



The potential of compost-based biobarriers for Cr(VI) removal from contaminated groundwater: Column test

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ABSTRACT

This paper presents the results of a column reactor test, aiming at evaluating the performance of a biological permeable barrier made of low-cost waste materials, for Cr(VI) removal from contaminated groundwater. A 1:1 by volume mixture of green compost and siliceous gravel was tested as reactive medium in the experimental activity. A 10 mg/l Cr(VI) contaminated solution was used and the residual Cr(VI) concentration along the column height and in the outlet was determined in the water samples collected daily. Also pH, redox potential and COD were analyzed. At the end of the test, the reactive medium was characterized in terms of Cr(VI) and total chromium.

The Cr(VI) removal efficiency was higher than 99% during the entire experimental activity. The influence of the biological activity on Cr(VI) removal efficiency was evaluated by varying the organic carbon and nitrogen dosages in the contaminated solution fed to the system; a removal decrease was observed when the organic carbon was not enough to sustain the microbial metabolism. The Cr(VI) removal was strictly linked to the biological activity of the native biomass of compost. No Cr(III) was detected in the outlet: the Cr(III) produced was entrapped in the solid matrix.

Two main processes involved were: adsorption on the organic-based matrix and reduction into Cr(III) mediated by the anaerobic microbial metabolism of the bacteria residing in green compost. Siliceous gravel was used as the structure matrix, since its contribution to the removal was almost negligible.

Thanks to the proven efficiency and to the low-cost, the reactive medium used can represent a valid alternative to conventional approaches to chromium remediation.

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1. Introduction

Groundwater is usually of excellent quality, being naturally filtered in its passing through the ground. Unfortunately, a threat is now posed by an ever-increasing number of soluble chemicals from urban and industrial activities and from modern agricultural practices. These chemicals are not completely removed by filtration as groundwater passes through the aquifer and some pose threat to human health. Contamination can render groundwater unsuitable for use and the cost of cleaning up contaminated water supplies is usually extremely high.

One of the most important chemical contaminant of concern is chromium (Cr), which exists in a series of oxidation states from -2 to $+6$ valence; the most important stable states are 0 (element metal), $+3$ (trivalent) and $+6$ (hexavalent). Cr(III) and Cr(VI) are released to environment primarily from stationary point sources resulting from human activities.

Contamination of groundwater by Cr at numerous localities primarily resulted from uncontrolled or accidental release of Cr-bearing solutions, used in various industrial applications (metallurgical, chemical, leather tanning, wood processing, textile and refractory), into the subsurface environment. Cr in such solutions mostly occurs as oxyacids and oxyanions of Cr(VI) [1,2]. It is this oxidation state in which Cr is highly soluble, mobile and toxic. Also solid wastes from chromate-processing facilities, when disposed improperly, can be source of groundwater contamination.

The entry routes of chromium into the human body are inhalation, ingestion and dermal adsorption. Cr(III) is an essential dietary mineral in low doses: it is required to potentiate insulin and for normal glucose metabolism. Because it is an essential nutrient and it exhibits low acute and chronic toxicity, and because no evidence exists to indicate that Cr(III) can cause cancer, Cr(III) has not been classified as a human carcinogen by the International Agency for Research on Cancer (IARC).

Cr(VI) compounds, which are powerful oxidizing agents and thus tend to be irritating and corrosive, appear to be much more toxic, systematically than Cr(III) compounds (about 1000 times more toxic). This variation in toxicity may be related to the great Cr(VI) solubility and to the ease with which Cr(VI) can pass

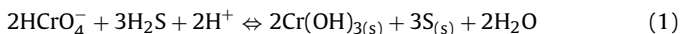
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through cell membranes and its subsequent intracellular reduction to reactive intermediated. Dose, exposure duration and the specific compound involved determine chromium's effects. Epidemiologic studies provide clear evidence of Cr(VI) carcinogenicity [3–5].

Thus removal of chromium from contaminated groundwater remains an important issue in environmental remediation. The most widespread *in situ* treatments used for hexavalent chromium-contaminated groundwater generally involve the reduction of Cr(VI) to Cr(III), which precipitates as hydroxide at pH above 5. Among such technologies, the permeable reactive barriers (PRBs) have gradually gained popularity, due to the high removal efficiency, the reduced overall costs, and the conceptual and applicative simplicity. In its simplest form, a permeable reactive barrier consists of a zone of reactive material, installed in the path of a contaminated groundwater plume. As the groundwater flows through this permeable barrier, the pollutants come in contact with the reactive medium and are degraded, adsorbed, precipitated depending on the reactive medium used. The main advantage of this system is that, generally, no pumping or aboveground treatment is required: the barrier acts passively after installation. Because there are not aboveground installed structures, the affected site can be put to productive use while it being cleaned up [6].

Most PRBs use reactive zero-valent iron reducing Cr(VI) into Cr(III), which precipitates as a mixed chromium–iron hydroxide solid solution and as a pure solid-phase hydroxide [7,8]. In the last years the biological removal of chromium has also been regarded to with increasing interest, because biotechnologies are generally cheap and do not require application of chemical reagents to the environment; the biological removal occurs according to different pathways:

- several species of bacteria, yeast and algae accumulate metal ions and many bacteria reduce Cr(VI) to Cr(III) [9];
- some dissimilatory metal reducing bacteria (DMRB) gain energy to support anaerobic growth by coupling the oxidation of H₂ or organic matter to the reduction of several multivalent metals, such as chromium, which precipitate [10];
- anaerobic sulphate-reducing bacteria (SRB) reduce Cr(VI) indirectly by the production of hydrogen sulphide, a strong reducing agent [11–13], according to the following reaction:



Moreover, vegetable-based waste materials have been used as natural adsorbent for Cr(VI): coirpith [14], sawdust [15], rice husk and rice husk carbon [16], hazelnut shell carbon [17] and debris of aquatic plants [18].

Batch tests on gravel, compost, sterilized compost and mixture of gravel + compost formerly carried out by the authors [19] proved that the gravel contribution to the Cr(VI) removal is quite negligible. Besides, the removal observed was predominantly due to the biomass activity, which converted Cr(VI) into Cr(III) under a stable form, such as Cr(OH)₃.

The aim of the present research was to evaluate the performance of an organic-based anoxic/anaerobic PRB for the treatment of Cr(VI) contaminated groundwater. A column test was carried out by using a mixture of the two low-cost waste materials previously used in the batch tests: green compost and siliceous gravel residual of cave activity; the former provided both the organic matter to be used by the SRB and the biomass, representing also the adsorbent medium for the abiotic chromium removal.

Besides, the waste materials used should be increased in values, through the definition of exploitation strategies alternative to landfilling.

2. Materials and methods

2.1. Materials

The siliceous gravel, used as a structure material and originated by effusive volcanic activities, was collected at the Vallerano cave, near Rome. The gravel had natural pH 8.7 and dry density 1.44 g/cm³. It was rich of cabasite and phillipsite, well known as natural cationic zeolites.

The green quality compost produced as amendment for agricultural use was collected at a composting plant near Rome, treating about 90 t/d waste (yard waste, wood cellulose waste, organic fraction of municipal and market waste collected separately), after about 90 days of biological stabilization in windrows. It is “green labelled”, as proved by the characterization data [20] shown in Table 2; due to the high organic content and the high pH value detected, such green compost can be considered as a peaty soil originated from the decomposition of plant organic fraction.

Leaching tests were carried out in order to assess the leaching behaviour of the materials and to check the feasibility of using compost in the aquifers. UNI-EN12457-2 test [21], using ultra pure water with a liquid to solid ratio (L/S) equal to 10 l/kg, was applied. The heavy metal release from both gravel and compost was quite negligible, representing only a percentage always below 3% of the total content in the solid phase reported in Table 1, matching with the requirements for the application of the two materials for an *in situ* treatment (Table 2).

2.2. Experimental system setup

A column test was carried out introducing a mix 1:1 by volume of compost and gravel [12] in a Perspex cylinder having height and diameter equal to 100 and 5 cm, respectively; the column is equipped with six sampling ports at the distance of 0 (inlet), 5 (port 1), 20 (port 2), 40 (port 3), 80 (port 4), 100 cm (outlet) from the bottom.

The Cr(VI) contaminated solution was fed upwards from a Tedlar bag (SKC) to the column through a multichannel peristaltic pump (ISMATEC IP, ±0.005 cm³/min precision), determining a flow rate within the column equal to 0.53 ml/min and a velocity equal to 1.86 m/d. One pore volume (PV) corresponded to about 411 ml, having a 13 h hydraulic retention time. The hydraulic retention time was equal to 0.65, 2.58, 5.16, 10.32 and 12.9 h, for sampling port 1, sampling port 2, sampling port 3, sampling port 4 and the outlet, respectively. A scheme of the column reactor is presented in Fig. 1.

The outlet was collected in a high density poly-ethylene (HDPE) bottle. Sampling was carried out daily from the sampling ports using Luer-Lock syringes and samples were immediately introduced in poly-ethylene (PE) vials and analyzed. All tubing and

Table 1
Compost characterization.

Parameter	Unit	Value
pH		8.48
Water content (U)	(%)	26.10
Total organic carbon (TOC)	(%)	31.95
Humic and fulvic Acids (HA + FA)	(%)	4.44
Total Kjeldahl nitrogen (TKN)	(%)	0.44
Ammonia nitrogen (NH ₄ ⁺ – N)	(%)	0.04
Chlorides (Cl ⁻)	(%)	0.80
Sulphates (SO ₄ ²⁻)	(%)	0.48
Cd	(mg/kgSS)	<d.l.
Cr	(mg/kgSS)	35.18
Cu	(mg/kgSS)	83.90
Ni	(mg/kgSS)	8.12
Pb	(mg/kgSS)	73.07
Zn	(mg/kgSS)	200.27

Table 2

Heavy metals leached by compost, compared to the Italian regulation limits for waste hazardousness definition.

Heavy metal	Leached in UNI-EN 12457-2 (mg/l)	Leached/total content (%)	Regulation limit for non-hazardous waste (mg/l)
Cd	<d.l.	<d.l.	0.02
Cr	0.02	0.57	1
Cu	0.19	2.26	5
Ni	0.07	8.62	1
Pb	0.14	1.92	1
Zn	0.45	2.24	5

connections were of Viton™. The experimental data were collected after 5 PVs run in the column in order to reach a steady-state condition.

2.3. Preparation of Cr(VI) contaminated solutions

The Cr(VI) contaminated solutions were realized by diluting $K_2Cr_2O_7$ (previously dried in oven at 105 °C for about 2 h and then stored at room temperature) in DDW, in order to obtain solutions containing 2 mgCr(VI)/l (solution A) and 10 mgCr(VI)/l (solution B).

Organic carbon (as acetic acid– CH_3COOH) and nitrogen (as ammonium hydroxide– NH_4OH) were added to the solution B in the ratio C:N equal to 100:5, obtaining a solution of chemical oxygen demand (COD) and ammonium nitrogen concentration equal to 400 mg/l and 10.8 mg/l, respectively (solution C); such a COD value was near the one of the compost used. In order to avoid too low pH in the feeding, during the experimental period the organic carbon was supplied as glucose instead of CH_3COOH , with the same COD and $NH_4^+ - N$ concentration (solution D); the substrate and nutrient dosage was then halved (solution E) and finally suspended until the end of the experimental activity,

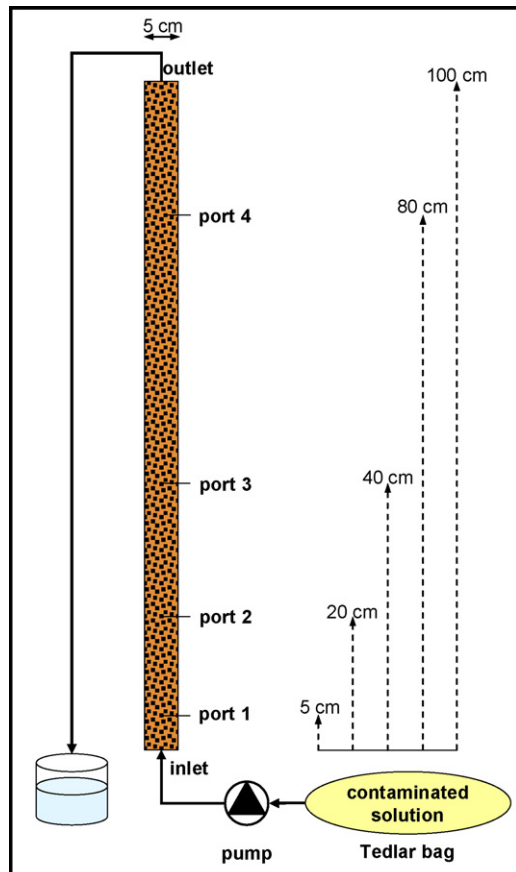


Fig. 1. Scheme of the column reactor.

Table 3

Experimental phases.

Phase	Solution fed to the column	Days
I	A	1–8
II	B	9–28
III	C	29–48
IV	D	49–64
V	E	65–86
VI	B	87–120

aiming at evaluating the influence of biological metabolism on the removal process. Depending on the solutions fed, the experimental activities are named as shown in Table 3.

2.4. Chemical analysis

2.4.1. Liquid phase characterization

pH, oxidation reduction potential (ORP), COD, Cr(VI) and total Cr were determined on the liquid phase collected from the column, following the APHA methods [22]. Cr concentration was determined by atomic absorption spectroscopy (Perkin Elmer 3030B) with flame and graphite furnace technique for Cr concentration above and below 0.01 mg/l, respectively.

2.4.2. Post-treatment solid phase characterization

At the end of the experimental activity, the materials used in the column test were characterized in terms of total and hexavalent chromium, through an acid [20] and an alkaline digestion [23], respectively.

Besides, a leaching test at L/S equal to 10 l/kg with DDW at pH 3 was performed, in order to evaluate the possible leaching of chromium which may occur after the treatment, under environmental conditions far from operating ones.

2.4.3. Chemicals

All the solutions were prepared with less than 50 $\mu S/cm$ conductivity deionised and distilled water (DDW). Glassware was cleaned with 1:1 nitric acid (HNO_3) solution and rinsed with DDW prior to use.

All the chemicals used (e.g. acetic acid, nitric acid, etc.) and potassium dichromate ($K_2Cr_2O_7$) were supplied by Carlo Erba and used as received.

3. Results and discussion

In the following paragraphs the results of the experimental activity are presented; such results concern both the liquid samples collected daily from the column and the solid phase at the end of the experimental period.

3.1. Liquid phase characterization

Fig. 2 and Fig. 3 report the Cr(VI), compared to the limit set by the Italian regulation in force for groundwater (5 $\mu g/l$), and the removal efficiency time profiles detected at each sampling port.

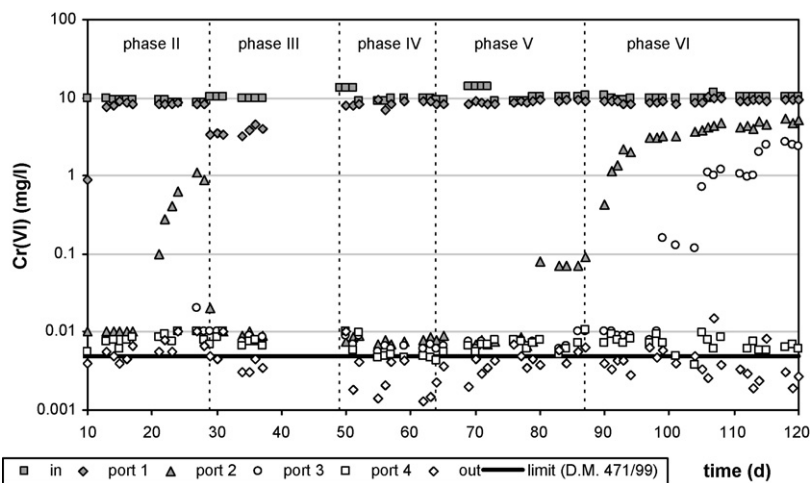


Fig. 2. Cr(VI) time profiles for each sampling port of the column and the regulation limit for groundwater.

3.1.1. Phase I

During the first experimental period (7 days) solution A was fed to the column (the results are not presented here); Cr(VI) concentration in the outlet and in the sampling ports 2, 3 and 4 was always below the detection limit for flame atomic adsorption spectrometry (0.01 mg/l), corresponding to an efficiency higher than 99%; in the first sampling port the removal efficiency was higher than 80%. Due to the high efficiencies obtained, the Cr(VI) content was increased in the feeding by using the solution B (phase II).

3.1.2. Phase II

In this phase Cr(VI) removal in the outlet and in the sampling port 4 was always higher than 99% (Fig. 3), with values at port 4 and in the outlet generally lower than 10 $\mu\text{g/l}$ and 4 $\mu\text{g/l}$, respectively (the Italian regulation for groundwater set a limit equal to 5 $\mu\text{g/l}$ for hexavalent chromium); a progressively decreasing efficiency was observed in the sampling ports 1 and 2, reaching 3% and 87% respectively after 20 days (the removal efficiencies were around 90 and 99% at the beginning of the experimental activity); the Cr(VI) concentrations were about 8.7 and 1.2 mg/l, respectively, in correspondence to a Cr(VI) concentration in the inlet of about 9 mg/l. Such a reduction was due to the exhaustion of the organic matter present in the compost, representing the only substrate for the heterotrophic biomass contributing to the Cr(VI) removal: in

fact, COD in the outlet was equal to about 30 mg/l at day 28, as shown in Fig. 4. Moreover, also the saturation of the adsorption sites on the compost [19] in the first centimetres of the column contributed to the Cr(VI) concentration increase at port 1 and 2; the residual adsorption capacity in the rest of the column ensured the maintenance of high removal efficiencies in the overall system.

3.1.3. Phase III

In order to resume the biological activity, since day 28 organic biodegradable substrate was supplied to the biomass by feeding the system with solution C, containing an organic carbon concentration similar to the one compost had at the beginning of the experimental activity (Fig. 4). This brought an improvement of the removal efficiency for the sampling ports 2 (up to 99%) and 1 (about 60%), as shown in Fig. 2 and Fig. 3. This seemed to confirm the significant contribution exerted by the biological activity on the reduction of Cr(VI) in a contaminated solution.

3.1.4. Phase IV

Due to an excessive pH decrease in the first centimetres of the column (<6), caused by the acetic acid present in the solution C, since day 49 CH_3COOH was substituted with glucose (solution D). The removal efficiencies were higher than 99%, except for the first sampling port, where concentrations similar to the inlet were

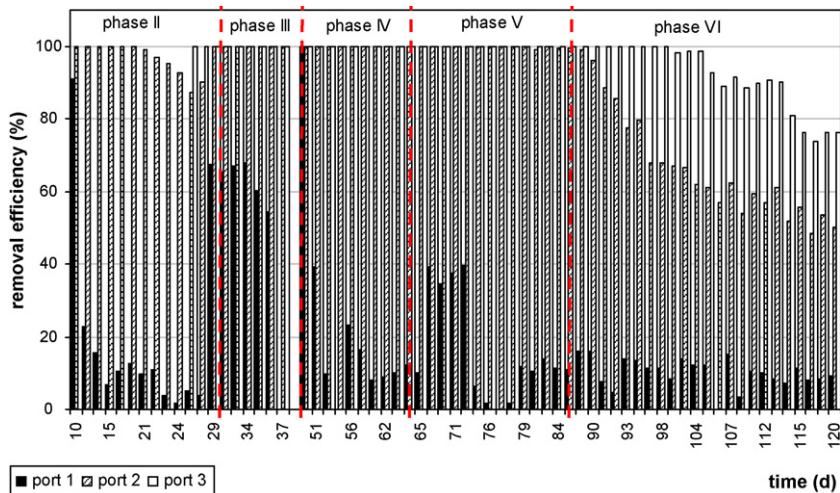


Fig. 3. Cr(VI) removal efficiencies at port 1, port 2 and port 3.

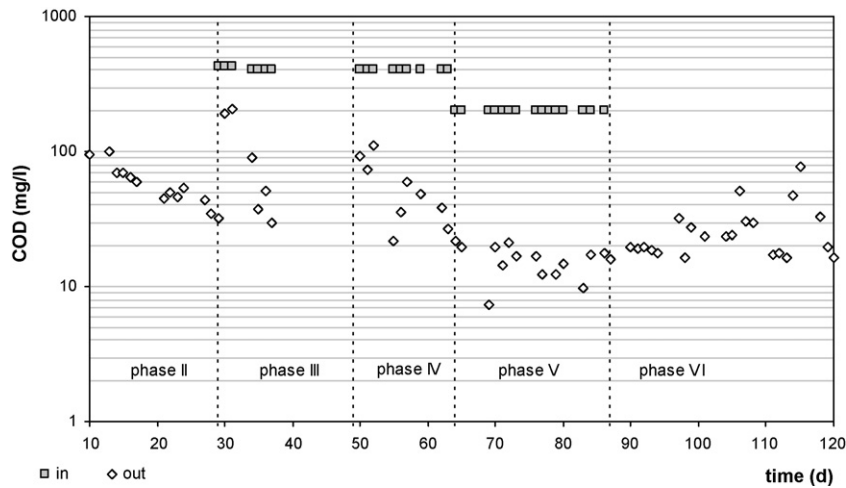


Fig. 4. COD time profiles in the inlet and in the outlet.

detected. The COD value in the outlet was generally below 50 mg/l, with a consumption in the column of about 350 mg/l (about 90%) (Fig. 4).

3.1.5. Phase V

In order to define the optimal COD and ammonia dosage, the solution E was fed to the column since day 64 until day 86. The efficiency did not seem to be strongly influenced, even if, as shown in Fig. 2, the Cr(VI) concentration in both port 4 and outlet was slightly higher than the one detected in the phase IV. An increase in the ORP values was observed also for sampling ports 2, 3 and 4 (Fig. 5). During this experimental phase the COD in the effluent was always below 20 mg/l (Fig. 4).

3.1.6. Phase VI

In order to evaluate the influence of the biological activity on Cr(VI) removal, in the last phase of the experimental period the organic substrate and nitrogen dosage was suspended and solution B was fed to the reactor. In this period, the following phenomena were observed in the sampling ports 2 and 3:

- an increase in the Cr(VI) concentrations, corresponding to a significant efficiency decrease especially at ports 2 and 3 (77% and 45%, respectively), as shown in Fig. 2 and Fig. 3;

- a significant ORP increase, with maximum values of about 200 mV detected at port 2 (Fig. 5).

The saturation of the adsorption sites in the first centimetres of the column and the inhibition of the biological activity caused by the lack of substrate led to a worsening of the performances at ports 1, 2 and 3.

In spite of this, a good removal efficiency was still shown in the port 4 and in the outlet, probably due to the residual adsorption capacity of compost.

3.2. Comments

3.2.1. ORP and Cr(VI) removal

The outlet concentration was always below the limit set by the regulation during the entire experimental activity; only in the experimental phases II and VI, when a lack in both organic substrate and nutrients was experienced, few samples occasionally presented Cr(VI) concentrations slightly higher than 5 $\mu\text{g/l}$.

The Cr(VI) time-profiles showed a good correlation with the ORP (Fig. 5 and Fig. 6). In fact, ORP in the ports 2, 3 and 4 was generally negative, corresponding to a reducing environment indicating that an anaerobic/anoxic microbial metabolism was taking place; it increased and turned into positive values only at the end of the experimental period, when the lack of nutrients and organic sub-

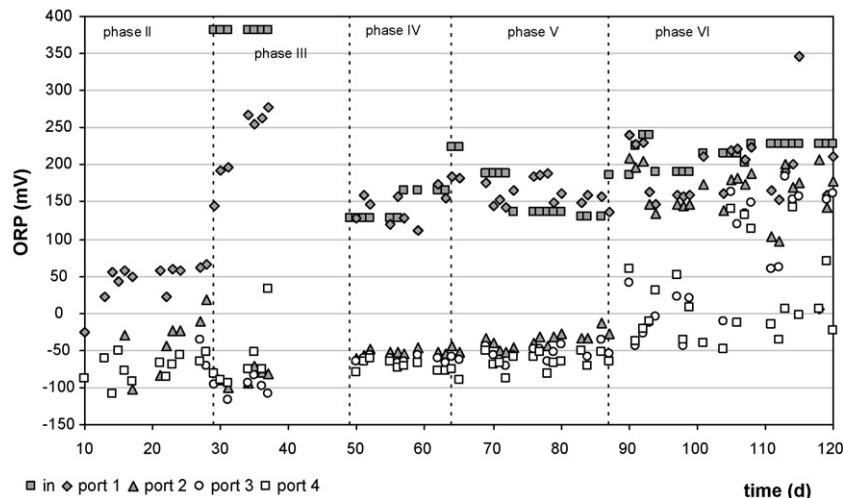


Fig. 5. ORP time profiles for each sampling port.

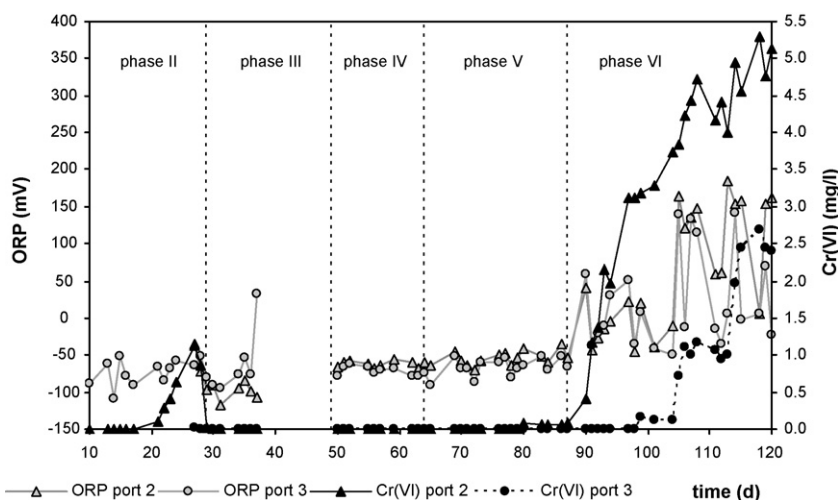


Fig. 6. ORP and Cr(VI) time profiles at sampling ports 2 and 3.

strate probably caused the slowdown or even the interruption of the anaerobic microorganisms biological activity. As the ORP turned to positive during phase VI, also Cr(VI) concentrations in the corresponding sampling ports increased significantly: from 8 $\mu\text{g/l}$ to 5.1 mg/l at port 2 and from 7 $\mu\text{g/l}$ to 3.1 mg/l at port 3 (Fig. 6).

At port 4 ORP was always negative. In the first sampling port the ORP was quite similar to the inlet one, which was slightly higher. The ORP data in the outlet are not reported since the outlet was collected in an open HDPE bottle and the prolonged contact with oxygenated air led to positive ORP values, non-representative of the phenomena occurring within the column.

The Cr(VI) profiles along the column height are presented in Fig. 7; in particular the curves relating to days 14, 21, 27 (phase II), 29, 34 and 37 (phase III), 51, 56, 62 (phase IV), 64, 71, 80, 86 (phase V), 91, 98, 104, 112, 120 (phase VI) were selected. The data obtained during each experimental phase are quite consistent and reproducible: in fact, the curves showed the same shape and almost the same slope. The highest removal rate occurred between the inlet and port 2 in the first 20 cm of the column in the first experimental phases (phase II, III, IV and V); only in the last experimental phase (phase VI) the highest removal rate was observed between port 2 and 3 (between port 3 and 4 in the last monitoring days). Such a behaviour was due to both the lack of organic substrate and the progressive saturation of the compost adsorption capacity at the bottom of the column. A decrease in the removal rate occurred also during phase II: on day 21 the inhibition of the biological activity led to a higher Cr(VI) concentration at port 2 and to a more rapid removal rate between ports 2 and 3. As organic carbon and nitrogen were fed, in the subsequent experimental phase the removal rate between the inlet and port 2 became higher.

Also the ORP decreased at the highest rate in correspondence to the first centimetres of the column, where the maximum Cr(VI) removal occurred. The ORP profile along the column during the same days selected for the Cr(VI) was almost reproducible in all the experimental phases (Fig. 8). After a strong decrease between the inlet and the second sampling port, ORP values were almost stable at about -50 mV and -100 mV in the phase II and III, respectively. The latter value resulted lower, due to the higher organic carbon availability, leading to an acceleration of the microbial metabolism contributing to the establishment of a reducing environment, as confirmed by the higher Cr(VI) removal. No significant changes were observed in the two subsequent phases IV and V; in phase VI the ORP values turned into positive (higher than 100 mV), decreasing to about -30 mV only in the last centimetres of the column.

ORP decrease occurred at the highest rate in correspondence to the maximum Cr(VI) removal, as a consequence of the biological metabolism.

3.2.2. pH

Also the pH profile along the column was almost reproducible in all the experimental phases, even if the initial pH in the inlet was quite different:

- about 6.6 for phase I;
- about 5 for phase II, due to the higher Cr(VI) content;

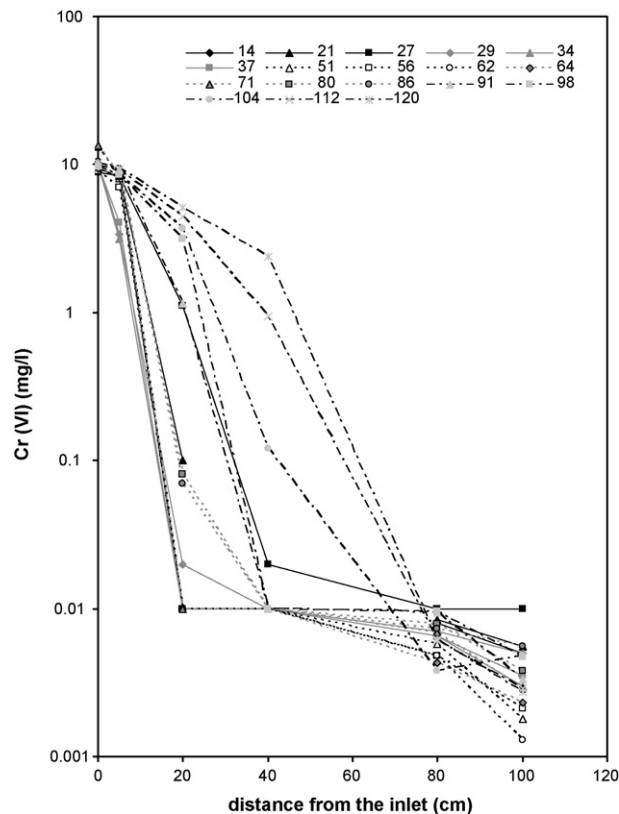


Fig. 7. Cr(VI) profiles along the column (phase II: black solid line; phase III: grey solid line; phase IV: black dotted line; phase V: grey dotted line; phase VI: black sketched line).

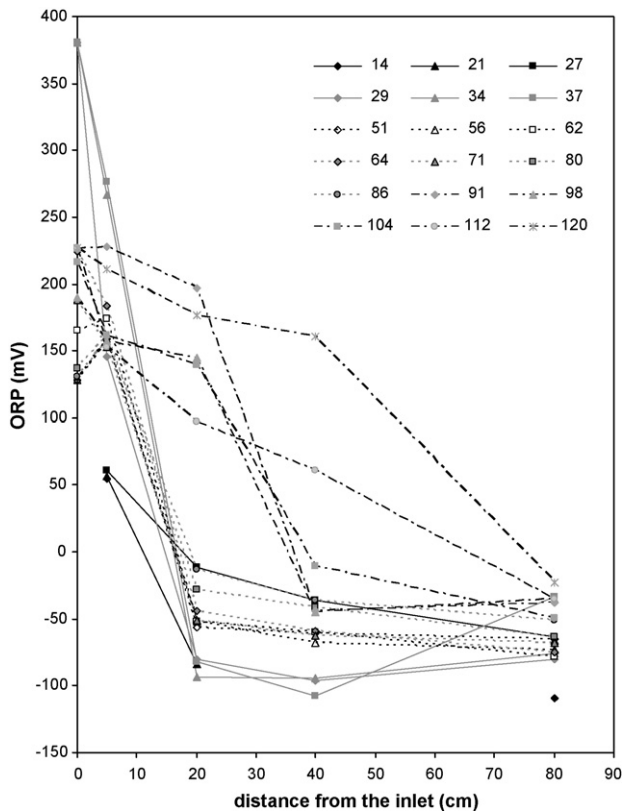


Fig. 8. ORP profiles along the column (phase II: black solid line; phase III: grey solid line; phase IV: black dotted line; phase V: grey dotted line; phase VI: black sketched line).

- about 3.8 for phase III, due to the addition of acetic acid;
- about 6.9 for phase IV, due to the addition of glucose, instead of acetic acid;
- about 6.1 for phase V, when the organic carbon and nitrogen concentration in the feeding was halved;
- about 5.4 for phase VI, near to the value obtained for the phase II, when the same solution was fed to the column.

After a strong increase between the inlet and the first sampling port, pH values gradually increased along the column until a stabilization at about 7.5 was reached; the pH increase was due to both

the high buffering effect exerted by the compost and the biologically mediated Cr(VI) reduction, as reported in equation 1.

pH increase occurred at the highest rate in correspondence to the maximum Cr(VI) removal, as a consequence of the biological metabolism.

3.2.3. Final comments

Based on these considerations, it can be concluded that the Cr(VI) removal in the present operating conditions was closely related to the biological activity, which contributed to the establishment of reducing conditions, as well as to the production of H_2S , thus leading to the hexavalent chromium reduction into Cr(III). Besides, no Cr(III) was detected in the samples collected daily from the column: the Cr(III) produced by the Cr(VI) reduction was under a solid non-soluble phase, as described in the following paragraph. Also the gravel contributed to such an “entrapment” of Cr(III); in fact, the natural cationic zeolites (phillipsite and cabasite) present in the gravel used bonded the metal cations as Cr(III). (It can be useful to remember that the hexavalent chromium is in solution under anion chromate, while the trivalent form is in solution as a cation.)

No clogging due to the biomass development seemed to occur within the column; in fact, at the end of the experimental period the hydraulic conductivity and the flow rate were approximately the same measured at the beginning. However, greater attention must be paid to the long-term behaviour and to the durability of such a system, in terms of its hydraulic properties.

3.3. Removal kinetic

Cr(VI) concentrations are plotted as a function of distance through the reactive column; when the flow rate and the porosity are known, distances through the column can be converted easily to residence times. A graph of Cr(VI) concentrations versus residence time can then be generated. If C_0 is the initial concentration of Cr(VI) and C is its concentration after time t , then a degradation rate constant (k) can be calculated for each concentration profile using a first-order kinetic:

$$C = C_0 e^{-kt}$$

$$\ln C = \ln C_0 - kt$$

When $\ln(C)$ is plotted against time in hours, the slope of the fitted line is the reaction rate k . The degree of fit can be determined by calculating the correlation coefficient (R^2), indicating how well the

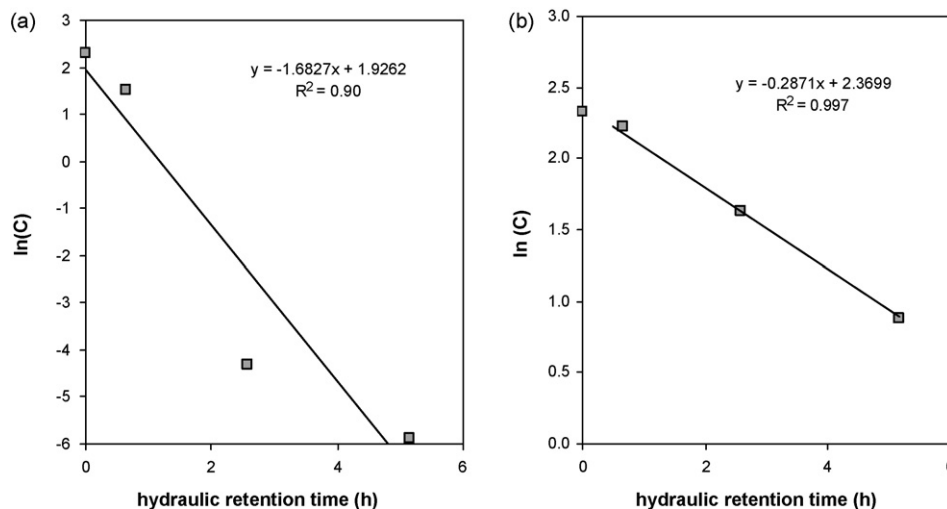


Fig. 9. Examples of linear regression of the experimental data in correspondence to day 36 (a) and day 120 (b).

Table 4
Mean half-life in each experimental phase.

Experimental phase	Solution fed to the column	Mean half-life (h)
II	B	0.84
III	C	0.41
IV	D	0.77
V	E	0.84
VI	B	1.16–2.66

first-order model fits the experimental data. Once the rate constant is known, a half-life ($t_{1/2}$) can be estimated for the contaminant [6]:

$$t_{1/2} = \frac{\ln 2}{k}$$

A half-life is the time period required to reduce the concentration of Cr by half.

The data presented in Fig. 7 allowed to calculate the Cr(VI) half-life. To such an aim, the first order kinetic (exponential decay) was applied between the inlet and port 3, fitting the experimental data with correlation coefficients generally higher than 0.9. In Fig. 9 two examples of the fitting line and the corresponding equation and correlation coefficient for day 36 (phase III) and day 120 (phase VI) are shown.

During the experimental period, $t_{1/2}$ varied in the range 0.41–2.66 h, as shown in Table 4. Such values are consistent with those obtained by other authors [24–27] for the Cr(VI) reduction by zero valent iron. In the phase I $t_{1/2}$ was equal to about 0.32 h, due both to the lower Cr(VI) concentration fed and to the organic carbon availability from compost. In general, it can be observed that the lowest $t_{1/2}$ values were reached when organic substrate was fed along with the contaminated solution (with the exception of phase I, when the compost organic content in the column was widely sufficient to sustain the biomass activity). The half-life strongly increased at the end of the experimental activity, when no nutrient was supplied: the values obtained were quite different if compared to those calculated for the phase II, when the same solution was used (solution B); such a behaviour was due to the complete consumption of organic matter by the microorganisms, enabling Cr(VI) reduction, as well as to the almost complete saturation of the adsorption sites at the bottom of the column.

3.4. Solid phase at the end of the experimental activity

At the end of the experimental period, the materials used in the column were characterized in terms of both total and hexavalent chromium content. The total chromium present in the solid phase is shown in Fig. 10: the highest Cr content was detected in the first centimetres of the column, where the maximum Cr(VI)

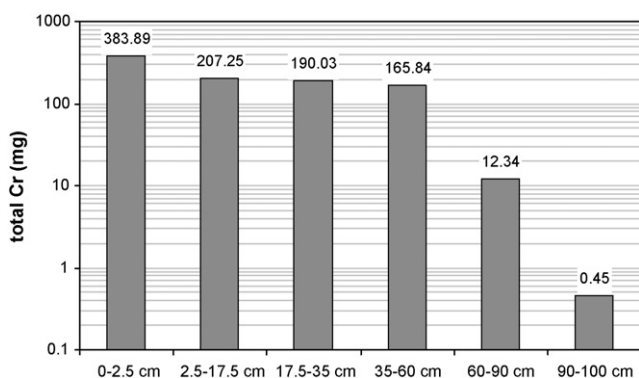


Fig. 10. Total Cr in the solid matrix at the end of the experimental activity.

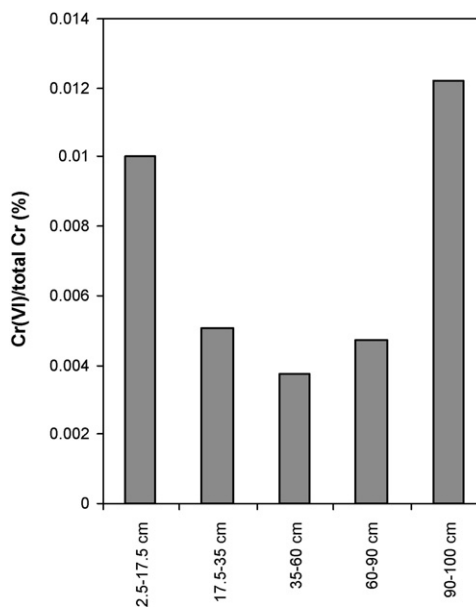


Fig. 11. Cr(VI) in the solid matrix at the end of the experimental activity, expressed as a percentage of the total chromium present in the column.

removal occurred; nevertheless, Cr(VI) represents only a negligible fraction of the total chromium entrapped in the solid matrix by adsorption, as shown in Fig. 11. Such results confirmed those previously obtained by the authors in the batch tests [19]: the Cr(VI) is almost completely biologically converted into the reduced trivalent form. Moreover, the negligible hexavalent chromium content was significantly below the regulation limit for soil.

As previously mentioned, a leaching test at pH 3 was performed on the solid matrix, in order to evaluate the leachable amount of chromium at extreme pH conditions, significantly far from the operating conditions of the experimental activity. A negligible release of chromium with respect to the total chromium content was observed (Fig. 12), confirming the high stability of the Cr(III) obtained as a product of Cr(VI) biologically mediated reduction.

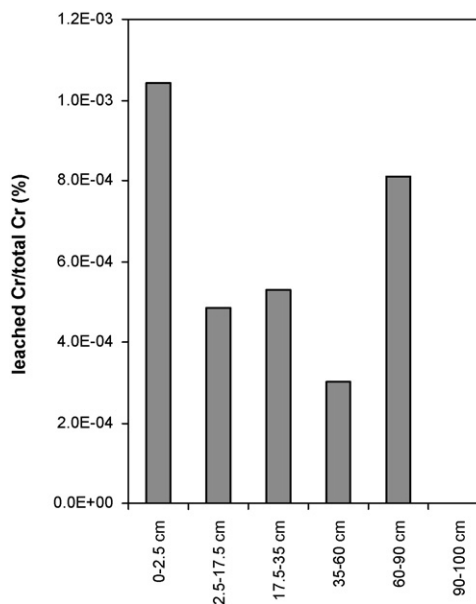


Fig. 12. Cr leached at pH 3 from the solid matrix at the end of the experimental activity, expressed as a percentage of the total chromium present in the column.

4. Conclusions

The results obtained showed the following:

- the organic based mixture allowed to reach high efficiencies in Cr(VI) removal from contaminated solutions;
- Cr(VI) removal was strictly linked to the anoxic/anaerobic biological activity of the native biomass of compost;
- almost all the Cr(VI) fed to the experimental system was converted into a stable and insoluble Cr(III) compounds.

The organic based mixture used represents a valid alternative to conventional approaches to chromium remediation, thanks to the proven efficiency and to the low cost of the materials tested.

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