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Reutilization of granite powder as a component of permeable reactive barriers for the treatment of Cr(VI)-contaminated waters

Reutilización de serrines graníticos como componente de barreras permeables reactivas para el tratamiento de aguas contaminadas con Cr(VI)
Reutilização de pó de serragem de granito como componente de barreiras permeáveis reactivas para o tratamento de água contaminada com Cr(VI)

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ABSTRACT

Permeable reactive barriers (PRBs) are efficient and cost-effective systems for groundwater remediation. Different types of material have been tested as reactive media for constructing PRBs. To this purpose, the use of waste materials is of particular interest, provided they meet some permeability and reactivity requirements. In the present study, the use of granite powder, a waste generated during the process of cutting granite, was evaluated as a component of PRB filler, mixed in different proportions with compost. The Cr(VI) adsorption capacity and desorption behaviour of granite powder, pine bark compost, composted municipal solid waste and mixtures containing different proportions of granite powder and compost was compared. Individually, the granite powder was not suitable for use as PRB filler because of its moderate permeability and Cr(VI) adsorption capacity. The addition of pine bark compost increased the hydraulic conductivity and improved the Cr(VI) adsorption capacity of the material, while decreasing Cr desorption. In turn, the addition of compost derived from municipal solid waste did not have the same beneficial effect, as it decreased the hydraulic conductivity of the mixtures and only slightly improved the adsorption capacity. In summary, mixtures containing 50 or 25% granite powder and 50 or 75% pine bark compost (v/v), respectively, were the best materials for use as a PRB in relation to cost/effectiveness.

RESUMEN

Las barreras permeables reactivas (BPRs) son sistemas eficaces y de bajo coste para la descontaminación de aguas subterráneas. Diversos materiales han sido ensayados como sustratos reactivos en la construcción de BPR's, siendo de interés la utilización de materiales residuales cuando cumplen unos requisitos de permeabilidad y reactividad. En este trabajo se ha evaluado la utilización para este fin de serrines procedentes del proceso de corte del granito, mezclados con compost, como componentes de relleno de BPRs. Para ello, se estudió la capacidad de adsorción de Cr(VI) de serrines graníticos, comparándola con la de compost de corteza de pino, compost de residuos sólidos urbanos y mezclas en diferentes proporciones de los serrines y compost. Los serrines graníticos, empleados sin mezcla con otros componentes reactivos, presentan como inconveniente para su uso como relleno de BPRs su moderada permeabilidad y capacidad de adsorción de Cr(VI). La adición de compost de corteza de pino compostada mejoró el comportamiento de los serrines, incrementando su conductividad hidráulica, al tiempo que aumentó la capacidad de adsorción de Cr(VI) y disminuyó su desorción. Por el contrario, el compost derivado de residuos sólidos urbanos no tuvo estos efectos beneficiosos, ya que redujo la permeabilidad y solo afectó ligeramente a la capacidad de adsorción y desorción de Cr. En resumen, las mezclas de serrines graníticos y compost de corteza de pino al 50 o 75% (v/v) de compost fueron las más adecuadas para su utilización como BPRs desde el punto de vista de su efectividad y coste.

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RESUMO

As barreiras permeáveis reativas (BPRs) são sistemas eficazes e de baixo custo para descontaminação de águas subterrâneas. Diversos matérias foram ensaiados como substratos reativos na construção de BPRs, sendo de interesse a utilização de materiais residuais desde que cumpram os requisitos de permeabilidade e reatividade. Neste trabalho avaliou-se a utilização para estes fins de pó de serragem de granito misturado com composto como componentes de enchimento de BPRs. Para tal estudou-se a capacidade de adsorção de Cr(VI) de pós graníticos, comparando-a com a do composto de casca de pinheiro, composto de resíduos sólidos urbanos e misturas em diferentes proporções de pós de granito e composto. Os pós graníticos usados individualmente apresentam como inconveniente para uso como substratos de BPRs a sua moderada permeabilidade e capacidade de adsorção de Cr(VI). A adição de composto de casca de pinheiro melhorou o comportamento dos pós graníticos, aumentando a sua condutividade hidráulica ao mesmo que tempo que aumentou a sua capacidade de adsorção de Cr(VI) e diminuiu a sua dessorção. Por outro lado, o composto derivado de resíduos sólidos urbanos não teve esses efeitos benéficos já que reduziu a permeabilidade e só afetou ligeiramente a capacidade de adsorção e dessorção de Cr. Em resumo, as misturas de pós graníticos com composto de casca de pinheiro numa proporção de 50 ou 75% de composto, foram as mais adequadas para a sua utilização como BPRs do ponto de vista custo/eficácia.

KEY WORDS
Decontamination, remediation, chromium, adsorption, reuse, waste

PALABRAS CLAVE
Descontaminación, cromo, adsorción, reutilización, residuos

PALAVRAS-CHAVE
Descontaminação, crómio, adsorção, reutilização, resíduos

1. Introduction

Chromium 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, which is highly toxic. Occasionally Cr reaches the soil through spillages and disposal, where it can be leached to deep layers and create contamination plumes that pollute the groundwater. Traditionally, Cr treatment technologies include chemical reduction followed by precipitation or ion exchange (Benefield et al. 1982). The use of biological materials has been proved as an alternative to the mentioned methods due to their removal efficiency and low cost (Miretzky and Cirell 2010).

Different technological systems are being developed to decontaminate groundwater, including permeable reactive barriers (PRBs). This technique is based on the *in situ* installation of a permeable reactive barrier, perpendicular to the flow of a contamination plume. The walls of the barrier are permeable and allow the passage of water, contacting the filler material (reactive material), which can absorb, precipitate or degrade the contaminants. As the contaminated water passes through the reactive zone of the barrier, the contaminants are immobilised or chemically transformed to less toxic forms, so that the water emerging on the other side of the barrier is cleaner (USEPA 1997). This system has been used successfully to treat effluents affected by contaminants such as dissolved metals, acid mine drainages or dissolved nutrients (Blowes et al. 2000). 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 Fe^0, which has been used to degrade organic compounds and to precipitate organic and inorganic substances (USEPA 1997). Particularly, PRBs filled with Fe^0 have been used to treat groundwater contaminated with Cr(VI), reducing Cr(VI) to Cr(III) and giving rise to a coprecipitate $Cr_xFe_{1-x}(OH)_3$ (James and Barlett 1983; Palmer and Wittbrodt 1991). Some iron compounds, such as iron sulphides and iron oxyhydroxides, also promote the reduction and precipitation of the chromate anion (Blowes et al. 2000).

The use of readily available and inexpensive waste materials to construct PRBs is of great interest, providing that the material is not detrimental from an environmental point of view, and complies with the minimum requisites of permeability and reactivity. In this study, the potential use of granite powder (GP) for constructing PRBs has been investigated. GP is a waste product generated in granite transformation plants during the cutting, polishing and finishing of the blocks extracted from quarries. During the cutting process, the metal (steel) blades that cut through the granite blocks are cooled by a solution of water containing calcium hydroxide and metal filings. The slurry generated during the cutting process is dried to produce GP, which contains mostly debris of ground granite along with components of the cooling solution. In previous studies, different potential applications for the reutilization of this waste have been evaluated, e.g as an amendment for acid soils (Barral et al. 2005; Silva et al. 2013), as a component of potting substrates and for land restoration (Coroneos et al. 1996; Paradelo et al. 2011). The presence of Fe oxyhydroxides in GP (Barral et al. 2005) potentially favours the use of the material for the retention of metals. Also, the high pH should favour the precipitation of certain metals as hydroxides; in the case of Cr, a high pH would also favourable for precipitation of Cr(III) as $Cr(OH)_3$. Additionally, the use of GP can be justified to provide weighting material for emplacement and matrix support, to reduce the amount of compaction after installation and to maintain the permeability of the mixture, as well as to stabilize the material (AFCEE 2008). To this end, sand and gravel are typically added at 40 to 60 percent by volume of the substrate mixture in the construction of biowalls (AFCEE 2008).

In the present study, with the aim of improving the properties of the material as an adsorbent of Cr(VI), the effect of mixing GP with compost has been investigated, on the basis of the cation and anion adsorption capacities of the organic matter-rich materials and their potential reducing effect. In this sense, different types of compost have been used successfully to treat soils and waters contaminated with organic contaminants (Tsui et al. 2003; Pereira et al. 2009) or inorganic substances (Smith, 2009; Paradelo and Barral 2012), and specifically to remove dissolved Cr(VI) (Bolan et al. 2003; Wei et al. 2005; Boni and Sbaffoni 2009).

In past decades, many authors have considered anionic adsorption as the only mechanism involved in Cr(VI) removal by organic rich materials. However the extensive work by Park et al. (2007, 2008a, 2008b, 2011), along with other studies undertaken by Módenes et al. (2010), Shen et al. (2010), Zheng et al. (2011) and López-García et al. (2013) demonstrate that the elimination mechanism involves adsorption-coupled reduction processes, producing the reduction of Cr(VI) (either in the aqueous phase or bound to positively charged groups on the biomaterial surface) to Cr(III) by contact with electron-donor groups of the organic matter. Low pH makes the biomaterial surface more positive, enhancing the binding of Cr(VI) ion species (Park et al. 2007); low pH also favours the reduction of Cr(VI) by the electron-donor groups of the biomass, but hinders the adsorption of Cr(III) to the binding sites (López-García et al. 2013). In addition, supplying a source of C and protons may stimulate microbial activity, thus favouring the reduction of Cr(VI) (Losi et al. 1994; Bolan et al. 2003). In turn, a high pH does not favour the binding of Cr(VI) on surface groups and the Cr(VI) reduction, but favours the precipitation of the reduced Cr(III) to $Cr(OH)_3$.

The aim of this study was to evaluate the use of a mixture of GP and compost as a reactive medium for the construction of PRBs. For this purpose, we compared the Cr(VI) adsorption capacities of granite powder, pine bark compost, municipal solid waste compost and mixtures of granite powder and each compost.

2. Materials and Methods

2.1. Granite powder and composts

To prepare the reactive material, GP was mixed with two different types of compost: compost M, produced by composting the organic fraction of municipal solid waste, and compost PB, obtained by composting pine bark. Each compost was mixed with GP in three different proportions (v/v): 75% GP/25% compost (PB25 and M25), 50% GP/50% compost (PB50 and M50), and 25% GP/75% compost (PB75 and M75). These proportions and their equivalences on a weight basis are shown in **Table 1**.

The granite powder comprised four samples of different origin, each of 30 kg, which were air-dried and gently crushed to < 2 mm and then combined into a single representative sample. The GP samples were obtained from granite manufacturing companies in Porriño (Pontevedra) and provided by the *Centro Tecnológico del Granito de Galicia*. 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 from this source has been previously characterized (Barral et al. 2005; Silva et al. 2013). GPs are silty loam, with the silt fraction representing around 80%. The composition of the powder is coincident with that typical of the granitic rocks from which it is originated, except for the concentrations of Ca, Fe and some trace elements which are higher in the granite powder (Barral et al. 2005; Silva et al. 2013), 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 (Barral et al. 2005).

For the analysis of the general properties of the materials, the Spanish UNE-EN version of the European CEN/TC 223 methods for the characterization of soil amendments and substrates was followed (AENOR 2001a,b,c; AENOR 2002); these included pH, electrical conductivity (EC), total organic matter (OM) and C, total N, and physical properties. Briefly, pH and electrical conductivity (EC) were determined in aqueous extracts (substrate/extractant ratio: 1/5 v/v) of fresh samples, using a glass electrode (Crison pH-Meter Basic 20) and a conductivity meter (HANNA HI 9033), respectively. Total organic matter (OM) was determined by weight loss on ignition of dried ground samples at 450 ºC, and total organic C (TOC) was calculated by multiplying OM by a factor of 0.58. Total N was measured by Kjeldahl digestion and steam distillation. The saturated hydraulic conductivity was determined in a constant head permeameter (Klute and Dirksen 1986).

Table 1. Proportion of compost in the mixtures of granite powder (percentage of PB or M compost in a volume basis, and on a wet and dry weight basis)

Mixture	Volume	Wet weight	Dry weight
PB25	25	11	4
PB50	50	27	10
PB75	75	53	20
M25	25	16	9
M50	50	36	20
M75	75	63	34

2.2. Adsorption kinetics

To study the adsorption time required to reach pseudo-equilibrium conditions, three grams of selected samples (GP, PB and PB50) were shaken for 15, 60, 120, 240, 480 and 1440 minutes with 150 ml of three different solutions of Cr(VI) (10, 100 and 500 mg L^{-1}) or with 150 ml of 0.1M potassium nitrate as a blank. After shaking, the suspensions were centrifuged for 10 min at 4000 rpm and the supernatant was filtered through cellulose filter paper. The filtrates were stored at 4 ºC until analysis. All of the experiments were carried out in triplicate. The concentration of Cr(VI) was measured by flame atomic absorption spectroscopy (Varian SpectraAA 220FS).

2.3. Adsorption curves

To study the Cr(VI) adsorption capacity, a series of batch experiments was carried out at a constant temperature of 20±2 ºC. A stock solution of potassium dichromate (1 g L^{-1}) in 0.01 M potassium nitrate was prepared and used to prepare solutions containing 1, 5, 10, 25, 50, 100, 250, and 500 mg Cr L^{-1}. Three grams of sample were added to 150 ml of each of the Cr(VI) solutions and the suspensions were shaken for 16 hours; 150 ml of 0.01M potassium nitrate were used as a blank and processed in the same way as the other solutions. After the shaking, the suspensions were centrifuged and filtered as described above. All of the experiments were carried out in triplicate. The pH of the extracts was determined and the concentration of Cr(VI) was measured as above. The concentrations of Cr(VI) in pseudo-equilibrium in the extracts were used to calculate the percentage of Cr adsorbed, with the following expression:

$$\%Cr\ adsorbed = 100\ \frac{([Cr]initial-[Cr]equilibrium)}{[Cr]\ initial} \quad \text{(Equation 1)}$$

The results are also expressed as mass of Cr(VI) adsorbed in the solid versus the equilibrium concentration of Cr(VI) in the solution. The amount of Cr adsorbed (in mg g^{-1}) was calculated using the following expression:

$$\frac{mg\ de\ Cr\ absorbed}{g} = 0.15\ \frac{([Cr]initial-[Cr]equilibrium)}{solid\ weight} \quad \text{(Equation 2)}$$

The adsorption curves were described using the Freundlich and Langmuir models, represented respectively by the following equations:

$$\log X = \log K_F + n \log C \quad \text{Freundlich isotherm (Equation 3)}$$

$$X^{-1} = (K_L X_m)^{-1}.C^{-1} + X_m^{-1} \quad \text{Langmuir isotherm (Equation 4)}$$

where X is the amount of Cr adsorbed (mg g^{-1}), C is the equilibrium concentration of Cr in solution (mg L^{-1}), and K_F, n, K_L and X_m are constants that depend on the type of adsorbent material and the chemical species. X_m represents the maximum adsorption capacity (mg g^{-1}) of the solid in the Langmuir model.

2.4. Desorption curves

The experiment was completed by determining the desorption of previously retained Cr(VI). For this purpose, the solid separated after the adsorption experiment was washed by shaking with 80 ml of acetone. The mixture was then centrifuged to separate the solid, which was then air-dried until complete evaporation of the acetone. The dried solid was weighed and added to 150 mL of a 0.01M solution of KNO_3; the mixture was shaken for 16 hours before being centrifuged for 10 min at 4000 rpm. The resulting supernatant was filtered through cellulose filter paper, and the concentration of Cr(VI) in the filtrate was then measured. The results were expressed as the percentage desorption of Cr(VI) relative to the total amount adsorbed.

3. Results and Discussion

3.1. Properties of the materials

The granite powder was characterized by low C and N contents, low electrical conductivity and alkaline pH (**Table 2**), as is usual for this type of waste. The high pH is considered to be a consequence of the sawing process (Barral et al. 2005), which involves the destruction of mineral networks and the dissolution of the alkaline cations (Ca, Mg, Na) present in minerals such as plagioclase and biotite, and reflects the predominance of unweathered primary minerals (Barral et al. 2005). The material was rich in total Fe, coming from Fe-bearing minerals in the rock and from the sawing additives, and had appreciable amounts of total Cr, although this element is not very soluble in GP at pHs close to neutrality (Barral et al. 2005).

The pine bark compost (P) was characterized by a low pH and a high percentage of organic matter, but a relatively low concentration of nitrogen, giving rise to a high C/N ratio, as is usual in this type of composted material. The pH and electrical conductivity of the compost M were higher than those of the pine bark compost, as is usual for compost derived from this municipal solid waste.

The pH of the granite powder slightly decreased by the addition of both types of compost, but never fell below pH 8. It has to be noted that although pine bark compost is acidic, it has a low neutralizing capacity (Paradelo et al. 2011). The electrical conductivity of the mixtures remained low (<1 dS m^{-1}), although the addition of compost M increased the value in proportion to the dose used. Likewise, the contents of C and N increased in all mixtures relative to the granite powder, and the apparent density also decreased. Permeability is an important parameter in this study, as it provides information about the rate at which a liquid will flow through the PRB, thus at least partly determining the efficiency of the barrier. Ideal retention time is one that allows the retention or degradation of pollutants, but that is not an obstacle to the flow of the contaminant plume. Although the saturated hydraulic conductivity (Ksat) of GP was in an acceptable range for PRBs (AFCEE 2008), it increased in proportion to the added amount of compost PB, whereas the addition of compost M had the opposite effect.

Table 2. Physicochemical properties of the mixtures. EC: electrical conductivity; OM: total organic matter; Ksat: saturated hydraulic conductivity; GP: granite powder; M: municipal solid waste compost; PB: pine bark compost; nd: not detected, - not determined

	GP	PB	M	PB25	PB50	PB75	M25	M50	M75
pH	9.2	5.3	7.95	8.7	8.4	8.2	8.9	8.7	8.4
EC (dS m^{-1})	0.23	0.37	1.11	0.23	0.22	0.22	0.46	0.62	0.87
Bulk density (g l^{-1})	1035	455	652	952	682	583	938	810	746
OM (%)	0.12	91.4	35.7	5.5	11.8	22.8	4.6	11.3	17.4
Total N (%)	nd	0.28	1.79	nd	0.03	0.08	0.23	0.60	1.00
Total organic C (%)	0.07	53.1	20.7	3.2	6.9	13.2	2.7	6.6	10.1
C/N	-	194	12	-	282	175	12	11	10
Total Fe (g kg^{-1})	75.7	3.1	11.1	72.7	68.4	61.5	70.1	63.0	53.5
Total Cr (mg kg^{-1})	192	9	33	184	174	156	178	161	137
Ksat (10^{-6} m s^{-1})	0.53	-	-	0.72	1.11	2.02	0.33	0.11	0.08

3.2. Adsorption kinetics

The objective of investigating the kinetics of the process is to determine the contact time required to attain pseudo-equilibrium in the laboratory adsorption experiments. Moreover, kinetics is also relevant for the estimation of the residence time in the reactive barrier required for adequate adsorption of the contaminant, and also the range of concentration in which the barrier will be most efficient. Cr(VI) adsorption varied depending on the initial concentration, contact time and sample studied (**Figure 1**).

The adsorbed Cr concentration increased with the Cr dose and was much greater for compost PB than for GP and PB50. The time required by PB to reach pseudo-equilibrium conditions increased with the initial Cr concentration, from 2 h for 10 mg L^{-1}, to 8 h for 100 and 500 mg L^{-1}, whereas for GP and PB50 pseudo-equilibrium was reached at 8 h, irrespective of the concentration considered. For PB a 100% adsorption percentage was achieved for all the initial Cr concentrations, whereas for GP and PB50 a maximum adsorption of 38% and 49% was observed, respectively.

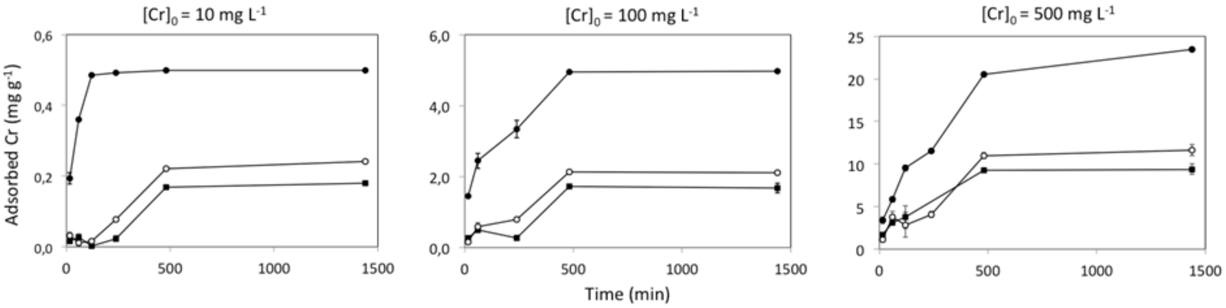

Figure 1. Cr(VI) adsorption over time from aqueous solution onto the granite powder (full squares), pine bark compost (full circles) and their mixture PB50 (open circles).

3.3. Adsorption curves

Irrespective of the concentration of Cr(VI) in solution, the pH values remained at approximately 7-8 for GP and the mixtures of GP and composts, whereas the final pH of the suspensions containing compost PB increased from 4.1 to 6.6 for the highest Cr concentration (**Table 3**).

Both composts differed in their adsorption capacities (**Figure 2**). For GP and compost M, as well as for their mixtures, the maximum percentage removal of Cr(VI) from solution was 30%. However, the percentage of adsorption was much greater for the compost PB, reaching 100% for Cr concentrations up to 100 mg L^{-1}. The addition of compost PB to GP also increased the adsorption percentage up to 45%, for the two highest doses of PB and for Cr concentrations in the range 50-300 mg L^{-1}. The better properties of the pine bark compost with respect to compost derived from municipal solid waste may be due to its higher percentage and different composition of organic matter, as well as to its lower native Cr concentration.

Several recent experiments have enabled evaluation of the role of compost in the decontamination of Cr(VI) and of the mechanisms involved in the process. Thus, in a soil incubation experiment, Bolan et al.

Table 3. Final pH of the extracts. GP: granite powder; M: municipal solid waste compost; PB: pine bark compost

[Cr]0 (mg L^{-1})	GP	PB	M	PB25	PB50	PB75	M25	M50	M75
0	7.8	4.1	7.1	7.6	7.5	7.5	7.4	7.0	7.2
1	7.8	4.2	7.5	7.8	7.6	7.6	7.3	7.0	7.2
5	7.7	4.4	7.2	7.9	7.6	7.6	7.4	6.9	7.2
10	7.7	4.1	7.2	7.8	7.7	7.6	7.4	7.0	7.1
25	7.7	4.4	7.3	7.8	7.7	7.7	7.5	7.0	7.3
50	7.9	4.7	7.1	7.8	7.8	7.6	7.6	7.1	7.3
100	8.0	5.0	7.2	7.8	7.7	7.5	7.7	7.3	7.2
250	7.9	5.9	7.4	7.6	7.5	7.2	7.5	7.4	7.3
500	7.2	6.6	7.3	7.1	6.7	6.8	7.2	7.1	7.1

(2003) observed that the addition of organic amendments to a contaminated soil gave rise to an increase in the fraction of Cr(VI) bound to the organic matter and to an increase in the reduction of Cr(VI) to Cr(III). Wei et al. (2005) studied the process of adsorption of Cr(VI) on compost and observed that between 18 and 25% of the chromium adsorbed was in the form of a precipitate, $Cr(OH)_3$, formed after reduction of the Cr(VI) by the compost. In this line, Park et al (2007) demonstrate that the elimination mechanism involves adsorption-coupled processes, promoting the reduction of Cr(VI) to Cr(III) by contact with electron-donor groups of the organic matter. In column experiments, Boni and Sbaffoni (2009) observed that a 1:1 mixture of compost and siliceous gravel was highly effective in removing dissolved Cr(VI), which was transformed into an insoluble Cr(III) compound. These authors considered that the mechanism of decontamination is a combination of adsorption on the organic matter followed by biological reduction and precipitation, and attributed this effect to the anoxic/anaerobic biological activity of the compost biomass.

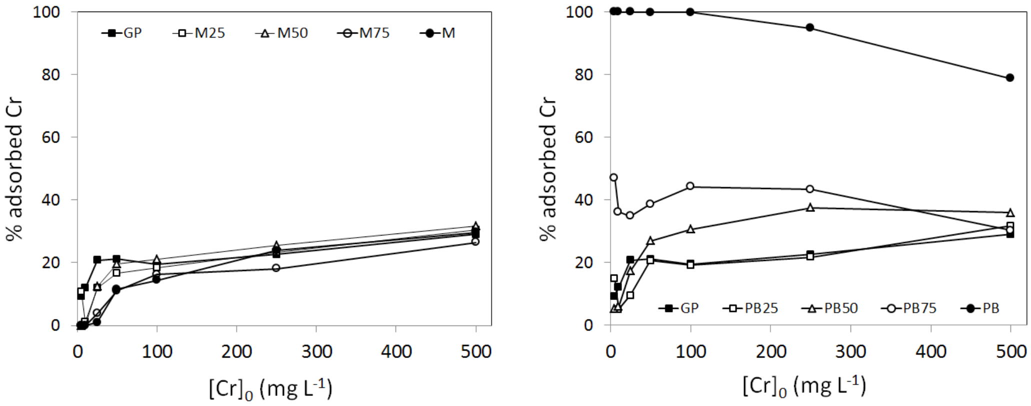

Figure 2. Percentage of Cr(VI) removal after the adsorption from aqueous solution onto the granite powder (GP), municipal solid waste compost (M), pine bark compost (PB) and their mixtures.

The adsorption curves for GP and the mixtures with composts were also very different (**Figure 3**). In general, compost M did not improve the adsorption capacity of the granite powder, giving rise to almost identical curves for all doses, whereas the highest doses of compost PB (50 and 75%) did increase the adsorption capacity, although not at the highest concentration of Cr(VI). However, none of the mixtures yielded such good results as compost PB alone, which proved to be an excellent adsorbent for Cr(VI). The values obtained of adsorbed Cr on PB were much greater than those found for several soils and biosorbents by Fernández-Pazos et al. (2013).

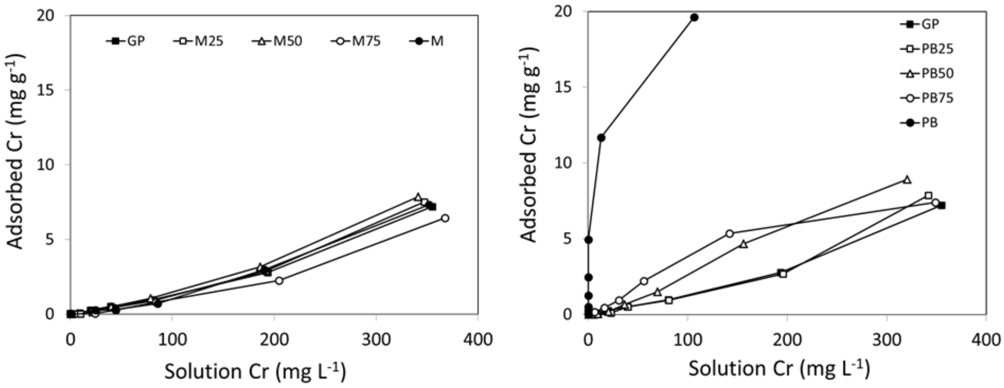

Figure 3. Cr(VI) adsorption curves for GP, compost M and PB, and their mixtures.

As indicated by the high values of R^2, Cr(VI) adsorption data for all the materials were satisfactorily fitted by the Freundlich model, whose fitting parameters are shown in **Table 4**. The values of K_F, which are proportional to the adsorption capacity of the material, reflect the greater adsorption capacity of compost PB and its mixtures with GP, relative to the other materials. Additionally, 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 Weil et al. (2005) for the adsorption of Cr(VI) on compost (36 mg g^{-1}).

Table 4. Freundlich isotherm parameters and correlation coefficients for the adsorption of Cr(VI) from aqueous solution onto the granite powder (GP), municipal solid waste compost (M), pine bark compost (PB) and their mixtures

	GP	M	PB	M25	M50	M75	PB25	PB50	PB75
K_F	0.0015	0.0009	6.5	0.0009	0.0018	0.0003	0.0003	0.018	0.141
n	1.44	1.53	0.23	1.55	1.44	1.67	1.74	1.08	0.69
R^2	0.9989	0.9994	0.9967	0.9996	0.9996	0.9985	0.9978	0.9972	0.9816

A suitable material for use as reactive component in PRBs should have a high adsorption capacity and low desorption capacity of the previously adsorbed Cr(VI). For GP, desorption of Cr(VI) was generally low, and appreciable concentrations (always under 4.5% of the adsorbed Cr) were only observed for samples previously incubated with Cr(VI) concentrations ≥ 25 mg L^{-1} (Figure 4). Similar desorption values were observed for the 25 and 50% mixtures of GP and compost M, whereas desorption was almost negligible in the 75% mixture and for compost M alone. For samples containing compost PB, desorption was considerably lower than for GP, below 0.1% for pure compost PB and never surpassing 1% of previously retained Cr(VI) for all the PB mixtures.

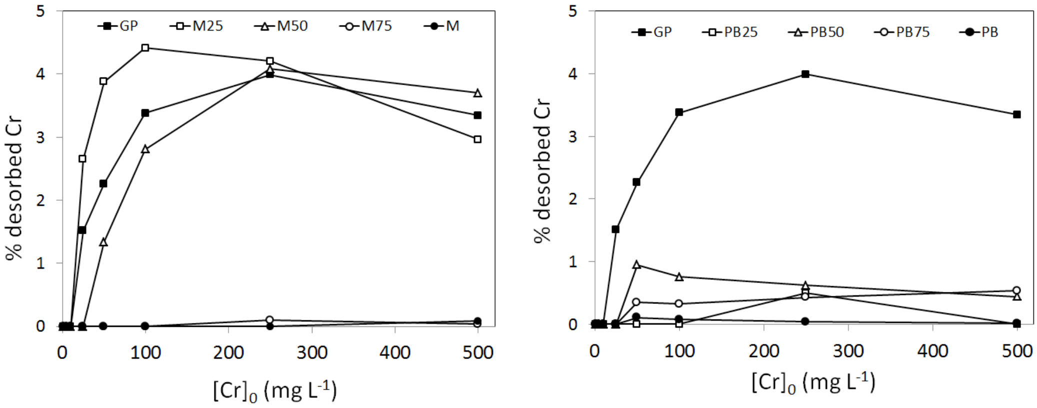

Figure 4. Percentage of Cr(VI) desorption for the granite powder (GP), municipal solid waste compost (M), pine bark compost (PB) and their mixtures.

For the selection of effective PRB fillers, it is necessary to take into account all the properties of the constituents. Granite powder possesses several good qualities in relation to the construction of PRBs: low degradability, ease of handling and more constant volume than organic materials such as compost. It is also an inexpensive waste material. However, its capacity to retain Cr(VI) is moderate. To improve this limiting characteristic, mixtures of GP with two types of compost with different properties were evaluated. One of the composts was produced from municipal solid waste and contains less than 50% organic matter, and the other from pine bark, containing more than 90% organic matter. The compost M displayed a low Cr(VI) adsorption capacity, similar to that of the granite powder, and combination with GP yielded a product with lower permeability; therefore these materials are not recommended as reactive fillers. In contrast, compost PB displayed a much higher Cr(VI) adsorption capacity than the granite powder and a much lower desorption, while the mixtures of these materials were more permeable than the pure granite powder. The combination of GP with 25% (v/v) of compost PB did not improve the properties of the granite powder, probably because the proportion of compost was only equivalent to 4% on a weight basis, and this mixture was then considered unsuitable. Combining the granite powder with 50 or 75% (v/v) pine bark compost, considerably improved the adsorption capacity of the granite powder, the mixture containing 75% compost yielding the best results. Nonetheless, the high cost of the pine bark compost relative to that of the granite powder must also be considered, so that an increase in the amount of compost in the mixture should be justified by a proportional increase in efficacy. Although compost is the most reactive component, the presence of granite is recommended as it provides physical support, reduces volume changes, and avoids compaction and the movement of compost inside the barrier (AFCEE 2008). In summary, mixtures of GP and 50 or 75% PB compost can be suitable as reactive medium for PRBs fillers, combining high adsorption and low Cr desorption with an adequate permeability.

4. Conclusions

The aim of this work was to combine the good properties of granite powder (GP) with those of compost, balanced by the price of each one. Although GP provides physical stability and matrix support to the barrier, it is not very effective as a reactive component of PRBs. Mixtures of GP with two types of compost with different properties were evaluated to overcome this limitation, one produced from municipal solid waste (compost M) and the other one from pine bark (compost PB). The compost M displays a low Cr(VI) adsorption capacity, similar to GP; moreover, the combination of these materials resulted in a product with reduced permeability. Consequently these materials cannot be recommended as reactive fillers. In contrast, the compost PB displays a much higher Cr(VI) adsorption capacity than GP, and a much lower desorption, being the mixtures of these materials more permeable than pure GP. Therefore, a combination of GP with 50 or 75% (v/v) compost PB is recommended for this use.

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