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Abstract

The removal of hexavalent chromium, Cr(VI), from a water-sediment system has been studied in vitro in different condition of soil water saturation, in order to simulate different possible occurring real scenarios. Two different approaches have been compared: the bio-mediated and the chemical Cr(VI) reduction. In the first technique three organic nutrients have been tested: glucose, trealose and β- cyclodextrin. For the chemical remediation reducing agents such as sodium sulphite, sodium metabisulphite and ascorbic acid were considered.

Both bio-mediated and chemical remediation approach yielded to the total abatement of Cr(VI) from a contaminated soil. No relevant drawbacks were observed in term of release of metal ions in solution or pH perturbation. Among the organic nutrients glucose showed the best performances while the best chemical reducing agent was ascorbic acid. Ascorbic acid can be considered more advantageous because its reaction with Cr(VI) is very fast (total Cr(VI) abatement in 24 hours) and allows a better control of the process parameters, not involving the action of microorganisms; moreover its higher cost compared to glucose, is compensated by the much lower amount necessary to attain 100% of Cr(VI) reduction.

In case of in-situ remediation of groundwater, the spreading on soil of ascorbic acid would contribute to reduce the leaching of Cr(VI), helping the overall site remediation.

Keywords: hexavalent chromium, soil remediation, groundwater remediation, organic nutrients, ascorbic acid.

1. Introduction

The contamination of natural ecosystems by hexavalent chromium, Cr(VI), is of major concern worldwide, since Cr(VI) has been recognized as highly toxic, mutagenic and cancerogenic for living organisms. It has been classified among the 20 most hazardous environmental pollutants of the last 15 years (Chrysochoou et al., 2012). The highest risk of release of Cr(VI) in the environment is due to industrial activities, such as plating, painting processes, metallurgy and tanning industry. An evaluation of the European Pollutants Emission Register referred to 2012, estimates the contribution of different sources to the release of Cr into waters and soils and also reports the contribution of each country (http://prtr.ec.europa.eu, 2017).

When present in soil-water systems Cr(VI) could be naturally reduced to trivalent chromium, Cr(III), being the latter specie much less toxic and with a very low solubility in the typical natural pH and redox potential ranges (Zayed and Terry, 2003). Chromate reduction in soils is mainly due to the action of iron, vanadium, sulfides and organic matter; the reduction efficiency increases when the pH decreases (Zayed and Terry, 2003). Nevertheless the capacity of soil is not enough to operate this reduction in reasonable times; indeed Cr(VI) can persist in soils and because of its high mobility, it can easily leach and contaminate ground waters (Fendorf, 1995).

The transformation of Cr(VI) into Cr(III) is controlled by many factors, both biotic and abiotic; as for the abiotic ones, the main physical parameters influencing the reduction on soil are pH and redox potential (Dhal et al., 2013 and references therein). On the other hand, from the biotic point of view, the Cr(VI) conversion to Cr(III) depends from the microorganisms present in soil, able to mediate the process (Valls and De Lorenzo, 2002). The microbial reduction of Cr(VI) to Cr(III) has been deeply studied and reviewed (Cervantes et al., 2001; Cheung and Gu, 2007); it can follow two different paths, i.e. direct or indirect reduction. The indirect mechanism involves reducing agents produced by the bacterial metabolism; the main

microorganisms involved in such a mechanism are iron and sulfate reducing bacteria, that transform Fe^{3+} and SO_4^{2-} into Fe^{2+} and HS^-. These latter compounds can react with Cr(VI) yielding to its conversion to Cr(III) (Arias and Tebo, 2003). On the other hand the direct process can be operated by a variety of reductase bacteria taking electrons from reduced organic substrates (amino acids, nucleotides, sugars, vitamin, organic acids or glutathione) (Martha et al., 2008).

The increasing diffuse contamination of anthropogenic origin poses the need of developing remediation technologies for soil and groundwater treatment. Starting from 80-ies many approaches have been followed, physic-chemical as well as biological, operating in-situ or ex-situ (Higgins et al., 1997), aiming in most cases to the transformation of Cr(VI) into Cr(III), not harmful. In the remediation of contaminated sites, microbial processes are of potential application for the removal of toxic metal species, by varying their oxidation state and therefore transforming toxic species into less harmful ones or less soluble ones, thus allowing their precipitation (Mulligan et al., 2001).

The bio-reduction of Cr(VI) represents an interesting alternative to the traditional approaches, mainly based on physic-chemical processes of soil washing or the use of chemical reducing agents. Such processes are expensive and energy consuming and can severely modify the soil characteristics (Jing et al., 2007). Bio-remediation is cheaper, and has a lower impact on soil properties (physical, chemical and biological); its kinetic could be favored by inoculation of selected bacteria resistant to Cr(VI) and with high capability to reduce Cr(VI) to Cr(III) (bioaugmentation) (Viti and Giovannetti, 2007).

Recently the use of organic nutrients has been proposed as a possible innovative bio-mediated approach (Leita et al., 2011; Smith et al., 2002; Tokunaga et al., 2003; Michail et al., 2015); in particular the use of glucose, cheap and non-toxic substance, could be of great interest. Indeed glucose is able to promote the growth of microorganisms naturally present in soils and

stimulate their reductive capability. The microorganisms action mechanism is rather complicate and can include a direct involvement, if bacteria can uptake Cr(VI) and transform it into Cr(III) enzymatically, as well as an indirect mechanism, if the Cr reduction is mediated by bacteria metabolism or decomposition (Gadd, 1992).

Among the drawbacks of the bio-mediated approach the slow kinetic and the difficulty of keep the system well controlled can be cited. In this direction, an alternative could be represented by the addition of reducing chemical substances; their advantage is represented by the usually very fast and complete reaction while a drawback could be the reagent cost and safety (Dhal et al., 2013).

When considering a real case of contamination, soil remediation is more difficult compared to groundwater remediation; in the latter case the redox agent can diffuse rather fast and efficiently, whereas the dispersion in a solid medium is much more difficult. Moreover it is of fundamental importance to plan both soil and water remediation; it is meaningless to remove Cr(VI) from groundwater if the soil is contaminated, because of the risk of leaching and re-contamination of the aqueous phase.

In any case, before applying a remediation process in field, a preliminary evaluation of its performances at laboratory scale would provide useful information on the effect of the experimental parameters on the process efficiency; it will allow also to evidence possible side effects, due to the eventually pH and redox condition modification.

The present work deals with the in vitro study of Cr(VI) removal from a water-sediment system in different condition of soil water saturation %.

The Cr(VI) removal was addressed following two different approaches: i) bio-mediated and ii) chemical Cr(VI) reduction. In the first case three organic nutrients have been tested: glucose, trealose and β- cyclodextrin. For the chemical remediation reducing agents such as sodium sulphite, sodium metabisulphite, and ascorbic acid were considered.

Since both biotic and abiotic process could affect water physical-chemical properties, a cascade effect on the chemistry of metal oxides present in the soil cannot be disregarded; a specific attention has therefore been devoted to the concentration of naturally occurring element such as Fe, Ni and Mn, whose content in solution has to be kept under control in order to guarantee the environmental suitability of the overall Cr(VI) abatement procedure.

2. Materials and methods.

The study area is located in the plain in the urban area of Turin city. The Turin Province consists of three distinct sectors: a plain (Turin Po Plain), an alpine area and a hilly area (Figure 1). The lowlands form the central section and are bordered by mountains and hills to the west and east, respectively.

The Turin Po Plain, consisting of fluvial sediments (Middle-Upper Pleistocene and Holocene) is formed by coarse gravel and sand with minor clayey silt, showing a generally high permeability. This complex of fluvial sediments represents an important shallow aquifer whose water table is directly connected to the surficial hydrographic network. This complex rests above a transitional villafranchian complex (Middle Pliocene-Lower Pleistocene) consists of alternating clayey silt, sand and minute gravel, forming a multilayer semi-confined aquifer.

The Turin Hill (Eocene-Pliocene) consists of marine consolidated sediments, mainly comprising marl, sand and clay, with gravel found only locally. The Alps are formed by impermeable metamorphic rocks .

A composite sample of soils from an area close to an industrial dismissed site in North Italy (Figure 1) was collected in a phreatic aquifer at about 10 meters depth; the sampled sediments were sandy gravels with minor clayey silt; they were sieved to <63 μm with a

Retsch Vibrotronic Type VE, air dried and stored at room temperature. In the same site a groundwater sample was also collected and used throughout the work.

2.1. Soil Characterization.

Soil pH was determined with glass combined electrode Metrohm mod. 6.0203.100 OF. Heavy metal content was evaluated after soil mineralization according to Gazzetta Ufficiale method, with ICP-OES spectrometry (Inductively Coupled Plasma – Atomic Emission Spectriometer) Perkin Elmer OPTIMA 7000 (Supplemento ordinario alla Gazzetta Ufficiale, 1999). The instrument is provided with a Echelle monochromator, a cyclonic spray chamber and a teflon Mira Mist nebulizer. The instrumental conditions were: plasma power 1.3 kW; sample aspiration rate 15 rpm; argon nebulizer flow 0.6 L/min; argon auxiliary flow 0.2 L/min and argon plasma flow 15 L/min. All the reagents used were of analytical grade. All metal solutions for external calibration were prepared from concentrated stock solutions (Merck-Millipore). High-purity water (HPW) produced with a Millipore Milli-Q Academic system was used throughout.

Soil mineralization is carried out by acid digestion assisted by microwave (CEM MARS 5 Model). Experiments were performed in triplicate: 0.5 grams of soil sample were introduced in PTFE® vessels and 5 ml of MilliQ water and 5 ml of HNO3 70% were added.

Solid/liquid partition coefficient of Cr(VI) was determined according to a procedure standardized for contaminated sites (APAT e ISS, Marzo 2007) introducing in airtight plastic conical tubes, soil and water in 2.5:1 and 5:1 ratio and 10 mg/Kg of Cr(VI); the samples were stirred at 25°C for 24 h, then 20 ml of deionized water were added and the samples were stirred for 16 h; afterwards they were centrifuged and filtered with a Millipore system at 0.45 μm; on the filtered solution, Cr(VI) and total chromium contents were determined.

2.2. Sample preparation and metal analysis.

The amount of water to yield soil saturation was preliminarily evaluated and corresponded to 40% W/W. For performing Cr(VI) reduction tests, different series of microcosms were prepared using 5 g of dried soil each and groundwater amounts to obtain 500%- 100% or 50% of the soil water saturation % (respectively, 10 mL – 2 mL or 1 mL); 10 mg/Kg of Cr(VI) (as K_2CrO_4) solution were added to each sample. The K_2CrO_4 working solution was prepared by diluting a potassium chromate standard (Sigma Aldrich, primary standard by ICP-OES spectrometry, 1000 mg/L).

After equilibration of water/soil system, reducing agent was added (see below in section 2.3), either biological or chemical compound. All tests were performed at 25 °C, into 50 ml polypropylene tubes with screw caps and an air swing. For biological remediation test, samples at 500% of the soil water saturation % were stirred for the whole duration of the test and analysed after 0, 1, 3, 7, 14, 21, 28, 40, 60 days of incubation. Samples at 50% and 100% of the soil water saturation % were incubated at 25 °C without stirring and analysed after 0, 3, 7, 14, 21, 28 days.

In chemical remediation samples were maintained in incubation for 24 hours.

At the end of incubation, samples at 500% of the soil water saturation % were centrifuged and the aqueous phase separated and filtered at 0.45 μm.

As regards samples at 50% and 100% of the soil water saturation %, 20 mL of deionized water were added to soil samples after the incubation time, and left 16 h under stirring at 25°C in order to obtain the Cr in an aqueous phase suitable to be analysed; afterwards samples were centrifuged and filtered.

Total Cr, Fe, Ni and Mn content were determined on all the obtained aqueous solutions by means of ICP-OES following the procedure detailed in section 2.1. Cr(VI) content was

determined by the diphenylcarbazide colorimetric assay, following EPA 7196 A method (http://www.epa.gov, 2017); hexavalent chromium reacts in acidic medium with diphenylcarbazide ($C_{12}H_{13}N_4O$), oxidizing it and forming a purple red product, which UV-VIS absorbance is measured at 540 nm.

2.3. Chemical reducing and bio-reducing agents.

For chemical reduction test sodium sulfite, sodium metabisulfite and ascorbic acid were used and different molar reducing agent/Cr(VI) ratio were considered, as reported below in section 3.3. On the other hand, for biological mediated reduction essays, three types of nutrients have been tested: glucose, trehalose and β-cyclodextrin, a monosaccharide, a disaccharide formed by two glucose units and an oligosaccharide formed by 7 glucose units, respectively. Solution at a concentration of 2.5 g/L were used.

3. Results and discussion

3.1. Preliminary soil and groundwater characterization

Before starting the study of Cr(VI) removal, the groundwater has been analyzed (see Table 1) and the soil sample has been characterized in terms of acidity and heavy metal content. The results reported in Table 2 indicate a soil composition that complies with the limit values established for a site to be reclaimed intended for industrial use (http://www.gesindsrl.it/it/). Based on the soil pH, that is 8.5, the soil can be classified as alkaline; usually the alkalinity is due to the presence of $CaCO_3$ (calcareous soil) and carbonates behave as strong buffer, hindering pH variations due to other reactions that could occur into the soil.

3.2. Bio-mediated remediation.

Before studying the bio-remediation on the whole soil-water system, two preliminary experiments were performed in the absence of soil, on a natural water sample spiked with 2.5 and 4 mg L^{-1} of Cr(VI); the addition of 1g L^{-1}glucose syrup does not yield significant decrease of Cr(VI), after 48 hours of contact (see results in Table 3). This means that Cr(VI) is not chemically reduced by glucose. Moreover, since the water used was not sterile, no bacterial activity stimulated by the presence of glucose was operating Cr(VI) reduction. Experiments have then been performed in the presence of organic nutrients (see section 2.3) at a concentration of 2.5 g L^{-1}, at different water/soil (w/w) ratio.

The experimental results have been reported as mg Kg^{-1} of residual Cr(VI) referred to the soil. As can be observed in the Figure 2, the kinetic and the efficiency of Cr(VI) abatement is influenced by the type of added nutrient, being the process faster and more effective in the presence of glucose (Leita et al., 2011, González et al., 2014 and references therein). After 21days, Cr(VI) content decreased below the law limits (< 2 mg Kg^{-1} in soils). With the other nutrients worst results have been obtained; the addition of different carbon sources is of great importance in Cr (VI) removal since they act as electron source for the microorganisms to achieve Cr (VI) reduction (Dey et al. 2012). It can be hypothesized that more complex nutrients have to be decomposed by microorganisms prior to be metabolized, thus slowing down the kinetic of the overall process.

In order to check eventually system variation related to Cr(VI) reduction, pH has been monitored and the results are reported in Table 4.

In all samples pH remains almost constant at a value about 8.5, with the only exception of samples added with glucose, where a more significant pH decrease has been observed (see Table 4). In bioremediation processes it has been reported that the best reduction of Cr (VI)

can be obtained at neutral pH; the reduction decreased with either increase or decrease of pH from neutral (Jeyasingh J., 2005).

Being glucose the nutrient that allowed to obtain the best Cr(VI) abatement, more experiments have been then performed using glucose, to deeper characterized its performances.

In particular, the effect of soil water saturation % was examined on two systems, at 50 and 100% of soil water saturation; the added Cr(VI) corresponded to a final concentration in soil of 10 mg Kg^{-1}.

The trials lasted 28 days and samples were taken and analyzed at 0, 1, 3, 7, 14, 21, 28 days.

Following the procedure described in the experimental section, Cr(VI), Fe, Ni and Mn were also determined. Results concerning the evolution of Cr(VI) concentration are reported in Figure 3; after 28 days 99.8%±0.1 and 98.1%±0.1 of Cr(VI) disappearance can be observed at 100 and 50% of soil water saturation, respectively, with a slightly faster kinetic for 100% of soil water saturation. Since in the absence of soil no Cr(VI) reduction has been observed, it could be hypothesized that the Cr(VI) abatement in the water/soil system, in the presence of glucose or other organic nutrients, preferentially occurs at the soil/water interface. Therefore increasing from 50 to 100% the soil water saturation a higher water/soil interface area is obtained, thus justifying the enhanced reduction rate. Moreover, in these conditions, no significant release in solution of Ni (0.01 mg kg^{-1}), Fe (0.09 mg kg^{-1}) and Mn (0.03 mg kg^{-1}) occurred compared to their concentration before the treatment.

In order to assess the influence of soil water saturation and glucose concentration/amount on the Cr(VI) reduction, an additional experiment has been performed, varying the soil water saturation % from 25 to 1000% and keeping constant the glucose amount at 5 g Kg^{-1} referred to the soil; experiments have been run in duplicate. The results are reported in Figure 4. When

increasing the saturation % (and consequently the added water) a relevant decrease in Cr(VI) abatement efficiency is evidenced.

The best results have been obtained at low soil water saturation %; at higher soil water saturation %, the solution is more diluted but the overall glucose content has been kept constant therefore similar Cr(VI) reduction rate would be expected, in case of bulk reaction. Since at lower glucose concentration corresponded lower reaction rate (and no Cr(VI) reduction was observed in the absence of soil), it can be confirmed the hypothesis that the Cr(VI) reduction did not occur in the bulk, rather at soil/water interface (Nancharaiah et al., 2013), in spite of the high Cr(VI) solubility in water.

3.3. Chemical remediation.

The chemical approach can be considered as an alternative to the bio-mediated one; in principle microorganisms are not involved and the process is expected to need significantly shorter times to reach the equilibrium.

Based on their redox potential three reagents have been selected, hereinafter reported following the increasing redox potential: sodium sulfite (NaSul), sodium metabisulfite (NaBisul) and ascorbic acid (AscAc).

Preliminary trials were performed in aqueous solution of Cr(VI), in the absence of soil, varying the pH and the molar ratio between Cr(VI) and reducing agent. In all these experiments the reaction time was 60 minutes, since for longer contact time no variation in the reduction yield has been observed.

3.3.1. Sodium sulfite

A molar ratio NaSul/Cr(VI) of 12 has been considered.

The reduction occurs immediately as can be visually noticed by the fast disappearance of the characteristic yellow color of a chromate solution; the effect of pH is clearly evidenced in the Figure 5; in the pH range 4- to 5 NaSul behaves as optimum reducing agent allowing to decrease the Cr(VI) amount more than 90%; the sulfite performances fall down at pH above 7 (about 5% of Cr(VI) abatement at pH =8). For application to real contaminated waters this aspect represents a relevant limit since many natural waters show pH values in the range 6 to 8.

3.3.2. Sodium metabisulfite

Three series of samples have been prepared with NaBisul/Cr(VI) molar ratio equal to 12, 6 and 3.

In this case better results can be obtained (see Figure 6); the Cr(VI) disappearance is still very fast and with the molar ratio of 12, in the pH range 4 to 9, 100% of Cr(VI) abatement can be attained. At lower NaBisul/Cr(VI) ratios the efficiency decreases when pH increases but even in the worst conditions an abatement of 40% of Cr(VI) can be reached.

3.3.3. Ascorbic acid

This compound (i.e. the Vitamin C) presents a very high solubility in water at room temperature (330 g L^{-1}). Five series of samples have been prepared at the following ascorbic acid/Cr(VI) molar ratio: 6, 3, 1.5, 1 and 0.5.

When observing the obtained results, reported in Figure 7, some interesting features can be evidenced. First of all, the capability of ascorbic acid to reduce Cr(VI) is not influenced by the pH in the range from 4 to 9. Moreover, to obtain 100% of Cr(VI) reduction lower molar ratio can be used compared to the other chemicals previously tested. Even for a molar ratio of 0.5 the efficiency is still about 50%. Such performances remain unmodified also in the presence of lower amount of Cr(VI).

After these preliminary tests performed in water, the efficiency of the reducing agents has been studied on the water/soil system.

3.4. Soil-water decontamination.

Based on the above discussed results Cr(VI) has been added to different natural water-soil samples, without any pH modification (therefore working at pH=8.5). Different reducing agent/Cr(VI) molar ratio have been considerd at three different soil water saturation %: 50%, 100%, 500%.

The results are reported in terms of percentage of Cr(VI) abatement.

Preliminary results showed that after 24 hours of contact time, there is not further variation of the Cr(VI) reduction yield; therefore samples were incubated for 24 hours. The best results have been obtained in the presence of ascorbic acid at a molar ratio of 6; as can be observed in Figure 8 the saturation is not affecting the reducing efficiency and 100% of Cr(VI) reduction can be attained. Only for lower molar ratio a decrease in Cr(VI) reduction can be observed when decreasing the saturation.

The effect of saturation is opposite to what observed in the bio-mediated approach; in chemical remediation the process can therefore be considered as a bulk process.

It is worth to be noticed that the use of ascorbic acid is not showing any drawbacks in term of release of other metal ions in solution. Actually, Mn, Fe and Ni have been quantified and in all case they are never present in concentration higher than few mg Kg^{-1}; in oversaturated system they are present below mg Kg^{-1} level.

4. Conclusions

The results demonstrated that both bio-mediated and chemical remediation approach can yield the total abatement of Cr(VI) from a contaminated soil.

No relevant drawbacks can be observed in term of release of toxic metal ions in solution or pH perturbation. Among the organic nutrients the best performances can be ascribed to the glucose while the best chemical reducing agent has been demonstrated to be the ascorbic acid. Despite the similar performance in term of efficiency, the chemical system is much simplified compared to the bio-mediated one and allows to obtain results in very short times (up to 24 hours) compared to the bio-ones (up to above 30 days). Under an economical point of view the higher cost of ascorbic acid compared to glucose is compensated by the much lower amount necessary to reach 100% of Cr(VI) reduction.

These results encourage an on-field testing of the chemical remediation with ascorbic acid on a contaminated groundwater; indeed solution of ascorbic acid can be directly spread on soil, to attain the overall site remediation.

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FIGURE CAPTIONS

Figure 1. The Turin Province territory. The Turin Po Plain (1), consisting of fluvial sediments, is interposed between the Alps (2) formed by metamorphic and Turin Hill (3), formed by sedimentary marine rocks . Red circle: area of study.

Figure 2. Evolution of Cr(VI) versus time in samples at 500% of soil water saturation in the presence of different organic nutrients: Glucose (empty squares), Trehalose (solid squares) and B-Ciclodextrin (solid triangles) in concentration of 2.5 g L^{-1}

Figure 3. Evolution of Cr (VI) vs time in the presence of glucose in concentration 5 g $Kg^{-1}$of soil, in samples prepared at 50% (solid squares) and 100% (empty squares) soil water saturation.

Figure 4. Residual concentration of Cr(VI) after 7 contact days in soil sample prepared at different soil water saturation % of soil water saturation, in the presence of glucose 5 g $Kg^{-1}$of soil.

Figure 5. Percentage of Cr(VI) abatement in 10 ml of an aqueous solution vs pH, in the presence of NaSul. NaSul/Cr(VI) molar ratio equal to 12

Figure 6. Percentage of Cr(VI) abatement in 10 ml of an aqueous solution vs pH, in the presence of NaBisul. NaBisul/Cr(VI) molar ratio equal to 12, 6 and 3.

Figure 7. Percentage of Cr(VI) abatement in 10 ml of an aqueous solution vs pH, in the presence of AscAc. AscAc/Cr(VI) molar ratio equal to 6-3-1.5-1-0.5.

Figure 8. Percentage of Cr(VI) abatement in the presence of AscAc.

AscAc/Cr(VI) molar ratio equal to 6-3-1.5-0.5. Sample soil water saturation equal to 50-100-500%.

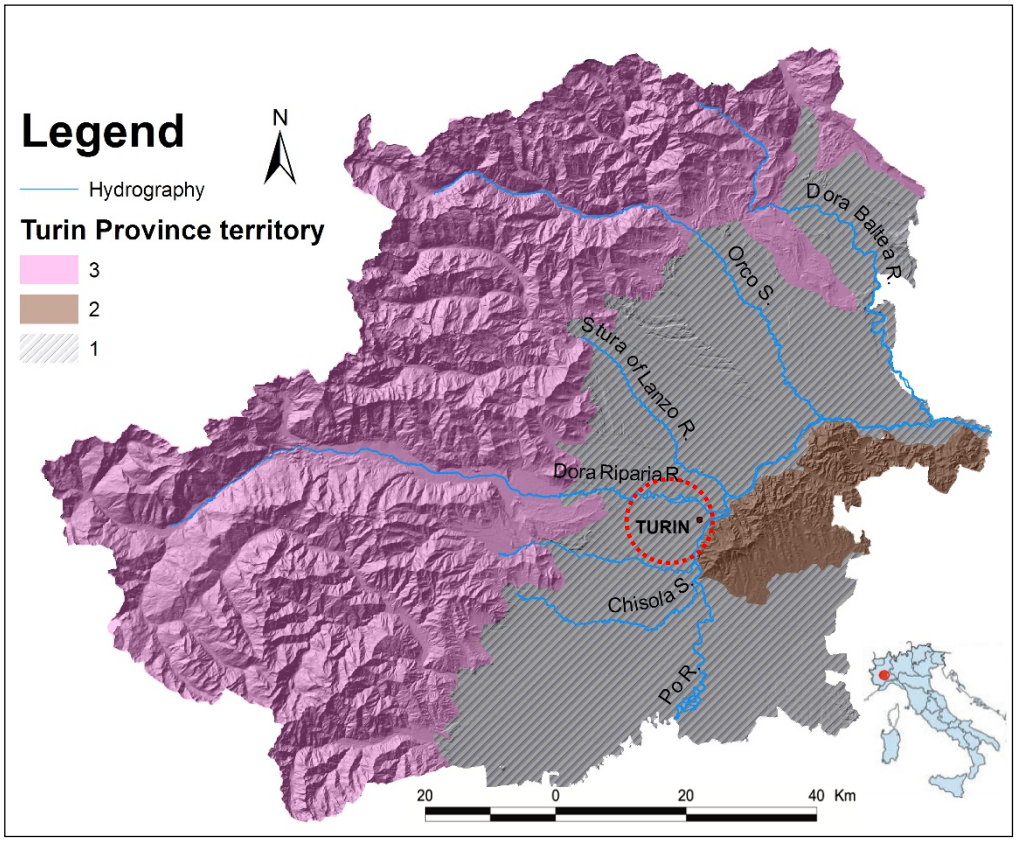
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Figure 1

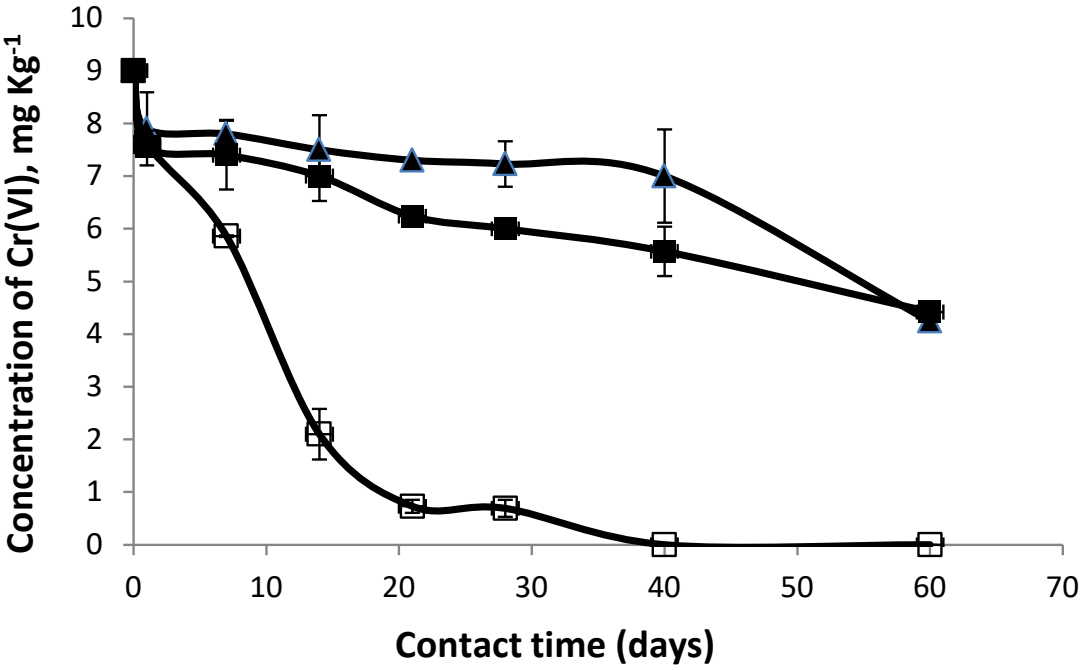
Concentration of Cr(VI), mg Kg-1
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
Contact time (days)

Figure 2

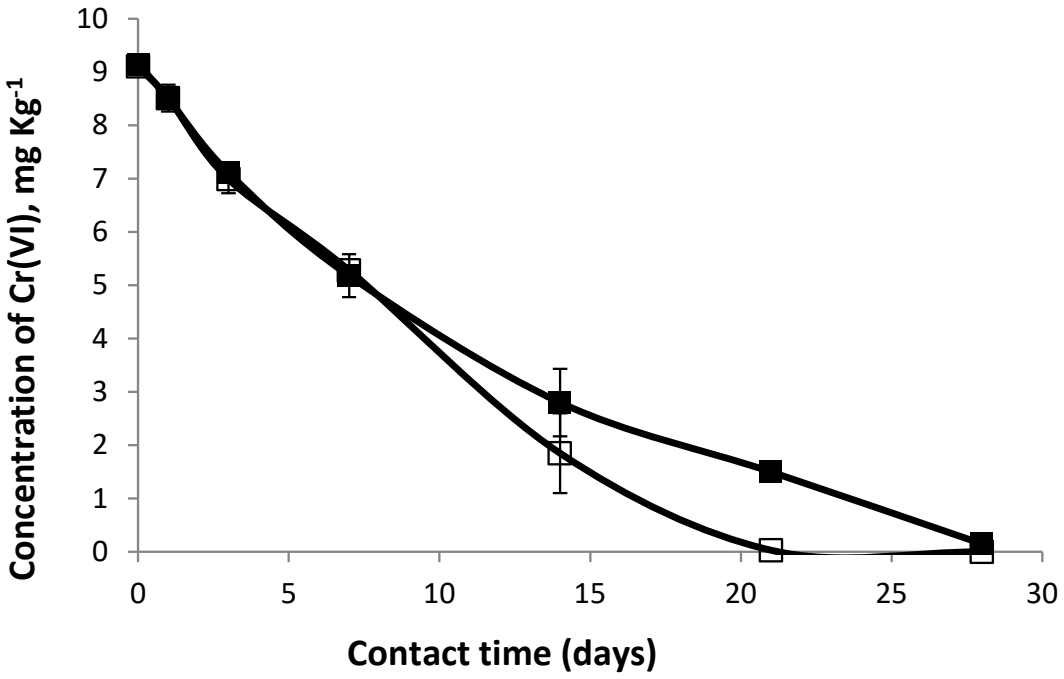
Concentration of Cr(VI), mg Kg-1
10
9
8
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
Contact time (days)

Figure 3

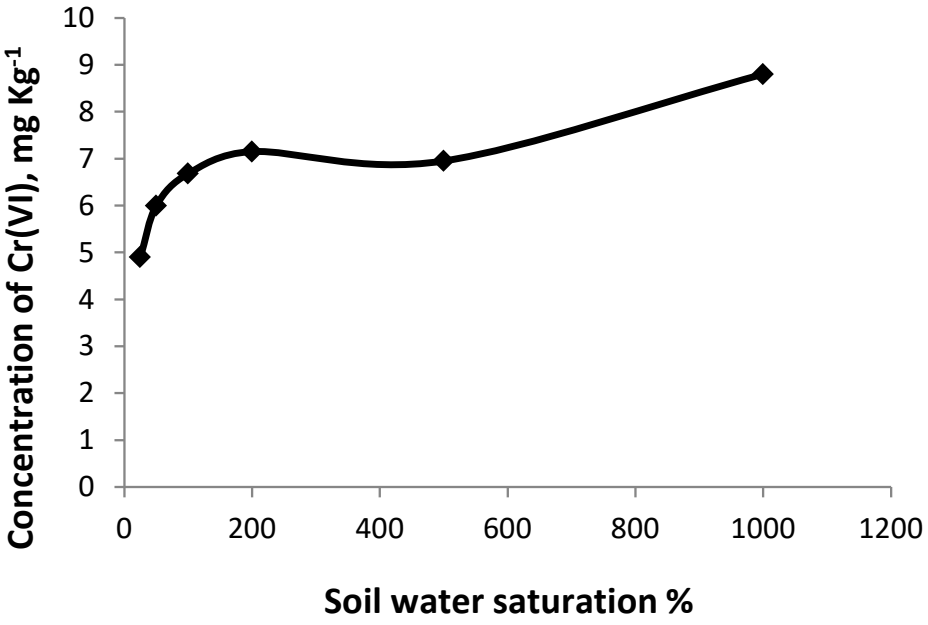
Concentration of Cr(VI), mg Kg-1
10
9
8
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
1200
Soil water saturation %

Figure 4

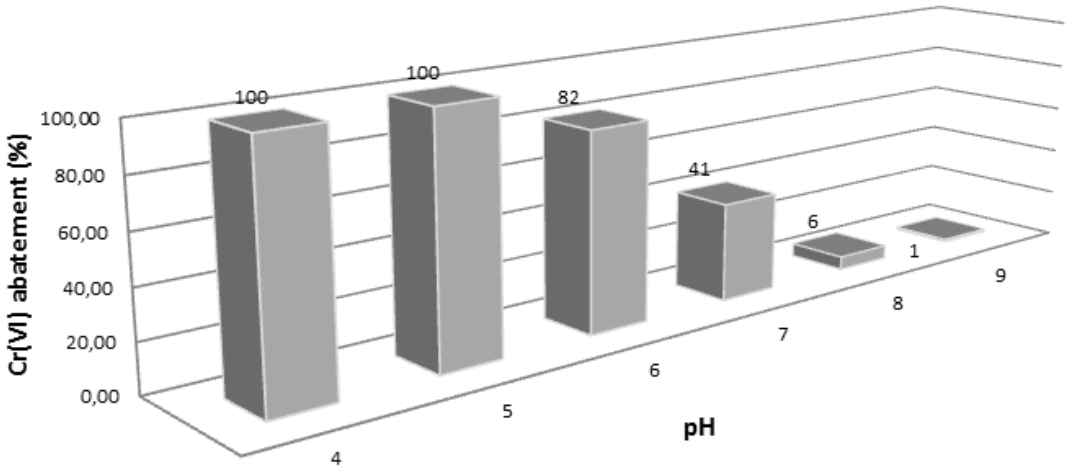
Cr(VI) abatement (%)
100,00
80,00
60,00
40,00
20,00
0,00
100
100
82
41
6
1
4
5
6
7
8
9
pH

Figure 5

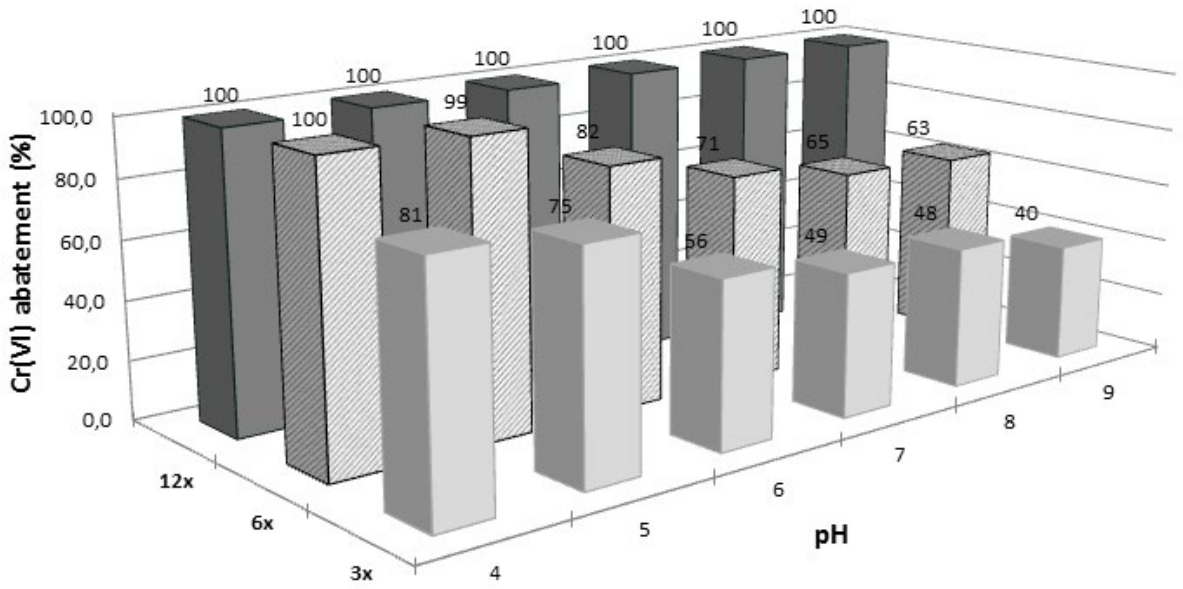
Cr(VI) abatement (%)
100,0
80,0
60,0
40,0
20,0
0,0
12x
6x
3x
4
5
6
7
8
9
pH
100
100
100
99
100
82
100
71
100
65
81
75
56
49
63
48
40

Figure 6

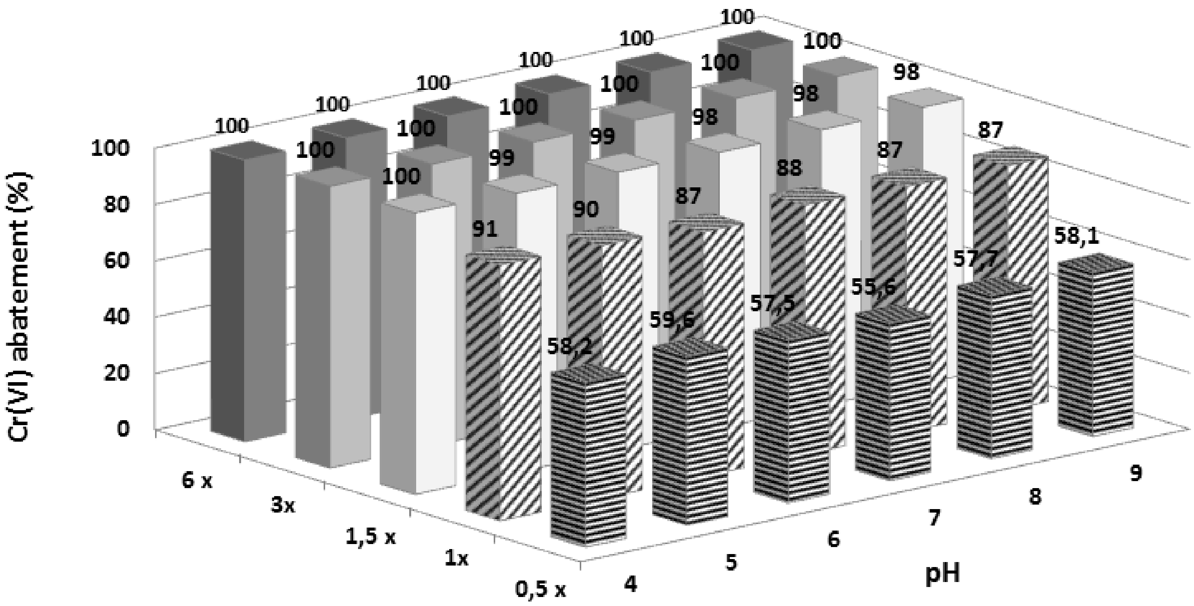
Cr(VI) abatement (%)
100
80
60
40
20
0
6 x
3x
1,5 x
1x
0,5 x
4
5
6
7
8
9
pH
100
100
100
100
100
100
100
100
100
100
100
98
100
99
99
98
98
98
91
90
87
88
87
87
58,2
59,6
57,5
55,6
57,7
58,1

Figure 7

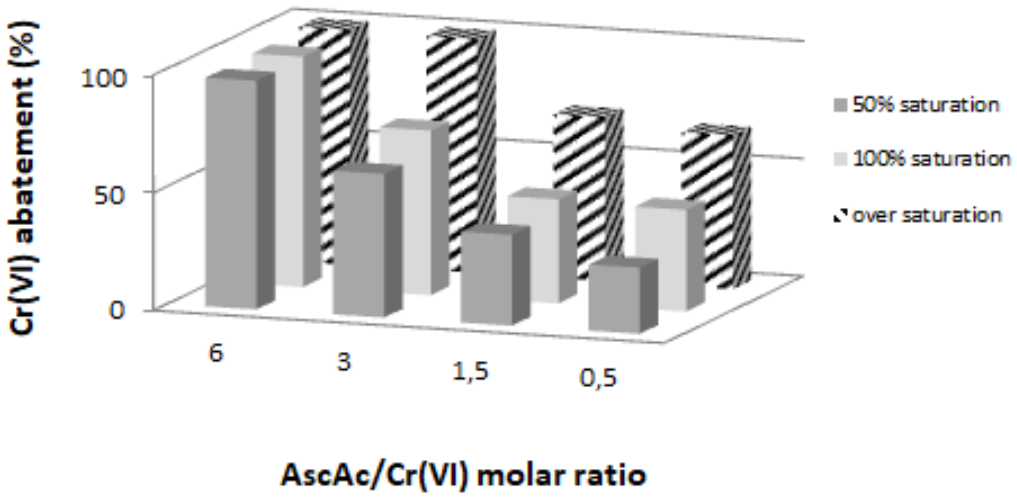
Cr(VI) abatement (%)
100
50
0
6
3
1,5
0,5
AscAc/Cr(VI) molar ratio
50% saturation
100% saturation
over saturation

Figure 8

Table 1. Results of groundwater characterization

Parameter	**Value**
pH	7.3
Total organic carbon	1.2 mg L^{-1}
Eh	0.25 mV
Cr tot	44.6 µg L^{-1}
Cr (VI)	42.6 µg L^{-1}
Fe	51.7 µg L^{-1}
Ni	20.6 µg L^{-1}
Mn	47.8 µg L^{-1}

Table 2. Metal concentration (mg Kg^{-1}) in soil digested in microwave in the presence of HNO_3 70%

Metal	mg Kg^{-1}	Standard Error (mg Kg^{-1})	LOD (mg Kg^{-1})
Cd	<0.05		0.05
Pb	43.12	1.1	2.0
Mn	118.06	2.6	0.5
Ni	48.97	5.2	1.0
Fe	44659.00	302	5.0
Cu	0.00254	2.5	1
Cr	767.47	2.8	0.2
Zn	228.51	5.3	1.0
Ba	140.72	10.3	0.5
Mg	56849.11	293	5.0
Al	26497.37	24.0	2.0
Na	2703.24	32	2.0
K	3157.58	27	5.0
Ca	1797.89	59	5.0

Table 3. Evolution of aqueous Cr(VI) solution upon glucose syrup addition

Sample	mgL^{-1} Cr(VI) in aqueous phase t=0	mgL^{-1} Cr(VI) in aqueous phase t=48 h
A	4.00	3.99
B	2.54	2.52
C	1.04	1.05

Table 4. pH measurements during Cr(VI) abatement

Added nutrient	ß-cyclodextrin		Trehalose		Glucose	
	Average pH	Standard error	Average pH	Standard error	Average pH	Standard error
t_0	8.71	0.092	8.71	0.001	8.56	0.035
t_1	8.43	0.007	8.51	0.007	8.52	0.014
t_7	8.20	0.014	8.20	0.032	7.88	0.007
t_{14}	8.22	0.018	8.23	0.085	7.78	0.025
t_{21}	8.13	0.004	8.17	0.014	7.81	0.004
t_{28}	8.31	0.007	8.34	0.025	7.91	0.007
t_{40}	8.19	0.032	8.18	0.014	7.91	0.004
t_{60}	8.29	0.007	8.18	0.042	7.92	0.004