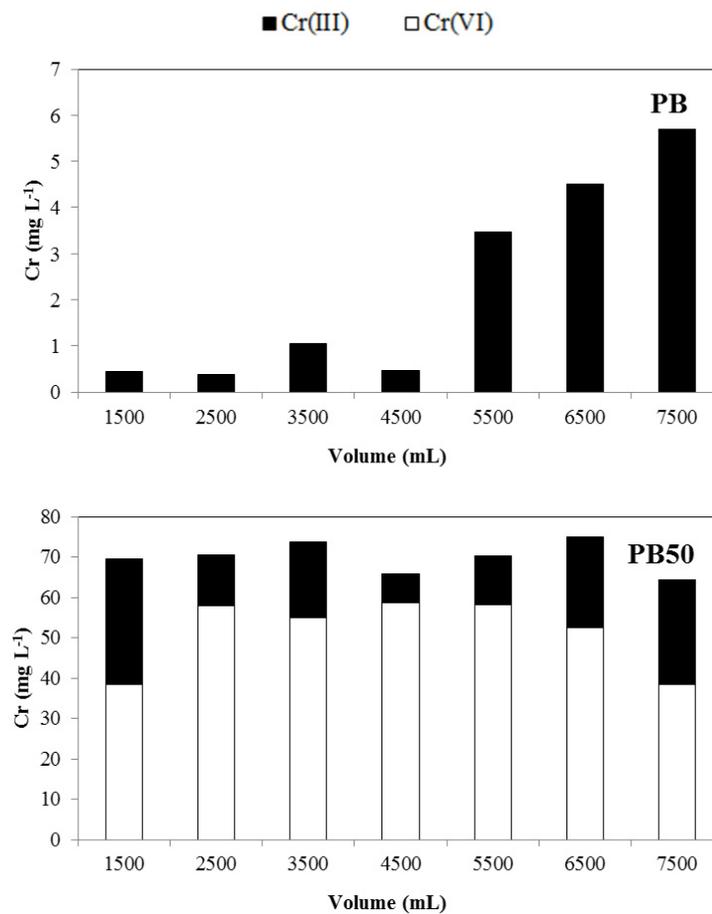


Figure 4. Cr speciation in the eluates from the retention step, as predicted by Visual Minteq applied to PB and PB50.

Adsorption is considered an efficient method for decontamination of polluted waters. The adsorbent properties of organic materials and particularly of compost have been frequently applied to soil and water decontamination (Blowes et al. 2000; Tsui et al. 2003; Farrell and Jones 2009; Pereira et al. 2009; Smith 2009; Park et al. 2011; Paradelo and Barral 2012), and specifically to remove dissolved Cr (VI). The Cr retention capacity of compost is attributed to the cation and anion adsorption capacities of the organic matter-rich materials and their potential reducing effect. Thus, in a soil incubation experiment, Bolan et al. (2003) observed that the addition of organic amendments to a contaminated soil increased the fraction of Cr (VI) associated with organic matter and favoured the reduction of Cr (VI) to Cr (III). Wei et al. (2005) observed that 18-25% of the Cr adsorbed by compost was in the form of precipitated $\text{Cr}(\text{OH})_3$ formed after reduction of Cr (VI) to Cr (III). In this line, Boni and Scaffoni (2009) observed a high retention and transformation of Cr (VI) in an insoluble compound of Cr (III) in experiments with columns filled with 1:1 compost and silica gravel, and considered that the mechanism of decontamination is a combination of adsorption on to the organic matrix followed by biological reduction and precipitation. Extensive work undertaken by Park et al (2007, 2008, 2011), along with Módenes et al. (2010), Shen et al. (2010), Zheng et al. (2011), demonstrated that the elimination mechanism involves adsorption-coupled reduction processes, promoting the reduction of Cr (VI) to Cr (III) by contact with electron-donor groups of the organic matter. Hydroxilic and carboxylic entities are the main functionalities involved on the adsorption-coupled reduction process (López-García et al. 2013). The lower pH of PB makes the adsorbent surfaces more positive, enhancing the binding of Cr (VI) species (Park et al. 2007) and favoring the reduction of Cr (VI) by the electron-donor groups of the biomass (Losi et al. 1994; Bolan et al. 2003), but hindering the adsorption of Cr (III) to the binding sites (López-García et al. 2013). This fact would contribute to the predominance of Cr (III) in the eluates of PB.

Overall, the results of this study indicate a good behaviour of PB as potential filler for PRBs, as it presents high Cr retention and low remobilization. Furthermore, the Cr (VI) introduced in the percolating solution is reduced to the less toxic Cr (III) which is mostly associated with DOM. The mixture PB50 was less effective than PB in the retention of Cr in the sorption step although previously sorbed Cr was firmly retained in the leaching step. Furthermore, Cr (VI) not associated with DOM was the predominant species in the eluates.

Although the compost PB is the most reactive component of the tested materials, it has several limitations to be used alone, as it can be easily displaced in the barrier and can experiment volume changes. It also shows an excessive permeability, making it difficult to achieve a sufficient residence time for the attenuation of contaminants (Barral et al. 2014). Therefore, mixing with GP is recommended as it provides physical support, reduces volume changes and avoids the movement of the compost inside the barrier (AFCEE 2008). Moreover, mixing compost and GP allows reaching suitable hydraulic conductivities (Barral et al. 2014). In this way, the mixtures of 50% GP and 50% PB compost could also be considered suitable as PRBs fillers, combining moderate adsorption and low Cr desorption with an acceptable permeability.

PRBs filled with PB should be also effective in retaining other metals with affinity for organic matter such as Cu. Other uses of PB for metal decontamination such as soil bioremediation or retention of metal spillages to water can be envisaged with promising perspectives.

4. Conclusions

The "reactive box" device, designed and used in this study to reproduce the operation of a permeable reactive barrier at a microcosm scale, proved to be suitable for this purpose, allowing for the evaluation of the retention capacity and release of pollutants. Pine bark compost was the most reactive filler material for the decontamination of Cr (VI) polluted waters, as it showed a high sorption capacity and low desorption both in saline 0.01M KNO₃ solution and in TCLP extracts. Moreover, Cr (VI) was reduced to the less toxic Cr (III) associated with organic matter in PB eluates. Nevertheless, the incorporation of the granite powder is useful from the viewpoint of construction and physical stability of the barrier. Its proportion in the filler mixture should be based on the criterion of achieving the hydraulic conductivity necessary to optimize retention and facilitate the construction of PRBs.

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