

Proceedings

Hexavalent Chromium Removal from Groundwater—A Low-Tech Approach †

Samiotis Georgios, Lefteri Lefteris, Mavromatidou Charoula, Tsiptsias Costas, Trikilidou Eleni, Batsi Anna and Amanatidou Elisavet *

Environmental Chemistry and Water & Wastewater Treatment Research Laboratory, University of Western Macedonia, Koila University Campus, 50100 Kozani, Greece; samiotis1982@hotmail.com (S.G.); lefteris1194@gmail.com (L.L.); xaroulam73@gmail.com (M.C.); ktsiopts@gmail.com (T.C.); etrikilido@yahoo.com (T.E.); annampatsi@gmail.com (B.A.)

* Correspondence: eamanatidou@uowm.gr; Tel.: +30-24610-68015

† Presented at the 4th EWaS International Conference: Valuing the Water, Carbon, Ecological Footprints of Human Activities, Online, 24–27 June 2020.

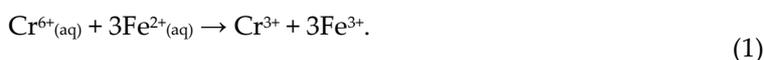
Published: 14 August 2020

Abstract: Chromium occurs in nature mainly in its trivalent or hexavalent form. Hexavalent chromium Cr(VI) is particularly toxic to humans, animals, and plants. The extensive pollution of groundwaters with Cr(VI) necessitates the complete understanding of natural chromium oxidation and reduction mechanisms, both for assessing the risk of hexavalent chromium formation and for the development of techniques for the reduction and removal of Cr(VI) from contaminated water bodies. In this work, the possibility of hexavalent chromium reduction by discarded or low-cost materials, which contain reducing compounds, is investigated regarding the creation of a compact, pump-and-treat filter for Cr(VI) removal from groundwater.

Keywords: chromates reduction; divalent iron; iron oxides inhibition; pump-and-treat

1. Introduction

Chromium (Cr) occurs in nature mainly in its trivalent (Cr(III)) or hexavalent (Cr(VI)) form. In most minerals, the form of Cr(III) is predominant and is favored by reducing and acidic conditions. Hexavalent chromium is a carcinogenic compound often encountered in contaminated aquifers. Cr(VI) can be found in groundwater either as the result of the natural oxidation of the Cr(III), mainly contained in ultramafic rocks and serpentinites of ophiolitic complexes, or as the result of a wide range of anthropogenic activities [1]. From an anthropogenic perspective, industrial and agricultural activities, the over-exploitation of groundwater, and urbanization are the most common causes that have been proven to introduce high concentrations of Cr(VI) into the environment [1–3]. Mn oxides are the only naturally occurring minerals capable of oxidizing Cr(III) to Cr(VI), while V^{2+} , Fe^{2+} , S^{2-} , HNO_2 , HSO_3^- and some organic species can reduce Cr(VI) [3–7]. Consequently, the reduction of Cr(VI) can be achieved by natural reductants, which can transform this toxic form to the less toxic trivalent form. Divalent iron has a significant effect on chromium chemistry because it reduces Cr(VI) to Cr(III) [8,9]. Numerous minerals in geological materials contain Fe(II), which potentially available for the reduction of Cr(VI). It is therefore concluded that Fe(II) found in certain iron-containing minerals, such as hematite and biotite, can have a significant effect on chromium removal even in an oxygenated aqueous system [3], contributing to the natural attenuation of the aquatic systems [9]. The general equation for the reduction of Cr(VI) by Fe(II) is presented in Equation (1) [10].



The reaction is rapid and completed in a few minutes. However, when iron is derived from mineral-containing iron oxides, such as hematite or biotite, the reaction can last from hours to days [10].

High Cr(VI) concentrations due to both the geology of the area and anthropogenic activities have been observed worldwide [11–18]. The extensive contamination of groundwaters with Cr(VI) (worldwide) necessitates the full understanding of the mechanisms of Cr(III) oxidation by Mn oxides in nature, both to determine the risk of Cr(VI) formation and to the development of techniques to reduce its formation.

The last decades various physio-chemical treatments for the removal of Cr(III) and Cr(VI) from aqueous solution have been utilized. These techniques include conventional methods such as chemical precipitation, ion exchange, adsorption, membrane filtration, etc.; and modern techniques, such as membrane electrolysis, photocatalytic reduction, adsorption, nanotechnology, liquid membrane, and electro dialysis [19,20]. However, most of the established treatment options are incapable of efficiently reducing the chromium concentrations to permissible levels. Additionally, most conventional treatment systems require secondary treatments before discharging effluents, making the process uneconomical [21]. Ion exchange and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater, but have a high operational cost. Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of higher than 1000 mg/L, but it raised the problem of sludge disposal [19]. Compared with others, adsorption has long been researched and it is effective, easy handling, flexible, and selective [19], but the cost is high and the Cr(VI) is just transferred but not removed [22]. Researchers showed a strong interest in low-cost adsorbents with high surface areas and adsorption capacities [19]. Various adsorbent materials, such as activated carbon, clay minerals, zeolites, agricultural wastes, nanosized metal oxides, and zero-valent iron, are applied in heavy metal removal [23]. The development of nanotechnology promotes the application of nano-adsorbents, which enhances chemical reactivity and adsorbate/adsorbent interactions [19]. Diverse functional nanomaterials (NMs, e.g., iron/iron oxide nanoparticles, carbon nanostructures, metal organic frameworks, and their commercial counterparts) have been studied in the treatment of Cr in aqueous environments, in relation to the adsorption capacity, removal efficiency, and partition coefficient. In addition, their performance was compared with the most common treatment options [21]. Considerable research efforts have been devoted in recent years to the synthesis of novel nanomaterials for the effective removal of Cr(VI) from waters, predominantly via adsorption, using chemically stable, energy effective, and recyclable nanomaterials with reduced operating and processing costs [21]. Iron-based NMs have been gaining traction in wastewater treatment due to their advanced properties [21,22]. The cost of these materials is also high compared to conventionally sized material [1]. Various approaches to reducing Cr(VI) in situ have been developed and tested. These methods usually involve adding some already reduced compound to act as a source of electrons. The application of technologies for the in situ treatment of Cr(VI)-contaminated aquifers presupposes large-scale interventions in the aquifer. Such techniques are the in situ biological reduction, the in situ chemical reduction (applied by direct injection of a chemical reducing agent either in liquid form into the aquifer or by placing a solid medium of chemical reductant in the path of water as permeable reactive barriers, or treatment walls), the in situ chemical precipitation, and the in situ chemical sorption [1,24,25]. Pump-and-treat remediation consists of the pumping of contaminated groundwater out of the aquifer and treating the surface of the ground. The treated groundwater can either be returned to the pumped aquifer, used, or discharged. This method suffers from serious disadvantages, due a series of subsurface processes and the high cost [26]. The process of natural attenuation relies just on natural processes in the environment to achieve the remediation goals at a contaminated site in a reasonable amount of time. Natural attenuation processes typically occur at most sites in the presence of natural reductants, but frequently are not rapid enough to prevent the migration of contaminants past the site boundaries, or allow the remediation of the site in the desired timeframe [25]. If Cr(VI) can be reduced and immobilized in the subsurface, as a result of interaction with naturally existing reductants, then expensive remedial measures may not be

required at certain sites [27]. During the last two decades, much research work has been published regarding the use of metallic iron (Fe^0) for the treatment of Cr(VI)-contaminated waters. Forms of tested Fe^0 materials include cast iron, granulated iron, iron chips, iron coils, iron composites, nano-scale iron, powdered iron, sponge iron, and steel wool. There are controversial reports in the Fe^0 literature attributed to the ill-defined nature of tested and used materials [28]. The well-accepted assumption of metallic iron (Fe^0) acting as an electron donor for environmental remediation has created an unstable domain of knowledge in the past few years. It is now imperative to develop an understanding to defend the difficulties of this assumption and re-orient Fe^0 -mediated remediation research as a whole [29].

In this work, chromium oxidation and reduction processes were studied, towards the creation of an innovative, low-cost, compact pump-and-treat filter for Cr(VI) reduction from groundwater by using natural or discarded iron materials.

2. Materials and Methods

In order to assess the reduction efficiency of Cr(VI) by low-cost iron materials (Fe^0) and to evaluate the possibility of its utilization for the construction of a filter for online applications, a series of experiments were conducted (Table S2, Supplementary Material). Preliminary Cr oxidation and reduction experiments using analytical-grade reagents, ophiolitic rocks of different composition, and fertile soil were also conducted. Forty-one experimental configurations containing various forms of metallic iron were set up and the reduction efficiency was assessed. Furthermore, the effect of granular-activated carbon on the adsorption and/or reduction of Cr(VI) was evaluated in experimental setups, as well as its applicability as a filtration medium of a multilayer sand-filter. The effect of a plating and/or oxidized iron coating on Cr(VI) reduction was assessed by replicate experiments using galvanized or oxidized iron scraps versus the same iron materials after immersion in hydrochloric acid (37% *w/w*) for 20 min and rinsing with ultrapure water for three times. Five different metallic iron materials were used for the experimental setups, iron wool, iron wires, iron screens, and scrap iron fillings and chips, as well as granulated activated carbon (Table S1, Supplementary Material).

For the assessment of Cr reduction, 100 $\mu\text{g/L}$ of Cr(VI) standard solution was used (with the use of ultrapure water at initial pH = 5.43). Before every series of experiments, the concentration of the standard solution was measured. The samples were filtered with 0.45 μm pore-size membrane filter prior to spectrophotometric measurements. Chromium oxidation or reduction by divalent iron was determined by Cr(III), Cr(VI), Total Cr, Fe(II), and total Fe concentration measurements, following standard methods. The manganese, pH, redox potential, dissolved oxygen, and conductivity were also determined using standard methods [30]. All the experiments and measurements were conducted at the accredited according to ISO 17025 "Laboratory of Environmental Chemistry & Water and Wastewater Treatment", of the University of Western Macedonia, Greece.

In Table S2 (Supplementary Material), a short description of the experimental setups and their results regarding Cr(VI) removal is presented, as well as important data for the evaluation of each experiment.

3. Results and Discussion

3.1. Preliminary Experimental Results

A plethora of experimental setups was conducted in order to confirm the mechanisms of geogenic chromium oxidation and reduction by manganese oxide and divalent iron, respectively. These experiments showed that:

- (a) The oxidation of Cr(III) to Cr(VI) by manganese oxide reagent, in solutions with ultrapure water, is rapid (within a few minutes) and almost complete, while the oxidation efficiency decreases in solutions with natural water (almost 40%) due to ion complex formation.

- (b) Oxidation of Cr(III) by Mn oxides, mainly contained in ultramafic rocks and serpentinites of ophiolitic complexes, increased the concentrations of Cr(VI), and lower concentrations of dissolved Mn(II) were observed at pH > 7.5 due to the desorption of chromates and the precipitation of Mn(II). The oxidation rate is decreased in time due to the gradual saturation of the available active centers of Mn(IV) to Cr(III).
- (c) The oxidation of Cr(III) to Cr(VI) by manganese oxide produces divalent manganese (Mn(II)), which cannot reduce Cr(VI) to Cr(III),
- (d) Soluble Fe(II) species can rapidly (within seconds) and completely reduce Cr(VI) from aqueous solutions. Surface area, contact time, mixing, and reactants concentration had a positive influence on the Cr(VI) reduction rate.
- (e) Oxidation of Fe(II) by Cr(VI) and Mn(IV) is thermodynamically favored to its oxidation by dissolved oxygen.
- (f) Cr(III) from the reduction of Cr(VI) precipitates in the presence of Fe(III) as a solid solution with the possible chemical formula $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$, which is an enmeshing agent for chromates [27–29].
- (g) Fe(II) can prevent the formation of Cr(VI) or naturally remediate natural waters. Therefore, scrap iron or low-cost iron compounds could be used in a pump-and-treat filter that is based on the principals of circular economy and has a low environmental and operational cost.
- (h) Fertile soils' reduction capacity is at least one order of magnitude higher than its oxidizing, even at soils with ultramafic rocks with a relatively high MnO_2 content. A soil's reduction capacity is attributed to its Fe(II) and organic compounds content and to its microbial activity.

3.2. First Experimental Series

In this series of experiments, the Cr(VI) reduction efficiency was estimated in relation to the contact time between Fe^0 and water containing Cr(VI), as well as to the active surface. Three polyethylene laboratory scale reactors (vessels) of 1.5 L volume were filled with 100 $\mu\text{g/L}$ Cr(VI) of standard solution, and a folded (4 times) iron wire (pretreated with 37% HCl for 20 min) of 1 m length was immersed in each reactor. Thereafter, a relatively slow, manual agitation (inversion of vessel every approximately 3 s) was applied continuously for 1.5 h. The samples were obtained at approximately 10 s, 30 s, 60 s, 3 min, 5 min, 60 min, and 20 h time intervals and were immediately filtered with 0.45 μm pore-size filters and analyzed.

All three experiments (1–1 to 1–3, Table S2, Supplementary Material) exhibited similar behavior regarding Cr(VI) reduction. During the first 5 min, less than 20% of Cr(VI) was reduced, while at 10 min the reduction efficiency reached 35%. After 1.5 h of continuous agitation, the reduction efficiency was approximately 65%, while after 20 h the complete reduction of Cr(VI) was observed. A linear relation ($R^2 = 0.73\text{--}0.84$) of the reduction rate versus time was observed.

3.3. Second Experimental Series

In this series of experiments (2-1 to 2-7, Table S2, Supplementary Material), for simulating a typical continuous-flow filter configuration, a 100 mL volumetric cylinder filled with reactive material and fed with the treatable solution (100 mL of 100 $\mu\text{g/L}$ Cr(VI) standard solution) was used. The fillings were (i) scrap iron fillings, (ii) scrap iron fillings and limestone sand, (iii) activated carbon, (iv) scrap iron fillings, activated carbon and fine limestone sand. The treated solution was immediately collected and analyzed. The hydraulic retention time (HRT)—i.e., contact time—was measured in each batch work, and the Cr(VI) reduction efficiency was calculated (Table S1—Supplementary Material).

The results of these experiments showed that, in relatively small contact times (0.8 to 15 s):

- (a) Scrap iron fillings may give low efficiencies in Cr(VI) reduction if they have been oxidized (<5% reduction efficiency) or if they contain galvanized iron compounds (<50% reduction efficiency).
- (b) Granular activated carbon offers an efficiency in Cr(VI) reduction of up to 27.1%, because the Cr(VI) species are adsorbed on the interior surface of the carbon and then Cr(VI) is reduced to

- Cr(III), which is adsorbed at the external carbon surface [1]. A higher contact time (up to 15 s) between activated carbon and Cr(VI) did not offer additional Cr(VI) removal efficiency.
- (c) Fine limestone sand can act as a barrier for the mechanical retention of trivalent iron and chromium precipitates.

3.4. Third Experimental Series

In this series of experiments (3-1 to 3-24, Table S2), the effect of iron materials' surface oxidation and galvanization on the Cr(VI) reduction was studied. Cr(VI) standard solution was added at 250 mL vessels containing different quantities of (i) mixed galvanized, oxidized, and non-galvanized iron feeling grains of <0.6 mm diameter (experiments 3-1 to 3-5); (ii) non-galvanized iron feeling grains of <0.6 mm diameter (experiments 3-6 to 3-10); (iii) mixed galvanized, oxidized, and non-galvanized iron feeling grains of 0.6 mm to 1.6 mm diameter (experiments 3-11 to 3-15); (iv) non-galvanized iron feeling grains of 0.6 mm to 1.6 mm diameter (experiments 3-16 to 3-20). A contact time of 10 s was obtained in all these experiments, while being on continuous manual, orbital stirring. At experiments 3-1 to 3-20, the effect of the iron filling mass was studied. Furthermore, the effect of sequential batch feed was also examined (experiments 3-21 to 3-24) by adding one volume of standard Cr(VI) solution (100 mL), rinsing with ultrapure water, and then again adding another volume of standard solution. This procedure was repeated five times.

The results of these experiments confirmed that the galvanization and oxidation of iron feelings inhibit the dissolution of Fe(II) from the metallic surface, due to the coating's, decreasing Cr(VI) reduction efficiency. In more detail, the oxidized iron fillings resulted a low Cr(VI) reduction efficiency (<5.3%), regardless of their granular size and added mass (experiments 3-1 to 3-5 and 3-11 to 3-15). On the contrary, the non-galvanized and non-oxidized iron fillings (experiments 3-6 to 3-10 and 3-16 to 3-20) resulted in high reduction efficiencies (up to 98.7%) at the same conditions. It is worth mentioning that each addition of one extra gram of iron fillings before each batch feed did not increase the Cr(VI) reduction efficiency. This suggests that the oxidation and consequently the passivation of metallic iron's surface is rapid and that periodic mechanical or chemical cleaning of its surface must be performed. This was also evident in the sequential batch feed experiments (3-21 to 3-24), where, after each of the five added volumes of Cr(VI) standard solution, the reduction efficiency gradually decreased (from 81.4% to 64.7%; from 86.1% to 26.4%; from 81.5% to 27.6%; and from 93.2% to 16.4% for experiments 3-21, 3-22, 3-23 and 3-24, respectively).

3.5. Fourth Experimental Series

In this series of experiments, two non-galvanized, irregularly folded, iron screen sheets (9 cm × 83 cm each; wire diameter 100 μm; square pore side's size 750 μm) were placed in 500 mL cylindrical tubes. In experiment 4-1, one volume (500 mL) of 100 μg/L Cr(VI) standard solution passed through the column and immediately collected and analyzed, while in experiment 4-2 an identical configuration was used for passing 5 volumes of standard solution. The contact time was measured in each batch work, and the Cr(VI) reduction efficiency was calculated (Table S2, Supplementary Material).

According to the results of these two experiments (4-1 and 4-2), at relatively small contact times (approximately 5 s), (a) high reduction efficiencies can be obtained (up to 94%), provided the iron compounds are non-galvanized and unoxidized; and (b) the oxidation of metallic screens resulted in relatively low reduction efficiencies (39.1% to 43%), but when mechanically cleaned a high reduction efficiency was obtained again (up to 91.4%).

In experiment 4-3, 100 mL of 100 μg/L Cr(VI) standard solution passed through a 100 mL column filled with 3.54 g of non-galvanized iron wool (fiber diameter 60 μm; specific density of 0.0076 g/m or 131,154 m/g) and was immediately collected and analyzed. Similar to the other two column experiments of this series (4-1 and 4-2), the reduction efficiency was high (89.6%) for a relatively small contact time of approximately 5 s. Finally, a standard solution of Cr(VI) prepared with natural water (at initial pH = 7.52) was reduced by iron wool with an efficiency of 98–100%.

3.6. Fifth Experimental Series

In this series of experiments (5-1 to 5-4, Table S1, Supplementary Material), 1 m-long iron wire/s that were previously bathed with HCL acid (37%) for 20 min and rinsed with ultrapure water, were placed into U-shaped (for complete wire immersion), 1m length propylene tubes of different diameters (0.35 cm; 0.75 cm; 1.00 cm). In experiment 5-4, instead of using one 1m iron wire, three 1m wires were used. The contact time and the Cr(VI) reduction efficiency was measured after each batch feed with 100 µg/L Cr(IV) standard solution, using a dosing pump with flow of approximately 3.5 L/h.

The contact times, which coincide with the hydraulic retention time, were 33, 46, and 79 s for experiments 5-1, 5-2, 5-3, and 5-4, respectively. The reduction efficiency was 35.7%, 26.5%, and 18.6% for experiments 5-1, 5-2, and 5-3, respectively. Experiment 5-4, which had 3m of iron wire instead of 1m (5-3), resulted in a greater reduction efficiency of 43.7%.

These results showed: (a) the effect of surface area on the reduction of Cr(VI), as the reduction efficiency was inversely proportional to the volume of the tubular U-shaped reactor and proportional to the surface of the iron wire; and (b) that a spiral tube configuration could be used for minimizing the size of a pump-and-treat filter.

4. Conclusions

In this work, low-cost iron materials (Fe⁰) were used for the reduction of 100 µg/L Cr(VI) of standard solution in order to evaluate the possibility of their utilization for the construction of a low-tech water filter for pump-and-treat applications. Five different metallic iron materials were used for the experimental setup: iron wool, iron wires, iron screens, and scrap iron fillings and chips, as well as granulated activated carbon. Different experimental setups were used (reactors, columns) in batch work or continuous flow. The contact time varied from 0.8 s to 20 h, and the reduction efficiency from 0.0% to 100.0% (Figure S1, Supplementary Material). In the absence of coatings and iron oxides from the surface of the iron materials, an almost complete reduction of chromates can be obtained, with small contact times. The chromate reduction efficiency drops significantly due to the oxidation of the metallic iron surface. This passivation problem can be addressed by means of the periodical, mechanical cleaning of the metallic iron surface.

Supplementary Materials: The following are available online at www.mdpi.com/2673-4931/2/1/25/s1: Table S1: Materials used for experimental setups; Table S2: Short description of the experimental setups and their results regarding Cr(VI) removal and important data for the evaluation of each experiment; Figure S1: Maximum Cr(VI) reduction/removal efficiency (%) in relation to contact time and experimental setups of Table S2.

Author Contributions: Conceptualization, A.E.; S.G.; methodology, S.G.; software, B.A.; validation, M.C.; formal analysis, S.G.; investigation, L.L.; S.G.; resources, T.E.; data curation, S.G.; writing—original draft preparation, S.G.; T.C.; writing—review and editing, A.E.; supervision, T.E.; project administration, A.E.; funding acquisition, A.E. All the authors have read and agree to the published version of the manuscript.

Funding: This research was funded by the University of Western Macedonia Research Committee, project number: 70278.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Theologou, E.; Panagiotakis, I.; Dermatas, D.; Chrysochoou, M.; Toskos, T. Remediation technologies for hexavalent chromium contaminated aquifers. In Proceedings of the 13th International Conference on Environmental Science and Technology, Athens, Greece, 5–7 September 2013.
2. Machiwal, D.; Jha, M.K. Identifying Sources of Groundwater Contamination in a Hard-Rock Aquifer System Using Multivariate Statistical Analyses and GIS-Based Geostatistical Modeling Techniques. *J. Hydrol. Reg. Stud.* **2015**, *4*, 80–110.
3. Fendorf, S.E. Surface reactions of chromium in soils and waters. *Geoderma* **1995**, *67*, 55–71.

4. Kimbrough, D.E.; Cohen, Y.; Winer, A.M.; Creelman, L.; Mabuni, C. A critical assessment of chromium in the environment. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 1–46.
5. Hausladen, D.M.; Fendorf, S. Hexavalent chromium generation within naturally structured soils and sediments. *Environ. Sci. Technol.* **2017**, *51*, 2058–2067.
6. Ndungu, K.; Friedrich, S.; Gonzalez, R.A.; Flegal, A.R. Chromium oxidation by manganese (hydr) oxides in a California aquifer. *Appl. Geochem.* **2010**, *25*, 377–381.
7. Zhong, L.; Jiewen, Y.; Liming, L.; Baoshan, X. Oxidation of Cr+3 on birnessite surfaces: The effect of goethite and kaolinite. *J. Environ. Sci.* **2015**, *37*, 8–14.
8. Gonzalez, A.R.; Ndungu, K.; Flegal, A.R. Natural occurrence of hexavalent chromium in the Aromas Red Sands Aquifer, California. *Environ. Sci. Technol.* **2005**, *39*, 5505–5511.
9. Jacobs, J. A., Testa, S. M. Overview of chromium (VI) in the environment: background and history. In: Guertin J, Jacobs JA, Avakian CP (eds) Chromium (VI) handbook. CRC, Boca Raton, FL, **2004**; pp 1–22
10. Rai, D.; Eary, L.E.; Zachara, J.M. Environmental chemistry of Chromium. *Sci. Total Environ.* **1989**, *86*, 15–23.
11. Pyrgaki, K.; Argyraki, A.; Kelepertzis, E.; Paraskevopoulou, V.; Botsou, F.; Dassenakis, E.; Mitsis, I.; Skourtsos, E. Occurrence of hexavalent chromium in the ophiolite related aquifers of Loutraki and Schinos areas. *BGS* **2016**, *50*, 2261–2270.
12. Dermatas, D.; Vatseris, C.; Panagiotakis, I.; Chrysochoou, M. Potential Contribution of Geogenic Chromium in Groundwater Contamination of a Greek Heavily Industrialized Area. *Chem. Eng. Trans.* **2012**, *28*, doi: 10.3303/CET1228037.
13. Dermatas, D.; Mpouras, T.; Chrysochoou, M.; Panagiotakis, I.; Vatseris, C.; Linardos, N.; Theologou, E.; Bompoti, N.; Xenidis, A.; Papassiopi, N.; et al. Origin and concentration profile of chromium in a Greek aquifer. *J. Hazard. Mater.* **2015**, *281*, 35–46.
14. Economou-Eliopoulos, M.; Megremi, I.; Vasilatos, C. Factors controlling the heterogeneous distribution of Cr(VI) in soil, plants and groundwater: Evidence from the Asopos basin, Greece. *Chemie der Erde* **2011**, *71*, 39–52.
15. Vengosh, A.; Coyte, R.; Karr, J.; Harkness, S.J.; Kondash, J.A.; Ruhl, S.L.; Merola, B.R.; Dywe, S.G. Origin of Hexavalent Chromium in Drinking Water Wells from the Piedmont Aquifers of North Carolina. *Environ. Sci. Technol. Lett.* **2016**, *3*, 409–414.
16. Izbicki, A.; John, W.; Michael, T.; Seymour, A.; McCleskey, W.; Blaine, R.; Fram, S.; Belitz, M.; Esser, K.; Bradley, K. Cr(VI) occurrence and geochemistry in water from public-supply wells in California. *Appl. Geochem.* **2015**, *63*, 203–217.
17. Vasileiou, E.; Papazotos, P.; Dimitrakopoulos, D.; Perraki, M. Expounding the origin of chromium in groundwater of the Sarigkiol basin, Western Macedonia, Greece: A cohesive statistical approach and hydrochemical study. *Environ. Monit. Assess.* **2019**, *191*, 509.
18. Remoundaki, E.; Vasileiou, E.; Philippou, A.; Perraki, M.; Kousi, P.; Hatzikioseyan, A.; Stamatis, G. Groundwater deterioration: The simultaneous effects of intense agricultural activity and heavy metals in soil. *Procedia Eng.* **2016**, *162*, 545–552.
19. Yuhua, Z.; Li, W. Physio-Chemical Treatment Technologies for Chromium Removal. In Proceedings of the 4th International Conference on Renewable Energy and Environmental Technology, Shenzhen, China, 30–31 December, 2016; p. 112.
20. Kurniawan, T.; Agustiono, C.; Gilbert, Y.S.; Wai-Hung, L.; Sandhya, B. Physico-Chemical Treatment Techniques for wastewater Laden with Heavy Metals. *Chem. Eng. J.* **2006**, *118*, 83–98.
21. Maitlo, H.A.; Kim, K.H.; Kumar, V.; Kim, S.; Park, J.W. Nanomaterials-Based treatment options for chromium in aqueous Environments. *Environ. Int.* **2019**, *130*, 104748.
22. Niu, S.F.; Xu, X.H.; Lou, Z.H. Removal of hexavalent chromium from aqueous solution by iron nanoparticles. *J. Zhejiang Univ. Sci. B* **2005**, *6*, 1022–1027.
23. Liu, J.; Dai, M.; Song, S.; Peng, C. Removal of Pb(II) and Cr(VI) from aqueous solutions using the prepared porous adsorbent-supported Fe/Ni nanoparticles. *RSC Adv.* **2018**, *8*, 32063.
24. Vermeul, V.R.; Szecsody, J.E.; Truex, M.J.; Burns, C.A.; Girvin, D.C.; Phillips, J.L.; Devary, B.J.; Fischer, A.E.; Li, S.-M.W. *Treatability Study of In Situ Technologies for Remediation of Hexavalent Chromium in Groundwater at the Puchack Well Field Superfund Site, New Jersey*; Pacific Northwest National Lab. (PNNL): Richland, WA, USA, 2006; doi:10.2172/896362.
25. Jonathan, F. In Situ Treatment of chromium contaminated groundwater. *Environ. Sci. Technol.* **2002**, *36*, 464–472.

26. Voudrias, E.A. Pump-and-treat remediation of groundwater contaminated by hazardous waste: Can it really be achieved? *Glob. Nest J.* **2001**, *3*, 1–10.
27. Palmer, C.D.; Puls, R.W. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils*; EPA Ground Water Issue; EPA/540/5-94/505; Kerr Environmental Research Laboratory: Oklahoma, OK, USA, **1994**.
28. Gheju, M. Progress in Understanding the Mechanism of CrVI Removal in Fe0-Based Filtration Systems. *Water* **2018**, *10*, 651.
29. Noubactep, C.; Makota, S.; Bandyopadhyay, A. Rescuing Fe0 remediation research from its systemic flaws. *Res. Rev. Insights* **2017**, *1*, 1–8.
30. APHA (American Public Health Association). *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; American Public Health Association: Washington, DC, USA, 2017.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).