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# Support Tool for Identifying In Situ Remediation Technology for Sites Contaminated by Hexavalent Chromium

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**Abstract:** Sites contaminated by hexavalent chromium raise concerns relating to the toxicity of the pollutant, as well as for the increased solubility of its compounds, which helps it to seep into aquifers. Chemical and biological in situ treatment technologies, with good potential in terms of environmental sustainability, have recently been designed and implemented on a wide scale. A useful support tool is shown in the manuscript in the preliminary phase of assessing possible technologies applicable according to the site-specific characteristics of sites. The actual efficacy of the technologies identified should nevertheless be verified in laboratory trials and pilot tests.

**Keywords:** hexavalent chromium; decision support tool; remediation technologies

## 1. Introduction

Wide scale industrial use of hexavalent chromium and its compounds has caused serious environmental pollution, generally relating to accidental or unlawful leakage of waste from production processes or illegal dumping of slags [1]. The presence of Cr (VI) in soil and groundwater has also been linked to geogenic processes, namely, weathering of ultramafic and mafic rocks in various areas around the world [2–4].

The increasing availability of scientific studies has progressively drawn attention to in situ remediation technologies. These are innovative compared to the “Dig and Dump” (D&D) of unsaturated soil and to the “Pump and Treat” (P&T) of groundwater. They enable the risks of the movement of contaminated matrices to be limited and a reduction in the remediation times, above all for the groundwater. Technologies for in situ treatment of Cr (VI), including the injection of reducing substances and bioremediation processes, do seem to ensure better results in terms of efficiency, with generally lower costs [5]. Full-scale application of these technologies is continuously growing, especially in the United States, with results appearing to confirm what has been illustrated on a smaller scale [6].

There are no written “Decision Guides” available for hexavalent chromium to refer to in choosing potentially the most suitable remediation technology depending on the site-specific conditions. Some tips are found in documents, such as those drawn up by the US Environmental Protection Agency [7,8] or the Savannah River National Laboratory [9], in which scenarios for sites contaminated by inorganic pollutants are set out. The scenario of greatest interest, on which this manuscript concentrates, is that of soil and groundwater in oxidising conditions, where the chromium remains in hexavalent form if not properly treated. The purpose is to provide a support tool useful in the

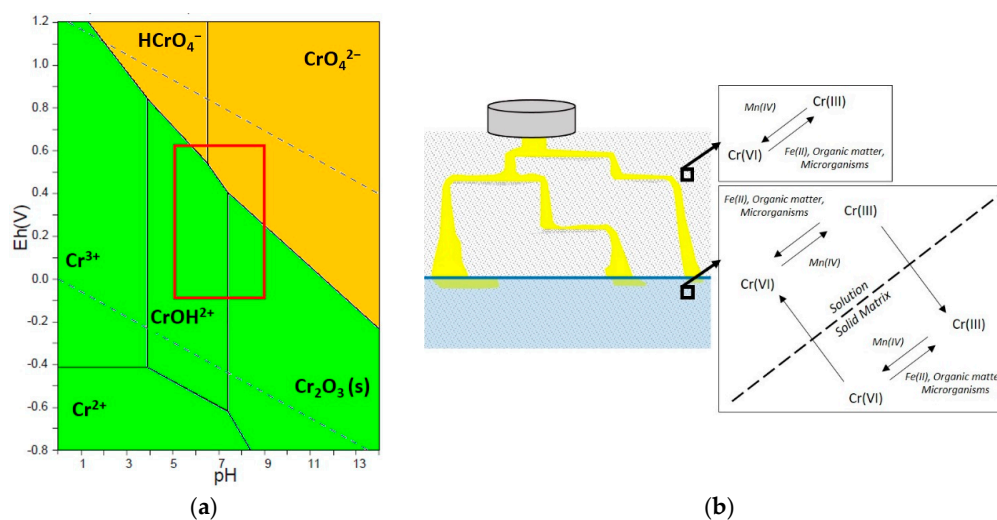
preliminary assessment of the remedial options to address further investigations on technologies with potential feasibility. In fact, due to the highly complex behaviour of inorganic pollutants in the environment and the numerous chemical species with which they can interact, a definite choice can only be made after site-specific tests.

## 2. Behaviour of Chromium in Soil and Groundwater

Chromium can have several oxidation states, but the most common forms in the soil are Cr (III) and Cr (VI) [10,11]. Cr (III) tends to form insoluble and low polluting compounds in water. Cr (VI) is generally present as hydrogen-chromate ion ( $\text{HCrO}_4^-$ ) and chromate ion ( $\text{CrO}_4^{2-}$ ) [2]; it has high mobility and high toxicity in a broad pH range [1,12,13], and is classified as a Class A carcinogen [14,15].

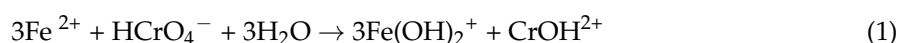
The state of oxidation and the chemical form of the chromium in the ground are jointly influenced by the pH and by the redox potential, as shown in the diagram of Pourbaix [16] (Figure 1a). The pH range of interest includes values between 5 (acidic) and 9 (alkaline), which can be considered the possible extremes for soil in natural conditions [17]; the potentials typically encountered in an aquifer are included in the range between  $-100$  and  $+600$  mV (vs. Standard Hydrogen Electrode—SHE) [18]. With reference to the area within the red box in Figure 1a, the prevalence of chemical species of Cr (VI) is located in the portion relating to the most basic pH and redox higher than  $+200$  mV. However, the theoretical Pourbaix diagram of Cr had to be properly adjusted to site-specific conditions, taking into account groundwater and soil composition.

Through redox processes, chromium changes dynamically from one state of oxidation to another (Figure 1b). Reducing species, which serve as electron donors (e.g., organic substances, such as carbohydrates, proteins, and humic acids), facilitate the reduction process of Cr (VI) to Cr (III); humic acids also form complexes with Cr (III) [9].

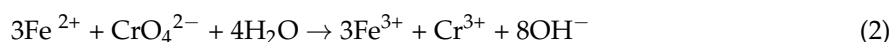


**Figure 1.** (a) Diagram of Pourbaix (redox potential Eh vs. SHE) for the chromium (in yellow Cr (VI) species, in green Cr (III) species); the red rectangle encloses the area of natural environmental conditions; (b) mechanisms of action on the chemical species of the chromium (in yellow) in the subsoil (in grey the unsaturated zone, in pale blue the saturated zone).

Amongst the most widespread electron donors, Fe (II) assumes special importance [19]. In aerated soil, with high redox potential, the iron has a trivalent form. In asphyxial soil, with low redox potential, the Fe (II) ions in solution are plentiful, depending also on the chemical composition of the soil, and are prone to react with hexavalent chromium. At pH 5–6, the redox reaction is [20]:



At pH > 7, the reduction mechanism of the hexavalent chromium follows the reaction [21]:



The formation of Cr (III) and Fe (III) species result from reactions (1) and (2). Reacting with each other, or with further dissolved Fe (II), means they do not remain in solution, but are removed in the form of hydroxides.

Strong oxidising conditions, generated, for example, by the presence of Mn (IV) oxides, can boost the transformation of Cr (III) precipitates into chemical Cr (VI) species [22]. That said, the significant instances of contamination by Cr (VI) are essentially linked to soils/aquifers in oxidising conditions, with greater intrinsic permeability of  $10^{-14} \text{ m}^2$  (coarser lithologies of fine silty sands); in fact, at a redox potential of around +500 mV (vs. SHE), the natural reduction of Cr (VI) to Cr (III) is widely disadvantaged [23]. Conditions of this type are typical of glacial/alluvial deposits with low organic substance and of fragmented rocks.

### 3. Technologies

In the last decade, numerous studies have been carried out, mainly based on laboratory scale and pilot tests, to assess the efficacy and sustainability of new technologies for the in-situ treatment of Cr (VI). Sustainability integrates many different, and sometimes competing, factors [24]; environmental, social, and economic factors must be considered and the final selected remediation plan will result in a balance of them [25].

In this chapter and in Table 1, the principal innovative technologies, which have reached full-scale application, are presented, subdivided according to the typology of mechanism used and potentially treatable zone. Some only apply in saturated or unsaturated zones; both unsaturated and saturated zones should also be further separated to take account of the fact that the full involvement of the contaminated matrix in the treatment is generally tied to the depth of the contamination from ground level (g.l.).

**Table 1.** Potential applicability (x: yes; -: no) of innovative technologies depending on the zone and maximum depth of soil to be treated.

Technology	Unsaturated 0–1 m	Unsaturated 1–10 m	Unsaturated > 10 m	Saturated < 10 m	Saturated 10–25 m	Saturated > 25 m
Chemical process with solutions or slurry	-	-	-	x	x	x
Chemical process with gaseous reagent	-	x	x	-	-	-
Indirect biological process	-	-	-	x	x	x
Biological process-Phytoremediation	x	-	-	-	-	-
Chemical-physical process-Electrokinetics	x	x	-	x	-	-
Chemical-physical process-Flushing	x	x	-	-	-	-

#### 3.1. Innovative Technologies for Cr (VI) Remediation

##### 3.1.1. Chemical Process

In general, applicable reagents for the chemical reduction of Cr (VI) in a saturated zone have an iron or sulphur based composition, and can act either directly or indirectly [26,27]. Amongst the iron-based species that act directly on the reduction of Cr (VI), the most commonly used is zerovalent

iron in the form of nano-particles. Acid conditions facilitate Cr (VI) reduction with Fe (0) [28–30]. The calcium polysulphurs ( $\text{CaS}_4$ ,  $\text{CaS}_5$ ) are also in common use [31]; Chrysochoou et al. [32] have shown that, when polysulphurs are used, the reducing conditions remain in the soil for a long time; neutral or basic pH values have provided greater reducing capacities [33]. Sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) acts mainly indirectly, converting Fe (III) to Fe (II) [34–36]. This ion plays an active role in the reduction of the pollutant, according to reactions (1) and (2). Under acidic conditions, the process is favoured. Ascorbic acid, or vitamin C ( $\text{C}_6\text{H}_8\text{O}_6$ ), like other organic acids, certainly represents a promising alternative, as it does not exhibit any toxic features. At  $\text{pH} \leq 7$ , it reduces Cr (VI) efficiently, transforming itself into dehydroascorbic acid [37]. Bianco Prevot et al. [38] have, however, encountered high levels of Cr (VI) reduction in the environment with a pH up to 9.

The in situ reduction of Cr (VI) in an unsaturated zone by means of gaseous injections [39] is an approach which has been little developed so far and principally concerns the use of hydrogen sulphide ( $\text{H}_2\text{S}$ ) diluted in air. The efficacy is limited to acid or more neutral environments; for  $\text{pH} > 7.5$ , a significant collapse in the efficiency of the process may occur [40]. The technology is especially suited to permeable soil, where the circulation of the gaseous reagent is enhanced. To promote the reduction of Cr (VI) to Cr (III) in unsaturated soil, there needs to be adequate moisture content in the soil or in the gas current injected [41].

### 3.1.2. Biological Process

With reference to biological processes in a saturated zone, the administration of carbonaceous substances aimed at supporting an indirect bacterial action can be assessed [38,42,43]. The mechanism is designed to create reducing conditions, with possible releases of Fe (II) from the solid phase of the soil. The quality of the treated soil is generally higher than that treated with chemicals [44]. The efficiency of Cr (VI) reduction through indirect biological processes tends to diminish as the concentration of the contaminant increases, because of the rise in toxicity [45]. This type of process is therefore not advised for environments with high concentrations of Cr (VI) and where there is a lack of iron. Chemical processes occasionally complement biological technologies, as, for example, in Němeček et al. [46], where there is the combined use of zerovalent iron and iron lactate. Many registered trademark reagents on the market incorporate the advantages of the two approaches.

For shallower unsaturated soil, phytoremediation treatment should be mentioned [47,48]. The process is certainly slow, but recent studies have shown how it can be accelerated, for example, by boosting the growth of the plants [49]. To define a phytoremediation treatment, it is crucial to evaluate whether the physical chemical features of the soil and the meteorological/climatic conditions of the site are compatible with the plant species to be used. In the case of phytoextraction, it is necessary also to take into account the periodic discharge of biomass, which contains chromium mainly in trivalent form [50]. The technology is not advised for environments with high concentrations of Cr (VI).

The injection of selected bacterial suspensions to reduce the Cr (VI) directly (chromium-reducing microorganisms) appears difficult to apply both in saturated and unsaturated zones. In fact, the in situ development and maintenance of these microorganisms is difficult [51–54]. As further proof, there is a lack of literature recording encouraging experiences.

### 3.1.3. Chemical-Physical Process

Electrokinetics is a remediation technique for both the saturated and the unsaturated soil zone, based on the application of a low constant electric field between two or more electrodes (positive/anode and negative/cathode) [55–57]. The field causes two important transport mechanisms, almost independent from soil intrinsic permeability: (a) Electromigration (transport of ionic species in bulk solution, according to the electric field direction); (b) electroosmosis (bulk pore fluid migration, including neutral or charged dissolved species, from the positive to negative electrode). The cathodic flow must be pumped out, whereas chromium can accumulate at the anode as a precipitate. Full-scale applications have been satisfactory, although significant limitations in the process were observed when

Cr (VI) concentration was low compared to non-target ion concentrations [58]. The equipment had to be optimised to reduce costs [59].

Soil flushing is used to treat unsaturated soil contaminated by leachable pollutants through suitable chemical agents [60,61]. In the case of Cr (VI), given its high solubility in water, the use of these latter may not be necessary [62]. Soil flushing for Cr (VI), in general, has satisfactory results in alkaline, permeable, and homogeneous soils whereas rocky formations or layers of less permeable soil help to create preferential flows that leave the untreated zone.

### 3.2. Full Scale Implementation

With reference to the above mentioned in situ remediation technologies for Cr (VI) requiring the injection of chemicals, they can be implemented in full scale using a range of approaches, depending on the technology, the zone to be treated, and the geological/hydrogeological features of the site. Reactive zones (RZ) and permeable reactive barriers (PRB) are discussed.

RZs involve the generation of a zone with suitable physical-chemical features in the portion of ground/aquifer to be treated by injecting appropriate reagents, without soil excavation. They are the most widely used, in view of their versatility and the possibility of reaching considerable depths [63]. The injections can take place upstream from the source of the contamination, next to it, and/or downstream. To intercept a plume in a saturated zone, lines of injection points can be used, perpendicular to the direction of the flow [64]. Within 10 m from g.l. and with lithology that is not excessively coarse (therefore, excluding gravel and pebbles), the reagents can be administered using “direct push” type systems, which require significant injection pressure to facilitate the distribution [65,66]. The zone of influence tends to diminish significantly as the viscosity of the fluid to be administered increases. The injection wells in a saturated zone can also reach very considerable depths, provided they use adequate pressure [67]. It is advisable to distribute the injection points along the vertical. It is also necessary to carry out pilot tests to evaluate the distribution of the chemicals in the subsoil [68].

In very heterogeneous soil, the creation of RZs can result in treatments of the contamination that are not homogeneous, with zones of finer lithology barely involved in the process [64]. The PRBs, which can only be used in saturated zones, consist of the substitution of the aquifer material with allocthonous material, through which the groundwater has to pass for the decontamination. This enables the achievement of a homogeneous treatment zone, regardless of the heterogeneity of the aquifer under examination. The PRBs are technically and economically sustainable if the depth of the installation does not exceed 25 m from g.l. [69–72]. Aquifers with high hydraulic conductivity are difficult to treat with this type of installation, because the reactive layer must have permeability of at least an order of magnitude greater than the aquifer to intercept effectively the contaminated plume. To increase the permeability of the barrier, it is necessary to increase its thickness so that the contaminant has an adequate hydraulic residence time in the RZs [73,74]. The use of reactive chemicals in the PRBs must consider possible problems of progressive fouling of the barrier. This is the case with the use of iron-based reagents, with the precipitation of the chemical species of Cr (III) and Fe (III) [75,76]. PRBs are well suited to the implementation of biological processes, in which case they are called “Biobarriers” [77].

## 4. Scenarios and Decision Support Tool

As already mentioned, in reducing environments (typically soil with low permeability, rich in organic substance), the redox conditions encourage the abundance of chemical species of Cr (III) rather than of Cr (VI); it is therefore rare to encounter significant contamination of Cr (VI) in these contexts [78]. The support tool proposed for the decisions, therefore, focuses on saturated or unsaturated permeable soil, in aerobic or, at most, anoxic conditions.

Table 2 shows the most influential factors on the choice of potentially applicable technologies: pH, concentration of Cr (VI), availability of iron in the soil, and homogeneity of the soil.

**Table 2.** Factors which influence the choice of technology.

Factor	Scenario	Value
Soil pH	Acid	5 ÷ 7
	Alkaline	7 ÷ 9
Cr (VI) concentration	Low	< 10 <sup>2</sup> mg unsaturated soil; < 10 mg L <sup>-1</sup> in aquifer
	High	> 10 <sup>2</sup> mg kg <sup>-1</sup> unsaturated soil; > 10 mg L <sup>-1</sup> in aquifer
Fe concentration in soil	Low	< 1 g Fe kg <sup>-1</sup>
	High	> 1 g Fe kg <sup>-1</sup>
Soil homogeneity	Yes	Variation of hydraulic conductivity or intrinsic permeability within 2 orders of magnitude
	No	Variation of hydraulic conductivity or intrinsic permeability more than 2 orders of magnitude

It is useful to subdivide soils according to their pH. The use of some reactive chemicals, for example, is advised for acid or neutral environments, in view of the significant loss of efficiency for basic pHs, or vice-versa. Soil flushing for chromium is not suitable in acid soils because of the lower mobility of its chemical species.

High concentrations of hexavalent chromium can limit the feasibility of some technologies. Regarding biological treatments, the capacity of the microorganisms to survive at high concentrations of Cr (VI) (up to a few grams per liter in water) could be mediated, not just by enzymes and/or very specific transport proteins, but also by sub-cellular structures, which interact with the metals themselves [79]. Many microorganisms are able to grow and survive at high concentrations of Cr (VI), developing mechanisms of resistance and tolerance to the pollutant [45,48,80]. The use of selected inoculations, if able to remain in situ, would therefore not have limitations, even in contexts with a high level of contamination. Vice-versa, action in indirect biological treatments could be inhibited with dissolved contamination above 10 mg L<sup>-1</sup> Cr (VI) or soil contamination above 10<sup>2</sup> mg kg<sup>-1</sup> [81].

The presence of Fe (II) ions allows redox reactions, with the reduction of Cr (VI). Releases of iron in solution are possible at the moment in which changes in the redox conditions promote the development of reducing conditions. For the technologies that promote this change, the presence of iron in the solid matrix is a determining factor. In general, the matrix is considered to be at a high iron content if the concentration exceeds 0.1% in weight, or 1 mg kg<sup>-1</sup> [82]; below this threshold, it becomes necessary to exclude technologies that use the iron as an essential element of the action mechanism. The releases of Fe (II) from the solid matrix must be sufficient to balance the quantity of Cr (VI) to be reduced; according to reactions (1) and (2), the indicative ratio in solution is Cr (VI): Fe (II) = 1:3 by weight [83].

Almost all natural soils are highly variable in their properties. The heterogeneity of the soil is linked to the presence of different lithologies [84]. The presence of heterogeneity limits the efficacy of the technologies, which envisage injection and dispersal of a reactive. As mentioned, the PRBs appear to overcome these problems. It is possible to quantify the homogeneity of the layer to be treated using parameters, such as the hydraulic conductivity or the intrinsic permeability of the layer to be treated [85].

Having taken the above into account, the support tool for the decisions is reflected in Table 3 where, for each innovative technology mentioned, the conditions of the factors of Table 2, which advise against/exclude its application, are specified; the zone of applicability of the different technologies reported in Table 1 is implied.



**Table 3.** Low applicability/inapplicability (shown by an “X”) of the innovative technologies examined, according to the factors in Table 2; the zone of potential application shown in Table 1 is implied.

pH <sup>1</sup>	Cr (VI) Concentration <sup>2</sup>	Fe Concentration in Soil <sup>3</sup>	Soil Homogeneity	Fe (0), C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> , H <sub>2</sub> S	Sodium Dithionite	Calcium Polysulphurs	Indirect Biological Process	Phytoremediation	Electrokinetics	Soil Flushing
A	L	L	Yes	-	X	X	X	-	X	X
A	L	L	No	X <sup>4</sup>	X	X	X	-	X	X
A	L	H	Yes	-	-	X	-	-	X	X
A	L	H	No	X <sup>4</sup>	X <sup>4</sup>	X	X <sup>4</sup>	-	X	X
A	H	L	Yes	-	X	X	X	X	-	X
A	H	L	No	X <sup>4</sup>	X	X	X	X	-	X
A	H	H	Yes	-	-	X	X	X	-	X
A	H	H	No	X <sup>4</sup>	X <sup>4</sup>	X	X	X	-	X
B	L	L	Yes	X	X	-	X	-	X	-
B	L	L	No	X	X	X <sup>4</sup>	X	-	X	X
B	L	H	Yes	X	X	-	-	-	X	-
B	L	H	No	X	X	X <sup>4</sup>	X <sup>4</sup>	-	X	X
B	H	L	Yes	X	X	-	X	X	-	-
B	H	L	No	X	X	X <sup>4</sup>	X	X	-	X
B	H	H	Yes	X	X	-	X	X	-	-
B	H	H	No	X	X	X <sup>4</sup>	X	X	-	X

<sup>1</sup> A = Acid, B = Alkaline; <sup>2</sup> H = High; L = Low; <sup>3</sup> H = High; L = Low; <sup>4</sup> Not recommended/Excluded only in case of injections.

## 5. Discussion and Conclusions

The intention of this manuscript is to provide support to operators and decision makers that wish to undertake the remediation of a site more directed towards a concept of sustainability [86]. The innovative technologies considered aim at greater sustainability than traditional approaches persisting more for established practice than for real advantage.

Frequently, in sites where the contamination from Cr (VI) is mainly found in shallow unsaturated soil, the remediation is limited to the removal of the soil and the transfer to a recycling centre or landfill site. The method is very onerous, particularly when the costs of transport are taken into consideration. On the other hand, despite inapplicability under certain conditions (see Table 3), phytoremediation, electrokinesis, and flushing can potentially be used. In relation to sustainability, time, and logistical limitations, phytoremediation is an interesting option from an economic and environmental standpoint, but cannot be used in sites with a high level of contamination, structures and/or land cover, and restricted remediation times.

Injections of reducing gases, electrokinesis, and flushing can potentially be used for unsaturated sub-surface soil; the latter two, however, are excluded for treating material more than 10 m from g.l. because the consequent technical-operational difficulties. Deep unsaturated ground (more than 10 m g.l.) therefore remains among the zones, with limited alternatives to treatment of the contamination by Cr (VI).

The contamination in a saturated zone can potentially be treated with all the innovative chemical and biological technologies mentioned and, in the case of depths within 10 m g.l., also with electrokinesis. In aquifers with low concentrations of Cr (VI), the indirect biological processes generally have lower costs, even if remediation times are usually longer than the one of purely chemical processes.

For all zones, among the technologies that are the most innovative and without significant site-specific limitations, electrokinesis is promising. Starting with this, there are also small-scale studies of remediation technologies underway, based on the application of low intensity electrical fields, for the reduction of chromium using electrochemical, biochemical, or bioelectrochemical processes.

From the perspective of full-scale implementation, the administration of chemical agents can be carried out using injections (in wells and/or with the direct push technique) and/or in PRBs. In groundwater within 25 m g.l., PRBs offer greater advantages in heterogeneous soils. However, there are significant implications in terms of the cost and time taken to excavate as well as the disposal of the material resulting from the installation of the work.

The final choice of the best remediation option in a site depends, in any case, on additional sustainability factors other than those considered in this manuscript, including the results of site-specific and laboratory tests. A lack of economic resources may lead in the direction of less onerous, but slower, technologies, just as the necessity of achieving quickly the remediation objectives for social purposes may lead to the exclusion of other technologies. Traditional treatment techniques should also not be excluded a priori from the assessment.

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## References

1. Guertin, J.; Jacobs, J.A.; Avakian, C.P. *Chromium (VI) Handbook*; CRC Press: Boca Raton, FL, USA, 2005.
2. Panagiotakis, I.; Dermatas, D.; Vatseris, C.; Chrysochoou, M.; Papassiopi, N.; Xenidis, A.; Vaxevanidou, K. Forensic investigation of a Chromium (VI) groundwater plume in Thiva, Greece. *J. Hazard. Mater.* **2015**, *281*, 27–34. [[CrossRef](#)] [[PubMed](#)]
3. Lilli, M.A.; Moraetis, D.; Nikolaidis, N.P.; Karatzas, G.P.; Kalogerakis, N. Characterization and mobility of geogenic chromium in soils and riverbed sediments of asopos basin. *J. Hazard. Mater.* **2015**, *281*, 12–19. [[CrossRef](#)] [[PubMed](#)]
4. Chrysochoou, M.; Theologou, E.; Bompoti, N.; Dermatas, D.; Panagiotakis, I. Occurrence, origin and transformation processes of geogenic chromium in soils and sediments. *Curr. Pollut. Rep.* **2016**, *2*, 224–235. [[CrossRef](#)]
5. United States Environmental Protection Agency. *In Situ Treatment of Soil and Groundwater Contaminated with Chromium—Technical Resource Guide*; United States Environmental Protection Agency: Washington, DC, USA, 2000.
6. United States Environmental Protection Agency. *Introduction to In Situ Bioremediation of Groundwater—Technical Resource Guide*; United States Environmental Protection Agency, Office of Solid Waste and Emergency Response: Cincinnati, OH, USA, 2013.
7. Bekele, T.C.; Bucklin, K.; Burger, S.; Martinez, L.; Parnass, B.; Renzi, E.; Rodriguez, M.; Wong, P. *Investigation and Remediation of Plating Facilities—Technical Resource Guide*; United States Environmental Protection Agency, Department of Toxic Substances Control: Sacramento, CA, USA, 2011.
8. California Environmental Protection Agency. *Proven Technologies and Remedies Guidance—Remediation of Metals in Soil*; California Environmental Protection Agency, Department of Toxic Substances Control: Sacramento, CA, USA, 2008.
9. Savannah River National Laboratory. *The Scenarios Approach to Attenuation-Based Remedies for Inorganic and Radionuclide Contaminants*; Savannah River National Laboratory: Aiken, SC, USA, 2011.
10. Unceta, N.; Séby, F.; Malherbe, J.; Donard, O.F.X. Chromium speciation in solid matrices and regulation: A review. *Anal. Bioanal. Chem.* **2010**, *397*, 1097–1111. [[CrossRef](#)] [[PubMed](#)]
11. Dhal, B.; Thatoi, H.N.; Das, N.N.; Pandey, B.D. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. *J. Hazard. Mater.* **2013**, *250*, 272–291. [[CrossRef](#)] [[PubMed](#)]
12. United States Environmental Protection Agency. *Toxicological Review of Hexavalent Chromium*; United States Environmental Protection Agency: Washington, DC, USA, 1998.
13. US Department of Labor Occupational Safety and Health Administration. *Hexavalent Chromium*; US Department of Labor Occupational Safety and Health Administration: Washington, DC, USA, 2009.
14. Canadian Council of Ministers of the Environment. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health—Chromium*; Canadian Council of Ministers of the Environment: Winnipeg, MB, Canada, 1999.
15. United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Toxicological Profile for Chromium. 2012. Available online: <https://www.atsdr.cdc.gov/toxprofiles/tp7.pdf> (accessed on 15 July 2018).
16. Pradhan, D.; Sukla, L.B.; Sawyer, M.; Rahman, P.K.S.M. Recent bioreduction of hexavalent chromium in wastewater treatment: A review. *J. Ind. Eng. Chem.* **2017**, *55*, 1–20. [[CrossRef](#)]
17. US Department of Agriculture. Soil Science Division Staff, 2017. In *Soil Survey Manual—Handbook No. 18*; US Department of Agriculture: Washington, DC, USA, 2017.
18. Ohio Environmental Protection Agency. *Reduction–Oxidation (Redox) Control in Ohio’s Ground Water Quality*; Ohio Environmental Protection Agency: Columbus, OH, USA, 2014.
19. Palmer, C.D.; Wittbrodt, P.R. Processes affecting the remediation of chromium contaminated sites. *Environ. Health Perspect.* **1991**, *92*, 25–40. [[CrossRef](#)] [[PubMed](#)]
20. Buerge, I.J.; Hug, S.J. Kinetics and pH dependence of Chromium (VI) reduction by Iron (II). *Environ. Sci. Technol.* **1997**, *3*, 1–7. [[CrossRef](#)]

21. He, Y. Chromate Reduction and Immobilization under High pH and High Ionic Strength Conditions. Ph.D. Thesis, The Ohio State University, Columbus, OH, USA, 2003.
22. Palmer, C.D.; Puls, R.W. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils*; USEPA, Office of Emergency and Remedial Response: Washington, DC, USA, 1994.
23. Sedlazeck, K.P.; Hollen, D.; Muller, P.; Mischitz, R.; Giere, R. Mineralogical and geochemical characterization of a chromium contamination in an aquifer—A combined analytical and modeling approach. *Appl. Geochem.* **2017**, *87*, 44–56. [[CrossRef](#)]
24. Network for Industrially Contaminated Land in Europe. How to Implement Sustainable Remediation in a Contaminated Land Management Project? 2012. Available online: <http://www.nicole.org/uploadedfiles/wg-sustainable-remediation-final-report.pdf> (accessed on 15 July 2018).
25. Department of Toxic Substances Control, California Environmental Protection Agency. *Interim Advisory for Green Remediation*; Department of Toxic Substances Control: Sacramento, CA, USA, 2009.
26. Beretta, G.P.; Pellegrini, R. *Linee Guida per la Verifica del Trattamento Chimico In Situ dei Terreni e Delle Acque Sotterranee*; Technical Report: Provincia di Milano, Italy, 2006. (In Italian)
27. Ludwig, R.D.; Su, C.; Lee, T.R.; Wilkin, R.T.; Acree, S.D.; Ross, R.R.; Keeley, A. In situ chemical reduction of Cr (VI) in groundwater using a combination of ferrous sulfate and sodium dithionite: A field investigation. *Environ. Sci. Technol.* **2007**, *41*, 5299–5305. [[CrossRef](#)] [[PubMed](#)]
28. Němeček, J.; Lhotský, O.; Cajthaml, T. Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations. *Sci. Total. Environ.* **2014**, *485*, 739–747. [[CrossRef](#)] [[PubMed](#)]
29. Li, X.; Lei, L.; Yang, C.; Zhang, W. Reduction of Cr (VI) by nanoscale zero valent Iron (nZVI): The reaction kinetics. In Proceedings of the 4th International Conference on Bioinformatics and Biomedical Engineering (IWBBIO 2016), Granada, Spain, 20–22 April 2016.
30. Yoon, I.H.; Kim, K.W. Effect of pH and Dissolved Oxygen on the Cr (VI) Removal by Zero-Valent Iron. Available online: [https://www.researchgate.net/publication/242201190\\_Effect\\_of\\_pH\\_and\\_Dissolved\\_Oxygen\\_on\\_the\\_CrVI\\_Removal\\_by\\_Zero-Valent\\_Iron](https://www.researchgate.net/publication/242201190_Effect_of_pH_and_Dissolved_Oxygen_on_the_CrVI_Removal_by_Zero-Valent_Iron) (accessed on 15 July 2018).
31. Storch, P.; Messer, A.; Palmer, D.; Pyrih, R. Pilot test for in situ geochemical fixation of chromium (VI) using calcium polysulfide. In *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds: pts 1a–2b*; Battelle Press: San Diego, CA, USA, 2002.
32. Chrysochoou, M.; Ferreira, D.R.; Johnston, C.P. Calcium polysulfide treatment of Cr (VI)-contaminated soil. *J. Hazard. Mater.* **2010**, *179*, 650–657. [[CrossRef](#)] [[PubMed](#)]
33. Chrysochoou, M.; Ting, A. A kinetic study of Cr (VI) reduction by calcium polysulfide. *Sci. Total. Environ.* **2011**, *409*, 4072–4077. [[CrossRef](#)] [[PubMed](#)]
34. Xie, Y.; Cwiertny, D.M. Use of dithionite to extend the reactive lifetime of nanoscale zero-valent iron treatment systems. *Environ. Sci. Technol.* **2010**, *44*, 8649–8655. [[CrossRef](#)] [[PubMed](#)]
35. Khan, F.A.; Plus, R.W. In situ abiotic detoxification and immobilization of hexavalent chromium. *Ground Water Monit. Remediat.* **2003**, *23*, 77–84. [[CrossRef](#)]
36. Beukes, J.P.; Pienaar, J.; J.; Lachmann, G.; Giesekke, E.W. The reduction of hexavalent chromium by sulphite in wastewater. *Water* **1999**, *25*, 363. Available online: <http://www.wrc.org.za> (accessed on 15 July 2018).
37. Xu, X.; Li, H.; Li, X.; Gu, J. Reduction of hexavalent chromium by ascorbic acid in aqueous solutions. *Chemosphere* **2004**, *57*, 609–613. [[CrossRef](#)] [[PubMed](#)]
38. Bianco Prevot, A.; Ginipro, M.; Peracaciolo, E.; Zelano, V.; De Luca, D.A. Chemical vs bio-mediated reduction of hexavalent chromium. An in-vitro study for soil and deep waters remediation. *Geoderma* **2018**, *312*, 17–23. [[CrossRef](#)]
39. Thornton, E.C.; Gilmore, T.J.; Olsen, K.B.; Giblin, J.T.; Phelan, J.M. Treatment of a chromate-contaminated soil site by in situ gaseous reduction. *Ground Water Monit. Remediat.* **2007**, *27*, 56–64. [[CrossRef](#)]
40. Kim, C.; Zhou, Q.; Deng, B.; Thornton, E.C.; Xu, H. Chromium (VI) reduction by hydrogen sulfide in aqueous media: stoichiometry and kinetics. *Environ. Sci. Technol.* **2001**, *35*, 2219–2225. [[CrossRef](#)] [[PubMed](#)]
41. Hua, B.; Deng, B. Influences of water vapor on Cr (VI) reduction by gaseous hydrogen sulfide. *Environ. Sci. Technol.* **2003**, *37*, 4771–4777. [[CrossRef](#)] [[PubMed](#)]

42. Ibbini, J.; Santharam, S.; Davis, L.C.; Erickson, L.E. Laboratory and Field Scale Bioremediation of Tetrachloroethene (PCE) Contaminated Groundwater. *Jordan J. Mech. Ind. Eng.* **2010**, *4*, 35–44.
43. Somenahally, A.C.; Mosher, J.J.; Yuan, T.; Podar, M.; Phelps, T.J.; Brown, S.D.; Yang, Z.K.; Hazen, T.C.; Arkin, A.P.; Palumbo, A.V.; et al. Hexavalent Chromium Reduction under Fermentative Conditions with Lactate Stimulated Native Microbial Communities. 2013. Available online: [www.plosone.org](http://www.plosone.org) (accessed on 15 July 2018).
44. Liao, Y.; Min, X.; Yang, Z.; Chai, L.; Zhang, S.; Wang, Y. Physicochemical and biological quality of soil in hexavalent chromium-contaminated soils as affected by chemical and microbial remediation. *Environ. Sci. Pollut. Res.* **2014**, *21*, 379–388. [[CrossRef](#)] [[PubMed](#)]
45. Viti, C.; Mini, A.; Ranalli, G.; Lustrato, G.; Giovannetti, L. Response of microbial communities to different doses of chromate in soil microcosms. *Appl. Soil Ecol.* **2006**, *34*, 125–139. [[CrossRef](#)]
46. Liu, J.; Duan, C.; Zhang, X.; Zhu, Y.; Lu, X. Potential of *leersia hexandra swartz* for phytoextraction of Cr from soil. *J. Hazard. Mater.* **2011**, *188*, 85–91. [[CrossRef](#)] [[PubMed](#)]
47. Nayak, A.K.; Panda, S.S.; Basu, A.; Dhal, N.K. Enhancement of toxic Cr (VI), Fe, and other heavy metals phytoremediation by the synergistic combination of native *Bacillus cereus* strain and *Vetiveria zizanioides* L. *Int. J. Phytoremediat.* **2018**, *20*, 682–691. [[CrossRef](#)] [[PubMed](#)]
48. Ashraf, M.A.; Hussain, I.; Rasheed, R.; Iqbal, M.; Riaz, M.; Arif, M. Advances in microbe-assisted reclamation of heavy metal contaminated soils over the last decade: A review. *J. Environ. Manag.* **2017**, *198*, 132–143. [[CrossRef](#)] [[PubMed](#)]
49. Ranieri, E.; Petros, G. Effects of plants for reduction and removal of hexavalent chromium from a contaminated soil. *Water Air Soil Pollut.* **2014**, *225*. [[CrossRef](#)]
50. Chai, L.; Huang, S.; Yang, Z.; Peng, B.; Huang, Y.; Chen, Y. Cr (VI) remediation by indigenous bacteria in soils contaminated by chromium-containing slag. *J. Hazard. Mater.* **2009**, *167*, 516–522. [[CrossRef](#)] [[PubMed](#)]
51. Höhener, P.; Ponsin, V. In situ vadose zone bioremediation. *Curr. Opin. Biotechnol.* **2014**, *27*, 1–7. [[CrossRef](#)] [[PubMed](#)]
52. Thatoi, H.; Das, S.; Mishra, J.; Rath, B.P.; Das, N. Bacterial chromate reductase, a potential enzyme for bioremediation of hexavalent chromium: A review. *J. Environ. Manag.* **2014**, *146*, 383–399. [[CrossRef](#)] [[PubMed](#)]
53. Qu, M.; Chen, J.; Huang, Q.; Chen, J.; Xu, Y.; Luo, J.; Wang, K.; Guo, W.; Zheng, Y. Bioremediation of hexavalent chromium contaminated soil by a bioleaching system with weak magnetic fields. *Int. Biodeterior. Biodegrad.* **2018**, *128*, 41–47. [[CrossRef](#)]
54. Němeček, J.; Pokorný, P.; Lhotský, O.; Knytl, V.; Najmanová, P.; Steinová, J.; Černík, M.; Filipová, A.; Filip, J.; Cajthaml, T. Combined nano-biotechnology for in-situ remediation of mixed contamination of groundwater by hexavalent chromium and chlorinated solvents. *Sci. Total Environ.* **2016**, *563*, 822–834. [[CrossRef](#)] [[PubMed](#)]
55. Zhang, P.; Jin, C.; Zhao, Z.; Tian, G. 2D crossed electric field for electrokinetic remediation of chromium contaminated soil. *J. Hazard. Mater.* **2010**, *177*, 1126–1133. [[CrossRef](#)] [[PubMed](#)]
56. Wei, X.; Guo, S.; Wu, B.; Li, F.; Li, G. Effects of reducing agent and approaching anodes on chromium removal in electrokinetic soil remediation. *Front. Environ. Sci. Eng.* **2016**, *10*, 253–261. [[CrossRef](#)]
57. Yan, Y.; Xue, F.; Muhammad, F.; Yu, L.; Xu, F.; Jiao, B.; Li, D. Application of iron-loaded activated carbon electrodes for electrokinetic remediation of chromium-contaminated soil in a three-dimensional electrode system. *Sci. Rep.* **2018**, *8*, 1–11. [[CrossRef](#)] [[PubMed](#)]
58. Contaminated Land: Applications in Real Environments. Electrokinetic Ferric Ion Remediation and Stabilisation (FIRS) of Hexavalent Chromium Contaminated Soils: An Ex Situ Field Scale Demonstration. Available online: <http://www.claire.co.uk> (accessed on 15 July 2018).
59. Voccianta, M.; Caretta, A.; Bua, L.; Bagatin, R.; Ferro, S. Enhancements in ElectroKinetic Remediation Technology: Environmental assessment in comparison with other configurations and consolidated solutions. *Chem. Eng. J.* **2016**, *289*, 123–134. [[CrossRef](#)]
60. Tang, S.; Yin, K.; Lo, I.M. Column study of Cr (VI) removal by cationic hydrogel for in-situ remediation of contaminated groundwater and soil. *J. Contam. Hydrol.* **2011**, *125*, 39–46. [[CrossRef](#)] [[PubMed](#)]

61. Yan, D.Y.; Lo, I.M. Pyrophosphate coupling with chelant-enhanced soil flushing of field contaminated soils for heavy metal extraction. *J. Hazard. Mater.* **2012**, *199*, 51–57. [[CrossRef](#)] [[PubMed](#)]
62. Yaqiao, S.; Lei, D. The influence mechanism of ash-flushing water from power plant on groundwater environment. In Proceedings of the 4th International Conference on Bioinformatics and Biomedical Engineering (IWBBIO 2016), Granada, Spain, 2016.
63. Fruchter, J. In situ treatment of chromium-contaminated groundwater. *Environ. Sci. Technol.* **2002**, *36*, 464A–472A. [[CrossRef](#)] [[PubMed](#)]
64. Jeyasingh, J.; Somasundaram, V.; Philip, L.; Bhallamudi, S.M. Pilot scale studies on the remediation of chromium contaminated aquifer using bio-barrier and reactive zone technologies. *Chem. Eng. J.* **2011**, *167*, 206–214. [[CrossRef](#)]
65. Ohio Environmental Protection Agency. Use of direct push technologies for soil and ground water sampling. In *Technical Resource Guide for Ground Water Investigations*; Ohio Environmental Protection Agency: Columbus, OH, USA, 2005.
66. ASTM International. *Standard Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization*; ASTM International: West Conshohocken, PA, USA, 2012.
67. United States Environmental Protection Agency. *Injection Wells: An Introduction to Their Use, Operation, and Regulation*; United States Environmental Protection Agency, Office of Drinking Water: Washington, DC, USA, 1989.
68. ASTM International. *Standard Guide for Development of Groundwater Monitoring Wells in Granular Aquifers*; ASTM International: West Conshohocken, PA, USA, 2013.
69. United States Environmental Protection Agency. *In Situ Permeable Reactive Barrier for Contaminated Groundwater at the U.S. Coast Guard Support Center Elisabeth City, North Carolina*; United States Environmental Protection Agency: Washington, DC, USA, 1988.
70. Sethi, R.; Day, S.; Di Molfetta, A. Clamshell vs. Backhoe excavation of permeable reactive barriers. *Am. J. Environ. Sci.* **2011**, *7*, 463–467. [[CrossRef](#)]
71. Obiri-Nyarko, F.; Grajales-Mesa, S.J.; Malina, G. An overview of permeable reactive barriers for in situ sustainable groundwater remediation. *Chemosphere* **2014**, *111*, 243–259. [[CrossRef](#)] [[PubMed](#)]
72. Faisal, A.A.; Rawaa, J.M. Performance of zero-valent iron barrier through the migration of lead-contaminated groundwater. *Assoc. Arab Univ. J. Eng. Sci.* **2018**, *25*, 132–144.
73. Scherer, M.M.; Richter, S.; Valentine, R.L.; Alvarez, P.J. Chemistry and microbiology of permeable reactive barriers for In Situ groundwater clean up. *Crit. Rev. Microbiol.* **2000**, *30*, 363–411. [[CrossRef](#)]
74. United States Environmental Protection Agency. A Citizen's guide to Permeable Reactive Barriers. 2012. Available online: [https://clu-in.org/download/Citizens/a\\_citizens\\_guide\\_to\\_permeable\\_reactive\\_barriers.pdf](https://clu-in.org/download/Citizens/a_citizens_guide_to_permeable_reactive_barriers.pdf) (accessed on 15 July 2018).
75. Fuller, S.J.; Stewart, D.I.; Ian, T.B. Chromate reduction in highly alkaline groundwater by zerovalent iron: implications for its use in a permeable reactive barrier. *Ind. Eng. Chem. Res.* **2013**, *52*, 4704–4714. [[CrossRef](#)]
76. Liu, Y.; Mou, H.; Chen, L.; Mirza, Z.A.; Liu, L. Cr (VI)-contaminated groundwater remediation with simulated permeable reactive barrier (PRB) filled with natural pyrite as reactive material: Environmental factors and effectiveness. *J. Hazard. Mater.* **2015**, *298*, 83–90. [[CrossRef](#)] [[PubMed](#)]
77. Careghini, A.; Saponaro, S.; Sezenna, E. Biobarriers for groundwater treatment: A review. *Water Sci. Technol.* **2013**, *67*, 453–468. [[CrossRef](#)] [[PubMed](#)]
78. Christoph, W.; Eggenberger, U.; Kurz, D.; Zink, S.; Mäder, U. A chromate-contaminated site in southern Switzerland—Part 1: Site characterization and the use of Cr isotopes to delineate fate and transport. *Appl. Geochem.* **2012**, *27*, 644–654.
79. Baldi, F.; Barbieri, P. *Microbiologia Ambientale ed Elementi di Ecologia Microbica*. 2008. Available online: <https://iris.unive.it/handle/10278/22405?mode=full.156#.W62VsbgRVPY> (accessed on 15 July 2018).
80. Kamaludden, S.P.B.; Arunkumar, K.R.; Avudainayagam, S.; Ramasamy, K. Bioremediation of chromium contaminated environments. *Indian J. Exp. Biol.* **2003**, *41*, 972–985.
81. Hassan, Z.; Ali, S.; Farid, M.; Rizwan, M.; Shahid, J. Effect of Chromium (Cr) on the Microbial and Enzymatic Activities in the Soil: A Review. 2017. Available online: [https://www.researchgate.net/publication/317167651\\_Effect\\_of\\_Chromium\\_Cr\\_on\\_the\\_Microbial\\_and\\_Enzymatic\\_Activities\\_in\\_the\\_Soil\\_A\\_Review](https://www.researchgate.net/publication/317167651_Effect_of_Chromium_Cr_on_the_Microbial_and_Enzymatic_Activities_in_the_Soil_A_Review) (accessed on 15 July 2018).

82. Dresel, P.E.; Wellman, D.M.; Cantrell, K.J.; Truex, M.J. Review: Technical and policy challenges in deep vadose zone remediation of metals and radionuclides. *Environ. Sci. Technol.* **2011**, *45*, 4207–4216. [[CrossRef](#)] [[PubMed](#)]
83. Mukhopadhyay, B.; Sundquist, J.; Schmitz, R.J. Removal of Cr (VI) from Cr-contaminated groundwater through electrochemical addition of Fe (II). *J. Environ. Manag.* **2007**, *82*, 66–76. [[CrossRef](#)] [[PubMed](#)]
84. Elkateb, T.; Chalaturnyk, R.; Robertson, P.K. An overview of soil heterogeneity: Quantification and implications on geotechnical field problems. *Can. Geotech. J.* **2003**, *40*, 1–15. [[CrossRef](#)]
85. Uzielli, M.; Simonini, P.; Cola, S. Statistical identification of homogeneous soil units for Venice lagoon soils. In Proceedings of the 3rd International Conference on Site Characterization, Taipei, Taiwan, 1–4 April 2008.
86. European Achievements in Soil Remediation and Brownfield Redevelopment. A Report of the European Information and Observation Network’s National Reference Centers for Soil. 2017. Available online: <http://publications.jrc.ec.europa.eu/repository/bitstream/JRC102681/kj0217891enn.pdf> (accessed on 15 July 2018).



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