

Article

Application of Metallic Iron and Ferrates in Water and Wastewater Treatment for Cr(VI) and Organic Contaminants Removal

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Abstract: Iron species can act as electron donors, electron acceptors or serve as a sorbent to co-precipitate contaminants. These properties, along with its relatively low cost as a material, make iron an ideal compound for environmental applications in the removal of pollutants from water and wastewater. This study assesses the use of metallic iron as a reductant for the removal of toxic Cr(VI) from aqueous solutions, as well as the use of hexavalent iron (ferrates) for the removal of organic compounds, turbidity and biological contaminants from water and wastewater. Laboratory-scale experiments show that the Cr(VI) removal efficiency of metallic iron filling materials, such as scrap iron fillings, via reduction to Cr(III) and the subsequent precipitation/filtration of aggregates can reach values over 99.0%. Moreover, the efficiency of ferrates, in situ synthesized via a low-cost Fe^0/Fe^0 electrochemical cell, in the removal of organic compounds, turbidity and biological contaminants from high-strength industrial wastewater, biologically treated wastewater and natural water can also reach values over 99.0%. The results showed that iron species can be applied in low-cost and environmentally friendly technologies for natural water remediation and wastewater treatment. Furthermore, the study showed that the challenge of an iron material's surface passivation, as well as of ferrates' procurement cost and stability, can be resolved via the application of ultrasounds and via in situ ferrate electro-synthesis.

Keywords: metallic iron; hexavalent iron; surface passivation; water treatment; wastewater; hexavalent chromium; disinfection; organic compounds removal



Citation: Samiotis, G.; Stimoniaris, A.; Ristanis, I.; Kemmou, L.; Mavromatidou, C.; Amanatidou, E. Application of Metallic Iron and Ferrates in Water and Wastewater Treatment for Cr(VI) and Organic Contaminants Removal. *Resources* **2023**, *12*, 39. <https://doi.org/10.3390/resources12030039>

Academic Editors: Eveliina Repo and Angel F. Mohedano

Received: 24 January 2023

Revised: 28 February 2023

Accepted: 14 March 2023

Published: 20 March 2023



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1. Introduction

Iron is an element that is present in rocks and soil minerals, usually as Fe(II) and Fe(III). Iron compounds can exhibit oxidation states from -4 to $+7$ and, thus, can act as reducing or oxidizing agents. Due to an abundance of iron minerals in the Earth's crust, the relatively low toxicity of iron species and their involvement in various physicochemical reactions and phenomena, iron compounds can be used for the development of sustainable environmental remediation processes, technologies and techniques. In this regard, the use of metallic iron (Fe^0) and hexavalent iron (Fe(VI)), in particular, has attracted interest from researchers involved in the fields of environmental remediation and water/wastewater treatment. Iron species can act as potent reductants, oxidants, adsorption materials and coagulants exhibiting high efficiency in the removal of various water contaminants including arsenic, bromate, chromate, halogenated organics, mercury, nitrate, nitroaromatics, pesticides, phenolic compounds, phosphates, selenium, uranium and zinc [1–5].

In regard to the mechanism involved in the reduction of contaminants from aqueous solutions, there is a debate among researchers regarding whether they are reduced by Fe(II) that is released upon the oxidation of Fe^0 by water or if they are directly reduced by their reaction with Fe^0 and by the release of Fe(II) products [6]. Nonetheless, there is a challenge regarding the use of metallic iron for the removal of pollutants from water or wastewater

streams due to the oxidation of its surface and its subsequent passivation. According to the critical reviews of Guan et al. and Noubactep [3,7], the creation of the oxide layer on Fe^0 materials, which leads to lower permeability and tandem loss of reactivity, is considered the most significant factor that affects the efficiency of Fe^0 -based remediation processes. Therefore, this challenge must be addressed in order to design and operate pilot-scale plants [8,9]. In accordance, the application of ultrasounds for addressing iron's surface passivation may be proved as an efficient solution [10] towards the development of novel Fe^0 -based water and wastewater treatment for the removal of various contaminants [11].

While Fe^0 and Fe(II) can act as reductants, the high valences of iron, such as hexavalent iron, are potent oxidants that can be utilized both in water/wastewater treatment and environmental remediation. Recently, novel wastewater treatment techniques that are considered environmentally friendly and are based on hexavalent iron species, namely ferrates ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe(VI) , $\text{Fe}^{\text{V}}\text{O}_4^{3-}$, Fe(V) and $\text{Fe}^{\text{IV}}\text{O}_4^{4-}$), are of particular interest due to their benign nature [12]. Ferrates present a high oxidation ability, and when transformed (reduced) to a non-toxic trivalent iron species, they present coagulant action [13]. Ferrates can oxidize organic compounds, microorganisms and spores that are present in water and wastewater; thus, the application of ferrates for water/wastewater treatment can result in the removal of organic compounds and biological contaminants. Ferrates have shown increased potential for the treatment of pharmaceuticals, personal care products and phenolic compounds, as well as for the removal of algae and water disinfection [14]. Ferrates performance can be enhanced and can be used for the removal of emerging micropollutants by synergizing ferrate with other techniques, such as the application of UV light, adsorbents, ozone, membrane filtration, chlorination and persulfate addition [15]. Nonetheless, the minimal stability of ferrates in environmental conditions renders them improper for commercial use both in terms of storage (poor shelf life) and provision (scarce and highly priced substance) [16]. If this challenge is addressed, a novel remediation tool can emerge for several applications including water/wastewater treatment, disinfection and feedstock preparation for biotechnological applications.

This study assesses the application of low-cost Fe^0 materials for the removal of highly toxic Cr(VI) and the use of ferrates, in situ electrosynthesized via a low-cost Fe^0/Fe^0 electrosynthesis cell, for the removal of organic compounds, turbidity and biological contaminants from water, wastewater and biologically treated wastewater. It presents valuable data regarding the efficiency of Fe^0 -based or ferrate-based treatment and tries to address the challenges at hand in the design and implementation of novel and sustainable treatment processes/techniques and environmental remediation technologies.

2. Materials and Methods

2.1. Setups for Fe^0 -Based Treatment

The reduction efficiency of Cr(VI) by Fe^0 was assessed in a series of experimental setups containing various low-cost iron materials. Five different low-cost metallic iron materials were used for the experimental setups: iron wool, iron wires, iron screens and scrap iron fillings and chips (Table 1). The scrap iron materials used were of industrial grade, but their exact composition is not known, since their origin is from discarded materials and industrial process wastes, except in the cases of iron wool, iron wire and iron screens (>99% purity, according to manufacturer). Cr(VI) reduction was assessed in relation to the contact time (1 s to 60 min) between iron materials and water containing Cr(VI) , as well as in relation to the active surface. Tests were set up in cylindrical tubes, each containing one of the five low-cost scrap iron fillings that were used in this study (Table 1). Contact time was regulated via an effluent valve installed at the bottom of the cylinder. The effluent from the cylindrical tube was then led to an in-line sand filter filled with limestone sand at mesh size <850 μm .

Table 1. Low-cost iron materials used in laboratory scale setups for Cr(VI) removal.

Material	Specifications
Iron wool	Wire diameter (mm) = 0.06 Specific weight (g/m) = 0.0076 Specific surface area (m ² /m) = 0.00038
Iron wire	Wire diameter (mm) = 1 Specific weight (g/m) = 0.0076 Specific surface area (m ² /m) = 0.00314
Iron screen	Wire diameter (mm) = 0.1 Specific weight (kg/m ²) = 0.255488 Specific surface area (m ² /m ²) = 0.00041867
Scrap iron chips	Wire diameter (mm) = 1 Specific weight (g/m) = 0.0076 Specific surface area (m ² /m) = 0.031557
Scrap iron fillings	Mesh (mm) = 0.6–1.6 and <0.6 Specific weight (kg/L) = 1884 and 1271.25 Specific surface area (m ² /kg) = 80.7 and 111.2

The effect of iron surface passivation was assessed in terms of Cr(VI) reduction efficiency in relation to treated water volume, expressed in terms of bed volume (BV = inflow water volume/reactive material volume). The techniques that were evaluated to counter iron material passivation were (i) chemical cleaning using HCl 36%, (ii) mechanical cleaning using a wire brush and (iii) cleaning via application of ultrasounds using a 200 W Hielscher (Teltow, Germany) ultrasonic processor, model UP200S.

The reduction of Cr(VI), the formation of Fe(III) aggregates and the effect of Fe⁰ material passivation were all assessed in laboratory setups in terms of Cr(VI) removal efficiency. Standard solutions of 100 µg/L, prepared using K₂Cr₂O₇ reagents (analysis grade) and ultrapure water, and natural water containing Cr(VI) at concentrations of 60 ± 7.3 µg L⁻¹, obtained from an artesian well in Village Kila (Western Macedonia, Greece), were used in the experimental setups. These Cr(VI) concentrations are considered significantly high for natural waters, and they are over the limit for drinking water set by Greece's legislation (50 µg L⁻¹) and Directive (EU) 2020/2184 (25 µg L⁻¹), which are established only for total Cr. It is worth mentioning that Cr(VI) is the prevailing form of chromium in natural waters due to the solubility and mobility of the chromate species [17–19]. The total Cr removal efficiency was assessed after the removal of Fe(III)/Cr(III) precipitants via sand filtration using limestone sand at mesh sizes <850 µm.

The effect of a plating and/or oxidized iron coating of scrap iron materials on Cr(VI) reduction was assessed by replicate experiments using galvanized or oxidized iron scraps versus the same iron materials after immersing them in hydrochloric acid (36% w/w) for 90 s and rinsing with ultrapure water three times.

2.2. Setups for Ferrate-Based Treatment

The adequacy of ferrates for water/wastewater treatment applications was assessed in experimental setups for the removal of both organic compounds and turbidity, as well as for disinfection efficiency.

The efficiency of ferrates for the removal of organic compounds was evaluated in terms of COD (chemical oxygen demand) and turbidity removal. For this series of experiments ferrates were applied in raw dairy wastewater, dairy industry's biologically treated wastewater and surface water of Aliakmon River.

The disinfection efficiency of ferrates was assessed by microbiological examinations and specifically in terms of total viable count (TVC at 22 °C) removal. For this series of experiments ferrates were applied in dairy industry's biologically treated wastewater, as well as in surface water of Aliakmon River. TVC was measured according to ISO 6222/99 and compared to the disinfectant's dosage, both of which are expressed as concentration

and concentration time (CT). CT is defined as the disinfectant residual concentration (C) multiplied by the effective contact time (T), and it is expressed as mg min L^{-1} .

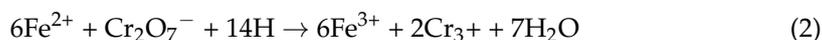
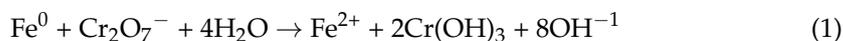
The ferrate solution was prepared in situ using an electrochemical Fe^0/Fe^0 cell in 25 M NaOH solution, as mentioned in Samiotis et al. [20]. A DC power generator, set at 15 V and 2A, was connected to two iron plate electrodes ($16 \text{ cm} \times 9 \text{ cm} \times 0.1 \text{ cm}$) having approximately 2 cm distance between them. The two plate electrodes were submerged 4 cm deep into a 500 mL vessel containing 250 mL of 25 M NaOH solution and agitated at 50 rpm with a magnetic stirrer. The concentration of Fe(VI) in the prepared solution was determined based on a modified indirect volumetric analytical method [21]. This method is based on the Cr(III) to Cr(VI) oxidation by Fe(VI). The resulting chromates are titrated against a known concentration of a divalent iron solution (0.025 N Ferrous ammonium sulphate solution) in order to determine Fe(VI) concentrations stoichiometrically. Cr(VI) was determined following the APHA 3500-Cr B standard colorimetric method [22]. The concentration of residual iron after ferrate treatment was assessed after sand filtration using limestone sand at mesh size $<850 \mu\text{m}$. All physicochemical and microbiological analyses were performed at the accredited according to ISO 17025 laboratory of Environmental Chemistry & Water and Wastewater Treatment of University of Western Macedonia, Greece, using standard methods [22] and having calculated measurement uncertainties [23,24].

3. Results and Discussion

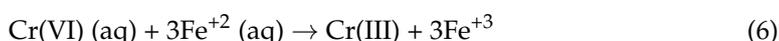
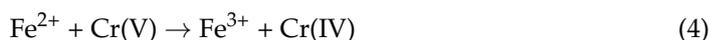
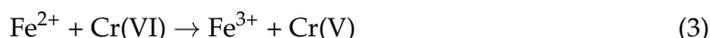
3.1. Iron-Induced Cr(VI) Removal from Natural Water

The experimental results showed that in aqueous solutions with a Cr(VI) concentration up to $100 \mu\text{g L}^{-1}$, the Fe^0 -induced reduction of Cr(VI) to Cr(III) can almost completely reach efficiencies of up to 100.0%. Given a necessary contact time and/or active surface area, all non-galvanized and non-oxidized metallic iron materials that were used in this study (Table 1) exhibited this nearly complete reduction of Cr(VI). The Fe^0 materials with the highest specific area could almost completely ($>99.0\%$ efficiency) reduce Cr(VI) within a few seconds (1 to 23 s). Other materials with a relatively low specific surface area required almost an hour of contact to reach this Cr(VI) reduction efficiency. The statistical interpretation of experimental data revealed a linear relation ($R^2 > 0.84$) of Cr(VI) reduction efficiency with the contact time, as well as with the surface area of iron materials.

The almost complete Cr(VI) removal efficiencies that were observed in experimental setups, which had pH levels from 6.5 to 7.2 without acid addition, are attributed to (i) the reduction of Cr(VI) by Fe^0 (Equation (1)) and (ii) by the formed Fe(II) (Equation (2)), as well as to the (iii) adsorption of chromates to the Cr(III) and Fe(III) precipitants. It is worth mentioning that pH significantly affects iron speciation in water, which can lead to significant results for Cr(VI) removal efficiency (for iron speciation diagram, see [25]).



The reduction of Cr(VI) by the released Fe(II) is a three-step process, as presented in Equations (3)–(5) [26], the general equation of which is presented in Equation (6) [27].



The experimental study of Cr(VI) reduction by Fe(II), which used aqueous solutions of Fe(II) and Cr(VI) prepared with analysis-grade reagents, showed that these reduction reactions occur within seconds, and they can result in the complete reduction of Cr(VI).

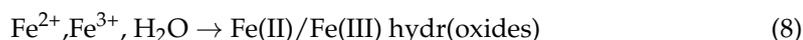
The reduction of Cr(VI) by Fe(II) can occur regardless of the pH, but it is significantly enhanced in acidic conditions [28]. On the other hand, the oxidation of Cr(III) species can naturally occur only in the presence of Mn^{IV} oxides (MnO²) and in oxidative conditions (Eh > 0), and oxidation is favored at pH > 6 [18,19]. Thus, upon Cr(VI) reduction in an Fe⁰-based water treatment configuration and in the absence of Mn^{IV} oxides, the resulting Cr(III) is not expected to be oxidized back to Cr(VI).

It is worth mentioning that at pH > 4, the Cr(III) precipitates in the presence of Fe(III) as a solid solution of brown color with the general chemical formula Cr_xFe_{1-x}(OH)₃ (most possible Cr_{0.25}Fe_{0.75}(OH)₃, which is an enmeshing agent for chromates [29–31]), assisting in Cr(VI) removal. At pH levels that are commonly encountered in natural waters, the resulting Cr(III) and Fe(III) species precipitate as insoluble species, presenting their maximum precipitation rate at pH levels of approximately 7 and 8, respectively [32,33]. Thus, depending on the pH of an aqueous solution, either the Cr(III) or the Fe(III) could enhance the precipitation of Cr_{0.25}Fe_{0.75}(OH)₃ due to co-precipitation phenomena, which further assists in the removal of Cr(VI) contaminants.

As mentioned in the introduction, it is debated in the literature whether the obtained Cr(VI) reduction is attributed to the mechanism described with Equations (1)–(6) or if it is attributed to the Cr(VI) reduction by Fe(II) that is released from the oxidation of Fe⁰ by H₂O (Equation (7)).



As presented in the literature review of Makota et al. [6], the redox chemistry of the Fe⁰/H₂O system involves the oxidation of Fe⁰ by H₂O in an acidic medium to form Fe(II) species (Equation (7)), which could be transformed to Fe(III) species or mixed Fe(II)/Fe(III) species (Equation (8)) that induce coagulation phenomena.



However, the described reaction of Equation (7) cannot occur in neutral to basic pH or without the presence of an acid. Only in the presence of oxidants in an aqueous solution, such as chromate ions, can the Fe⁰ be oxidized to release Fe(II) that is as potent as a reducing agent. Thus, the reduction of Cr(VI) from freshwater, which usually exhibits pH levels between 6.5 and 9.0 [34], can only be attributed to the mechanism presented with Equations (1)–(6).

Consequently, Cr(VI) removal in the Fe⁰/aqueous solution system is attributed to the oxidation of Fe⁰ and the tandem reduction of Cr(VI) in contact with a metallic material's surface, enhanced by the formed Fe(II) species and the adsorption of chromates by Cr(III)/Fe(III) and Fe(II)/Fe(III) hydroxides.

3.1.1. Effect of Iron Coating and Surface Passivation on Cr(VI) Reduction

The coated (galvanized) scrap iron materials, as well as the oxidized scrap iron materials that were evaluated in the experimental investigation, exhibited significantly lower Cr(VI) reduction efficiency (maximum reduction efficiency of 47.3% using synthetic solutions with a Cr(VI) concentration of 100 µg L⁻¹ after a 1 h contact time) than that of the non-galvanized and non-oxidized scrap iron materials. This is attributed to the fact that the zinc coating, which is the most common coating material used in galvanization processes, as well as the precipitating Fe₂O₃ oxides from Fe⁰ oxidation, created a barrier between the metallic iron and the aqueous solution. These layers hindered the direct oxidation of Fe⁰ with Cr(VI) and the creation of Fe(II). By removing the coating and/or the iron oxide layers from iron materials via immersion in an HCl bath, the Cr(VI) reduction efficiency reached up to 100.0% within seconds of contact with Fe⁰. However, the oxidation of Fe⁰ and Fe(II) by Cr(VI), and the formation of insoluble precipitating species, resulted in the creation of a contact-hindering layer that once again decreased reduction efficiency.

The experimental investigation revealed that the creation of the iron oxide coating due to iron species oxidation with Cr(VI) has a profound effect on Cr(VI) reduction efficiency. As evident in Figure 1, Cr(VI) reduction efficiency in experimental setups linearly decreased

in relation to the treated water volume, as expressed in terms of the bed volume (BV). This reveals the creation of a barrier between iron materials' surface and water, which leads to the gradual passivation of iron materials.

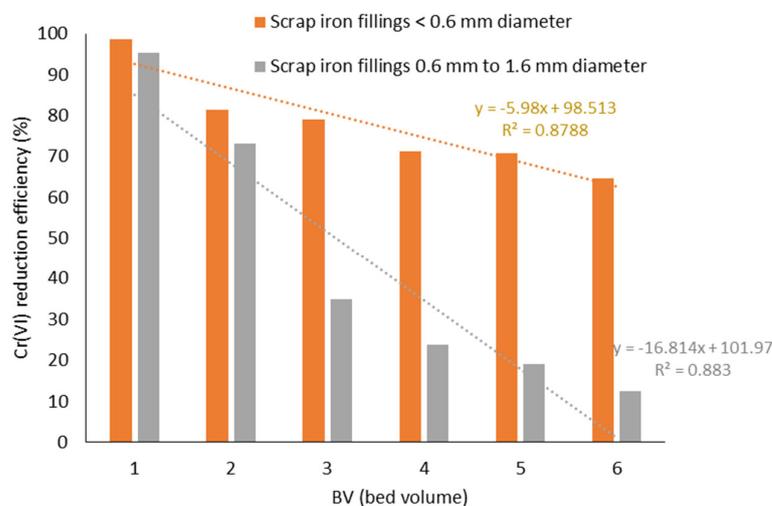


Figure 1. Impact of the treated water volume, in terms of BV, on Cr(VI) reduction efficiency using scrap iron fillings of different particle diameters.

As shown in Figure 1, the passivation of iron materials is more evident in the setups using scrap iron fillings of higher particle size diameters, i.e., materials with smaller active surfaces. This is attributed to the fact that the smaller the active surface of a reducing material, the faster this surface will be oxidized and covered with insoluble and precipitating species. Thus, the selection of an iron material's particle size is a key parameter in the design of more efficient iron-based water/wastewater treatment configurations. Particle size can dictate the duration of operation cycles, i.e., when the replacement or regeneration of iron material is to be performed; hence, the use of scrap iron fillings and their periodic regeneration for the removal of contact-hindering layers is proposed for the development of a water/wastewater treatment configuration that is based on the concept of circular economy, i.e., reduce, reuse and recycle.

The experimental investigation revealed that the passivation of an iron surface is an issue that can be addressed by chemical means or mechanical means (scrubbing). As illustrated in Figure 2, the periodic regeneration of an iron sheet's surface via chemical means (a bath in 36% HCl solution for 90 s and a subsequent rinsing with water) or mechanical means (scrubbing of the surface by folding/unfolding iron sheets five times and subsequent rinsing with water) exhibited similar results.

As shown in Figure 2, after the chemical or mechanical cleaning of iron sheet fillings, which was performed after four cycles (1 cycle = 4 BV of Cr(VI) of contaminated natural water treatment, the Cr(VI) reduction efficiency was restored from values below 50% to values over 90%.

Despite the efficient regeneration of Fe^0 , the use of chemicals is not considered an environmentally friendly and sustainable option for removing iron oxide from iron surfaces. Moreover, invasive mechanical cleaning is considered challenging for full-scale implementations due to the technical complexity and/or the increased labor intensity associated with such systems.

Hence, to reduce the environmental footprint and simplify the regeneration process of Fe^0 fillings, the non-invasive scrubbing of iron surfaces via ultrasound applications was experimentally assessed (Figure 3). The use of ultrasounds for the removal of the contact-hindering layer from a material's surface is considered an environmentally friendly regeneration technique that does not require the use of chemicals or the management of

regeneration solutions and rinsing water. Moreover, it can easily become a completely automated process with minimal operational and maintenance requirements.

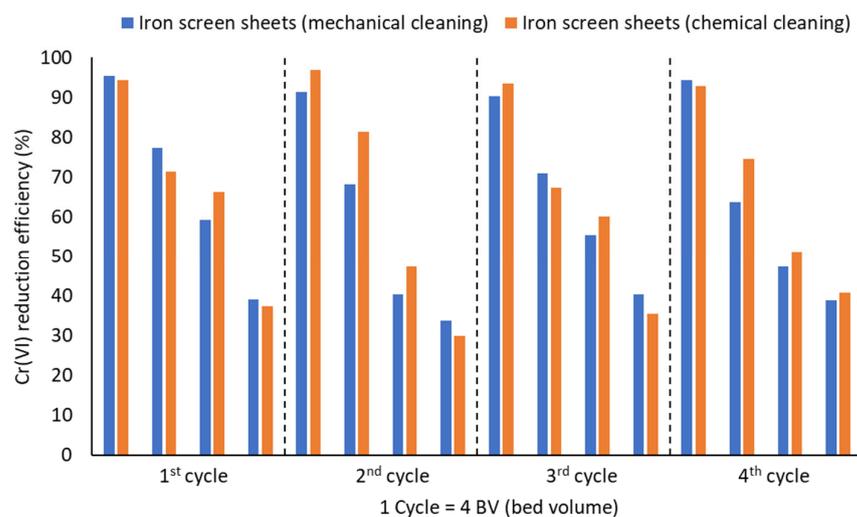


Figure 2. Effect of mechanical cleaning (blue bars) and chemical cleaning on Cr(VI) reduction efficiency by iron sheet fillings.

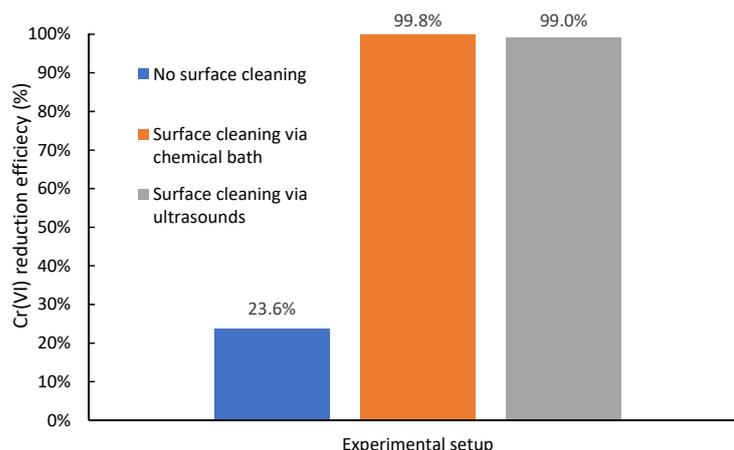


Figure 3. Effect of sonication on Cr(VI) reduction efficiency by iron sheet fillings.

As evident in Figure 3, the reduction efficiency of Cr(VI) by Fe^0 reaches values over 99% when regeneration via the application of ultrasounds or chemical cleaning is applied. Based on the presented experimental results, it is concluded that scrap iron or low-cost iron compounds could be used in a water treatment process at low environmental and operational costs. Moreover, periodic mechanical cleaning, preferably via vibration upon ultrasound application, is suggested for the regeneration of iron materials used for Cr(VI) reduction. Based on the data from the experimental sonication configuration setups, a rough cost estimate of sonication for the regeneration of iron screen fillings is approximately 0.83 USD m^{-3} by taking into account an energy cost of $0.25 \text{ USD kWh}^{-1}$. It should be mentioned that this cost is calculated at the imposed operational conditions of sonication configuration. Further studies should be undertaken to find the optimal conditions for regenerating iron materials via sonication.

3.1.2. Removal of Precipitants

The efficiency of an in-line low-cost sand filter for the removal of the insoluble Fe(III) and Cr(III) species that formed during Cr(VI) removal in the Fe^0 -based treatment process was evaluated in laboratory-scale experimental setups using fine limestone sand (mesh

size <850 µm). The evaluation was performed by measuring the total and soluble iron and chromium concentrations of the influents and effluents of the sand filter (Figure 4).

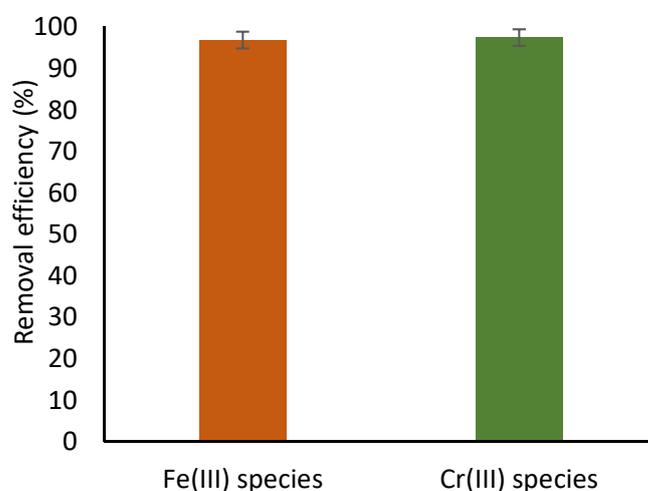
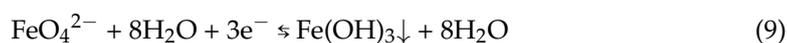


Figure 4. Particulate iron and chromium compounds removal via sand filtration.

As evident in Figure 4, the removal efficiency of particulate Fe and Cr species can reach up to 99.9%, indicating that the use of a low-cost sand filter is suitable for the polishing stage of an Fe⁰-based water treatment process.

3.2. Ferrates for the Removal of Organic Compounds from Water and Wastewater

The efficiency of ferrates in the removal of organic compounds from surface water, raw wastewater and biologically treated wastewater was evaluated in terms of COD removal. Turbidity removal was also evaluated, as it is an indicator of the removal of particulate matter and colloidal organic compounds due to the excellent coagulation and adsorption ability of reduced ferrate compounds, i.e., ferric hydroxides (Equation (9)) [35,36].



According to the conducted experiments (Figure 5), ferrates can almost completely remove organic compounds and turbidity from surface water with removal efficiencies reaching over 99% at a ferrate concentration of approximately 4 mg L⁻¹. At this concentration, the total iron content of the treated surface water, after sand filtration, increased from <0.01 mg L⁻¹ to 0.02 mg L⁻¹, values that are far below Greece's legislation limit regarding the concentration of iron in surface waters intended for human use and/or consumption (1 mg L⁻¹). At concentrations of 56 mg L⁻¹, ferrates exhibited significantly high removal efficiencies for the removal of organic compounds and turbidity from raw wastewater (up to 89% and 94% for COD and turbidity, respectively), as well as from biologically treated wastewater (up to 84% and 97% for COD and turbidity, respectively). At this ferrate's dosage, the measured total iron concentration after sand filtration was 0.14 mg L⁻¹ for the raw wastewater and 0.19 mg L⁻¹ for the biologically treated wastewater from initial concentrations of 0.22 mg L⁻¹ and 0.07 mg L⁻¹, respectively. According to Greece's legislation regarding the characteristics of treated wastewater disposed in surface waters, the total iron concentration should not exceed the value of 2 mg L⁻¹.

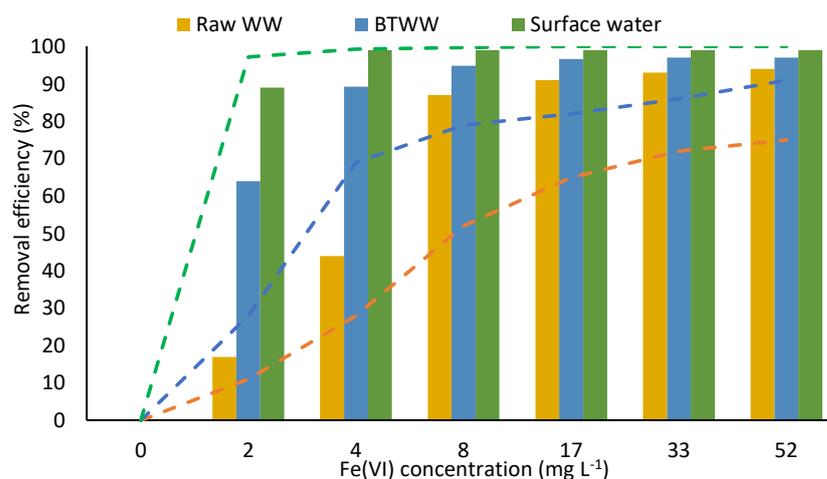


Figure 5. Removal efficiency of COD (dashed lines) and turbidity (columns) in relation to Fe(VI) concentrations in raw wastewater (Raw WW), biologically treated wastewater (BTWW) and surface water samples.

As evident in Figure 5, there is a concentration of ferrates at which removal efficiencies reach a plateau phase, the value of which differs between samples. The higher the initial organic compounds concentration, the lower the value at which the plateau is observed. This is probably attributed to the increased content of recalcitrant organic compounds, which characterizes wastewater compared to natural waters. These recalcitrant organic compounds cannot be readily oxidized and removed via conventional biological treatment processes; however, high solids retention time (SRT) activated sludge processes have shown to be capable of removing organic compounds that are considered non-biodegradable [37,38].

In order to evaluate the ability of ferrates to remove recalcitrant organics from wastewater, higher ferrate concentrations of up to 120 mg/L were tested in order to achieve complete COD removal from the evaluated samples. At this concentration of ferrates, the initial COD content of the raw wastewater was reduced from 3064 mg L⁻¹ to 30 mg L⁻¹, while the COD content of the biologically treated wastewater was reduced from 147 mg/L⁻¹ to values <4 mg/L⁻¹. The experimental investigation revealed that almost the complete elimination of organic compounds can be achieved (COD removal efficiencies over 99%), which is attributed to both oxidation and coagulation phenomena; this is in accordance with other studies that assessed the application of ferrates in water and wastewater treatment [13,35,39–42]. Even at such high ferrate dosages, the total iron concentration of the treated samples, after sand filtration, was significantly lower than the threshold value of 2 mg L⁻¹. For raw wastewater, it was 0.35 mg L⁻¹, and for biologically treated wastewater, it was 0.47 mg L⁻¹. The low concentrations of total iron, which were obtained after ferrates treatment and sand filtration, reveal the instability of ferrates, as they are readily reduced to Fe(III) species and retained as solid particles in the sand filter. It should be noted that there was an evident increase in pH after the addition of ferrates in all tested samples, which is attributed to the alkaline nature of the electrosynthesized ferrates solution (the use of 25M NaOH as an electrolyte). The pH of the surface water increased from 7.7 to 7.8 at a ferrate concentration of 4.2 mg L⁻¹, while the pH of the raw wastewater and the biologically treated wastewater increased from 6.7 to 7.2 and from 7.1 to 7.5, respectively, at a ferrate concentration of 120 mg L⁻¹.

3.3. Ferrates for Water and Wastewater Disinfection

The disinfection efficiency of ferrates was assessed in comparison to two commonly applied chemical disinfectants: sodium hypochlorite (NaClO) and hydrogen peroxide (H₂O₂). There was no pH adjustment during the application of the three disinfectants; thus, their efficiency was evaluated with unbuffered aqueous solutions with pH 7.1 to 7.8. As evident in Figure 6, ferrates presented the highest disinfection efficiency in relation to

the chemical dosage regarding the treatment of biologically treated wastewater samples from the dairy industry. There is an evident logarithmic relationship between disinfectant concentration and disinfection efficiency, as is evident from the graphs of Figure 6 that are plotted on a base-4 logarithmic X-axis. This means that the higher the dosage, the lower the disinfection efficiency gain.

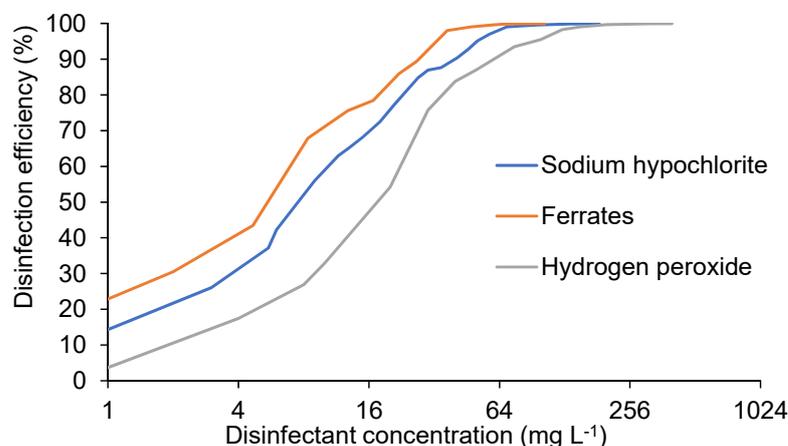


Figure 6. Disinfection efficiency of ferrates, sodium hypochlorite and hydrogen peroxide, in terms of TVC removal from biologically treated wastewater, at different disinfectant dosages.

Even though disinfection efficiency reached 99.99% in terms of TVC removal, none of the evaluated disinfectants could provide the complete disinfection of wastewater samples, even at considerably high disinfectant dosages (over 100 mg L⁻¹) and CT values (over 3000 mg min L⁻¹). On the contrary, the complete disinfection of the artesian well water sample was achieved at relatively low NaClO, H₂O₂ and Fe(VI) dosages of approximately 0.5 mg L⁻¹ and CT of 15 mg min L⁻¹. The incomplete disinfection of wastewater samples is attributed to the presence of particulate matter (TSS 16.3 ± 3.7 mg L⁻¹), which may provide a shelter for microorganisms and spores to avoid contact with chemical disinfectants.

This was experimentally confirmed in this study by applying chemical disinfection on wastewater samples that had been previously subjected to low-cost sand filtration (limestone sand at mesh size <850 μm) for the removal of large size particulates. While a considerable count of viable microbial species remained in wastewater samples after filtration, their complete disinfection could be achieved at CT values of 270 mg min L⁻¹, 380 mg min L⁻¹ and 157 mg min L⁻¹ for NaClO, H₂O₂ and Fe(VI), respectively. Once again, ferrates presented the highest disinfection efficiency compared with NaClO and H₂O₂. It should be mentioned that the oxidizing power of each of the chemical disinfectants used in this study can be significantly affected by the pH of the solution. The oxidizing power of H₂O₂ and ferrates increases with decreasing pH, while the oxidizing power of NaClO increases with increasing pH [43,44]. As Jiang and Lloyd [45] highlighted, at acidic pH, the oxidizing power of ferrates is higher than the most commonly used chemical disinfectants (chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, oxygen, permanganate, etc.). Interestingly, ferrates' highest oxidizing efficiency is obtained at pH values between 9 and 10, which indicates the importance of the ferrate compound's stability, which is enhanced with increasing pH [46].

The results of the present study indicate that a ferrate-based disinfection process could offer a more sustainable and green solution in water and wastewater treatment sectors. The challenge at hand regarding the minimal stability and high procurement cost of ferrate compounds can be addressed by the in situ electrochemical preparation of ferrate solutions in a strongly basic environment using a simple low-cost Fe⁰/Fe⁰ electro-synthesis cell. The maintenance of strongly basic conditions during the electro-synthesis of ferrates ensures the highest stability of ferrate compounds, since ferrates are stable in basic solutions and very unstable in neutral and acidic solutions [47].

The experimental assessment of the stability of the ferrate solution, which was produced in the Fe^0/Fe^0 electrosynthesis cell, revealed its minimal stability even under the alkaline conditions induced by the use of the 25M NaOH solution as an electrolyte. Approximately 6 h after the electrosynthesis of a ferrate solution, its concentration dropped from the initial value of 836.8 mg L^{-1} to 376.3 mg L^{-1} , corresponding to a 55% reduction in ferrates. Due to this evident degradation of the ferrate solution, the in situ electrosynthesis of only the necessary quantities of ferrate solution is proposed for the full-scale implementation of a ferrate-based process. This would increase the viability of the technology, since it would minimize the reduction of ferrates in the solution and, thus, energy losses.

In a scenario where a volumetric load of $100 \text{ m}^3 \text{ d}^{-1}$ of biologically treated wastewater is subjected to disinfection via electrosynthesized ferrates, the energy requirement for ferrates synthesis is under 0.1 kWh d^{-1} , corresponding to 0.001 kWh m^{-3} and approximately USD 0.00025 m^{-3} (accounted energy cost at USD 0.25 kWh^{-1}). The daily consumption of NaOH is calculated at approximately 2.8 kg . By taking into account a procurement cost of NaOH at USD 0.5 kg^{-1} (the approximate price of industrial grade reagent in the Greek market), the resulting NaOH procurement cost is approximately USD 1.4 d^{-1} , corresponding to USD 0.014 m^{-3} . Thus, the total operational cost of a biologically treated wastewater disinfection process by in situ prepared ferrates is estimated at USD 0.1425 m^{-3} . This is based on the cost for the disinfection of 100 m^3 of treated wastewater using other commonly applied techniques, which for chlorination and ozonation is approximately USD 1.06 m^{-3} and USD 0.38 m^{-3} , respectively [48].

The experimental study of ferrates application for disinfection revealed (i) the higher disinfection efficiency of ferrates compared to sodium hypochlorite and hydrogen peroxide, (ii) that ferrates can readily transform to non-toxic Fe(III) species that can be easily retained via low-cost filter configurations and, thus, (iii) that they do not produce residuals to an extent that would affect water or treated wastewater characteristics and uses.

4. Conclusions

The results of this study indicate that low-cost iron-based or ferrate-based treatment stages could be used for natural water remediation, as well as for the treatment of wastewater, either as a preliminary treatment stage or as an advanced treatment stage. The use of low-cost and/or scrap iron materials showed that Fe^0 is an agent that can rapidly and almost completely reduce Cr(VI) from aqueous solutions. The mechanism involves the oxidation of Fe^0 to Fe(II) with Cr(VI), followed by Fe(II) to Fe(III) oxidation. The co-precipitation of the generated, relatively insoluble Cr(III) and Fe(III) species can offer efficient chromium removal when coupled with low-cost separation techniques, such as sand filtration. The formation of iron oxide on the metallic iron surface minimizes Fe^0 reactivity, leading to its passivation. The non-invasive regeneration technique of sonication can restore Fe^0 reactivity with equal efficiency to the chemical baths in strong acid solutions. Regarding the use of ferrates as a green alternative to chemical disinfection and advanced water and wastewater treatment processes, the study showed that the in situ electrosynthesis of ferrates via a simple Fe^0/Fe^0 electrochemical cell can provide an efficient and low-cost solution for the removal of microbial contaminants, turbidity and recalcitrant organic compounds.

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

Funding: This research was funded by Region of Western Macedonia's (MIS) 5047197 project.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are available upon request.

Conflicts of Interest: The authors declare no conflict of interest.

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