Article

Comparison between Different Technologies (Zerovalent Iron, Coagulation-Flocculation, Adsorption) for Arsenic Treatment at High Concentrations

Luis E. Lan [1], Fernando D. Reina [2], Graciela E. De Seta [1,2], Jorge M. Meichtry [2,3] and Marta I. Litter [4,*]

[1] Unidad Docente Básica (UDB)-Química, Facultad Regional Buenos Aires, Universidad Tecnológica Nacional, Mozart 2300, Buenos Aires City 1407, Argentina; llan@frba.utn.edu.ar (L.E.L.); egdeseta@frba.utn.edu.ar (G.E.D.S.)

[2] Centro de Tecnologías Químicas, Facultad Regional Buenos Aires, Universidad Tecnológica Nacional, Medrano 951, Buenos Aires City 1425, Argentina; freina@frba.utn.edu.ar (F.D.R.); jmeichtry@frba.utn.edu.ar (J.M.M.)

[3] División Química de la Remediación Ambiental, Gerencia Química, Comisión Nacional de Energía Atómica and CONICET, Av. Gral. Paz, 1499, San Martín 1650, Buenos Aires Province, Argentina

[4] Escuela de Hábitat y Sostenibilidad, Universidad Nacional de General San Martín, 25 de Mayo y Francia, San Martín 1650, Buenos Aires Province, Argentina

* Correspondence: mlitter@unsam.edu.ar or martalitter24@gmail.com

Abstract: The presence of arsenic in water for human consumption is of concern, especially in developing countries, and the design of simple and economic treatments for arsenic removal is imperative. In this paper, three low-cost technologies were evaluated for As(V) or As(III) (5 mg L^{-1}) removal: (1) zerovalent iron (Fe(0)), as powdered (μFe(0)) and iron wool (wFe(0)); (2) coagulation-flocculation with $Al_2(SO_4)_3$ or $FeCl_3$; and (3) adsorption on a natural clay. μFe(0) was more efficient than wFe(0), requiring a minimal dose of 0.25 g L^{-1} to achieve [As(V)] < 0.01 mg L^{-1} after 288 h; the reaction time was reduced to 168 h under stirring. When starting from As(III), partial oxidation to As(V) was observed, and removal was not complete even after 648 h with 1 g L^{-1} μFe(0). As(V) removal using $FeCl_3$ and $Al_2(SO_4)_3$ was very fast and completed in 15 min with 0.25 g L^{-1} of both reagents. However, $Al_2(SO_4)_3$ was not efficient to remove As(III). With the clay, doses higher than 50 g L^{-1} and times longer than 648 h were needed to remove both As species. Arsenic leached from μFe(0) used to treat As(III) was almost negligible. Thus, Fe(0) may be the best alternative for low-cost, small-scale applications.

Keywords: arsenic; zerovalent iron; coagulation-flocculation; clay; adsorption
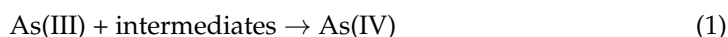
1. Introduction

Arsenic is the twentieth element in abundance in the earth's crust, the fourteenth in the oceans, and the twelfth in the human body [1,2]. It is toxic for animals and plants, associated with numerous chronic effects that include skin lesions, cardiovascular diseases, neurological effects, and various types of cancers [3–6]), leading to oxidative stress and genotoxicity [7]. For these reasons, it is at the top of the list of priority substances of the Agency for Toxic Substances and Disease Registry (ATSDR, Atlanta, GA, USA) [8] and is considered the largest case of mass poisoning in the history [4]. In general, inorganic species are predominant in groundwater [5], with As(V) being the thermodynamically stable species under moderately oxidizing conditions and neutral to alkaline pH. As(III) has greater toxicity and mobility in water than As(V), and organic species are less toxic [2,5,9]. For both humans and animals, the ingestion of As-contaminated water is the main source of exposure [10,11]. The World Health Organization (WHO) recommends a maximum limit of 10 μg L^{-1} of total As (As$_T$) in water for human consumption [12].

The greatest impact of As contamination is natural and observed in groundwater, coming from the dissolution of rocks and ash of volcanic origin [9–11,13]. Minor As contamination is related to human activities such as mining, electronics, agriculture, and disposal of municipal and industrial waste [9,10]. The population potentially exposed to dangerous levels of As in water has gone from 46 million in 2002 [10] to 226 million in 2012 [14]. At the end of 2017, the WHO reported that at least 140 million people consumed water with an As content greater than 10 μg L^{-1} [15].

Although it is known that in Latin America the population may have suffered arsenicosis 7000 years ago [16], the first reports of this impact on health in our subcontinent date from one century ago and correspond to the locality of Bell Ville, Córdoba, Argentina [16,17]. In this country, the presence of As in groundwater has been observed in the Chaco-Pampean plain, Puna, Cuyo, and Patagonia in concentrations ranging from 200 μg L^{-1} to 15,000 μg L^{-1} and has affected around four million people [18–20]. Its consumption has been related to Endemic Regional Chronic Hydroarsenicism (HACRE), a series of clinical manifestations characterized by skin lesions and cancers [9,14,16]. In general, in Latin America, As is found almost exclusively as inorganic As(V) [10,13,16].

For these reasons, it is necessary to improve conventional methods and develop new technologies for the treatment of As contaminated water. The most used physicochemical processes for As removal are coagulation-flocculation, adsorption, ion exchange, and membrane processes (e.g., [1,9,10,21–28]). In this paper, three conventional technologies, Fe(0), coagulation-precipitation with $Al_2(SO_4)_3$ and $FeCl_3$, and adsorption on a natural clay for the treatment of aqueous solutions of As(V) and As(III) are compared. Thus, details about these technologies are given below.

Processes based on the use of Fe(0) tend to be very efficient (e.g., [29–35]), with a high capacity and a low As desorption rate [36]. In general, the As removal mechanisms with Fe(0) involve the generation of Fe(II) or Fe(III), followed by partial oxidation of Fe(II) and coprecipitation of As(III)/As(V) species with these ions (e.g., $FeAsO_4$), or by adsorption of As on Fe(III) oxides and oxyhydroxides (FeOx) (e.g., [23,27,34,37–50]). This is mainly due to the great affinity between the Fe(II) and Fe(III) ions generated in the Fe(0) corrosion with As(III) and As(V). Among the FeOx, hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), wustite (FeO), goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (δ-FeOOH), and "green rust", can be mentioned [24,44,46]. Other works suggest that As forms strong surface complexes with iron [38,39]. The general well-accepted (simplified) mechanism involved in systems using Fe(0) is indicated in Equations (S1)–(S10) of the Supplementary Material Section (SI) (e.g., [46,48,51,52]). Removal of As(V) then occurs through reactions displayed in Equations (S11) and (S12). The corrosion process of Fe(0) also generates reactive oxygen species (ROS, such as superoxide ($O_2^{\bullet-}$), H_2O_2, or HO$^{\bullet}$) or Fe(IV) coming from Fe(II) oxidation by dissolved O_2 (DO), all species capable of oxidizing As(III) to As(IV) and then to As(V) [46]:

$$\text{As(III)} + \text{intermediates} \rightarrow \text{As(IV)} \tag{1}$$

$$\text{As(IV)} + O_2 \rightarrow \text{As(V)} + O_2^{\bullet-} \tag{2}$$

Treatment of As with Fe(0) is usually slow [38,41,53] and removal is greater and faster under oxic conditions [34,45,54]. In addition, the corrosion rate of Fe(0) depends on the characteristics of the Fe(0) material (e.g., specific area), on pH, DO concentration, electrical conductivity (EC), mixing conditions, and presence of ions, such as phosphate, silicate, or calcium in the treated water [48,55,56]; even the presence of As(V) and As(III) affects the formation of the FeOx, significantly decreasing the Fe(0) corrosion rate [38,41,48]. Use of nanoparticulate Fe(0) (nZVI) is more rapid but this material has a short lifetime under oxic conditions and requires immobilization before its use in filters. There is a large number of publications on the use of nZVI for As removal (e.g., [27]); thus, no specific references will be included in the present paper.

In coagulation-precipitation, salts of aluminum ($Al_2(SO_4)_3$ or aluminum polychloride), or iron ($FeCl_3$ or $FeSO_4$) are used. It is a simple method and one of the most widely used [24,57,58] with numerous examples of applications at pilot and commercial level, especially in large-scale treatment plants [24], such as the ARCIS-UNR process developed in Argentina [9,18,26]. Fe-based coagulants are more efficient than Al-based coagulants, especially at pH > 7 [21,24,28]. In the process, precipitation, coprecipitation, or adsorption of dissolved As on the formed surface of oxo-hydroxides or retained in suspended particles takes place. However, this method has the disadvantage of requiring a continuous addition of reagents, and of generating a large volume of hazardous waste that must be properly disposed of [24,25]. The mechanisms of removal of As by coagulation-precipitation are similar to that described for Fe(0) by Equations (S1)–(S10), but when coagulation-flocculation is used with Fe(II), reactions (S1)–(S3) are not involved, and when $FeCl_3$ or $Al_2(SO_4)_3$ is used, reactions (S4)–(S9) are not involved either, replacing Fe(III) by Al(III) when aluminum sulfate is employed.

Adsorption technologies for As removal from water have been extensively studied and applied. Thus, the involved processes will not be described here and can be consulted in several articles (e.g., [21,22,59–61]). In particular, clays or soils from the Misiones province in Argentina have been used, leading to good removal yields [62–66].

As said previously, the present paper compares the use of Fe(0), coagulation with $Al_2(SO_4)_3$ and $FeCl_3$, and adsorption on a natural clay for the removal of As(V) or As(III) from aqueous solutions. The leachability of As removed after Fe(0) and clay treatment of As(III) solution is also studied.

2. Methodology

2.1. Materials and Reagents

In the experiments with Fe(0), two different materials were evaluated: (a) zerovalent iron powder (μFe(0), Sigma Aldrich, Saint Louis, MO, USA) of high purity (>99.8%) with a particle diameter between 0.84 mm and 0.074 mm (>95%), and (b) a commercial steel wool (Virulana®, Garín, Buenos Aires, Argentina, wFe(0)), purity > 97%, formed by wires with a diameter of approximately 0.2 mm.

In the coagulation-flocculation experiments, $Al_2(SO_4)_3$ (99%, Sigma Aldrich) and $FeCl_3$ (98%, Alfa Aesar, Ward Hill, MA, USA) of analytical quality were used.

The natural clay used for the adsorption experiments was collected in the Misiones province, Argentina. Prior to use, it was processed in a mortar and sieved through a 20-mesh filter (particle size < 0.84 mm). The characterization of the clay is briefly described in Section S2 of the Supplementary Information, extracted from ref. [66]. The chemical composition with respect to Fe, Al, and Mn in the clay is similar to that reported for other samples of Misiones province [65,66] and are indicated in Table S1.

Na_2HAsO_4 (98%, Baker, Radnor, PA, USA) and As_2O_3 (99.95%, Sigma Aldrich) were used to prepare the solutions of As(V) and As(III), respectively. Ascorbic acid ($C_6H_8O_6$, 99.7%), ammonium molybdate (($NH_4)_6Mo_7O_{24}.4H_2O$, 81–83% as MoO) and sulfuric acid (H_2SO_4, 98%) were Merck (Darmstadt, Germany); antimony tartrate ($C_8H_4K_2O_{12}Sb_2.3H_2O$, 99%) was Baker, and sodium hydroxide (NaOH, 97%) and calcium hydroxide ($Ca(OH)_2$, 96%) were Cicarelli (San Lorenzo, Santa Fe, Argentina). The other reagents were of analytical quality. Low EC (1 μS cm^{-1}) distilled water was used for the experiments.

Solutions of As(V) and As(III) (5 mg L^{-1}) were prepared from concentrated solutions (1000 mg L^{-1}). That concentration was in the range of initial As concentrations used in other studies [34]. For pH adjustments, freshly prepared dilute solutions of NaOH or H_2SO_4 were used. In all cases, the experiments were completed at room temperature (RT, 16–20 °C). Experiments were performed by duplicate for all studied conditions.

2.2. Experiments with Fe(0) and Natural Clay

The experiments were performed in Erlenmeyer flasks of 250 mL, in which 200 mL of the As solution (previously adjusted to the desired pH) were placed. Next, the desired

amount of solid material was added under orbital agitation (100 rpm, Ferca, Buenos Aires, Argentina) for one min; in the experiments without agitation, it was interrupted after this time and restarted for one min prior to sampling, while under agitation, it remained constant throughout the test.

2.3. Coagulation-Flocculation Experiments

The experiments were performed using a Jar Test equipment (Parsec, model Aries VII, Morón, Buenos Aires, Argentina) in beakers of 1000 mL, in which 400 mL of the As solution (previously adjusted to the desired pH) were placed. Next, the desired amount of the solid coagulant was added under mechanical agitation, the pH was adjusted to 7 using $Ca(OH)_2$ and the system was stirred for 1 min at 100 rpm, then for 14 min at 25 rpm, after which the agitation was interrupted to allow the growth of flocs.

2.4. Experiments of As Stability on the Generated Solids

At the end of the experiments of As(III) removal with $\mu Fe(0)$, clay and the mixture $\mu Fe(0)$ + clay, the content of the Erlenmeyer flasks was vacuum filtered through a cellulose nitrate filter of 0.22 μm pore and 47 mm diameter (Sartorius, Göttingen, Germany), and the solids obtained were dried at 100 °C for 10 days in a San Jor SI60 (San Martín, Buenos Aires, Argentina) stove. Next, 1 g of the solid was taken, and 25 mL of distilled water was added, leaving it in contact for 14 days, after which the concentrations of As(III) and As(V) in solution were determined. Due to the low amount of solids generated, this procedure was not applied to As(III) solutions treated by coagulation-flocculation.

2.5. Analytical Techniques

Changes in As(V) concentration in solution were measured by the spectrophotometric arsenomolybdate technique at 868 nm [21], with a modification to measure As_T and As(III) with excess potassium permanganate [67]. Quartz spectrophotometric cells of 1 cm (limit of quantification: 50 $\mu g\ L^{-1}$), or 10 cm optical path (limit of quantification: 10 $\mu g\ L^{-1}$), were used in a Shimadzu (Kyoto, Japan) dual-beam spectrophotometer, model UV-1700. In all cases, periodic samples of 1 mL or 5 mL were taken for measurements, which were filtered through a Sartorius cellulose nitrate filter of 0.22 μm pore and 25 mm diameter and brought to volume in flasks of 10 mL or 25 mL, respectively. The determination of pH and EC was performed by potentiometry directly in the treated solution with a Hanna (Woonsocket, RI, USA) C114 multiparametric equipment.

3. Results and Discussion

3.1. Removal of As(V) with Fe(0)

The majority of experiments with $\mu Fe(0)$ and $wFe(0)$ were performed with As(V) because it is the main As species in groundwater of Latin America [10,13,16]. The initial concentration was fixed in 5 mg L^{-1} to cover a wide range taking into account the values found in Argentina [18,19]. The experiments were performed without agitation, to simulate the operating conditions of Fe(0) within a filter, and the doses of Fe(0) were between 0.25 g L^{-1} and 5 g L^{-1}, i.e., in the range of the values reported in other references (e.g., [34,48]). The working pH was 7 and the system was open to the air ($[O_2] \geq 1$ mg L^{-1}). Periodic samples were taken until no significant changes in As(V) concentration were observed; the results are shown in Figures 1 and 2.

Figures 1 and 2 show that the removal of As(V) using these Fe(0) materials is slow, requiring at least 96 h (4 days) to achieve a removal $\geq 99\%$ of the initial As(V) concentration when using 5.0 g L^{-1} and 2.5 g L^{-1} of the materials. The results also show that $\mu Fe(0)$ requires a dose of 0.25 g L^{-1} and 288 h (12 days) to achieve a complete As(V) removal ($[As(V)] \leq 10\ \mu g\ L^{-1}$), while for $wFe(0)$ a tenfold higher dose after 168 h (7 days) was needed.

The effect on As(V) removal of stirring, use of partially corroded Fe(0) and pH was evaluated employing 0.25 g L^{-1} of μFe(0), i.e., the minimum dose required to achieve the complete removal of As(V) (Figure 1). The results are presented in Figure 3.
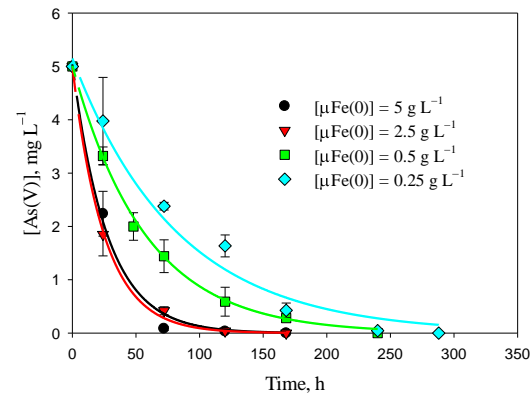

Figure 1. Temporal profiles of As(V) concentration in contact with different doses of μFe(0). Conditions: [As(V)]$_0$ = 5 mg L^{-1}, pH 7, RT, EC = 0.03 mS cm^{-1}, without stirring. Error bars represent the standard deviation between duplicates, while full lines are the adjustment to a pseudo-first-order kinetics using Equation (3).

Figure 2. Temporal profiles of As(V) concentration in contact with different doses of wFe(0). Conditions: [As(V)]$_0$ = 5 mg L^{-1}, pH 7, RT, EC = 0.03 mS cm^{-1}, without stirring. Error bars represent the standard deviation between duplicates, while full lines are the adjustment to a pseudo-first-order kinetics using Equation (3).
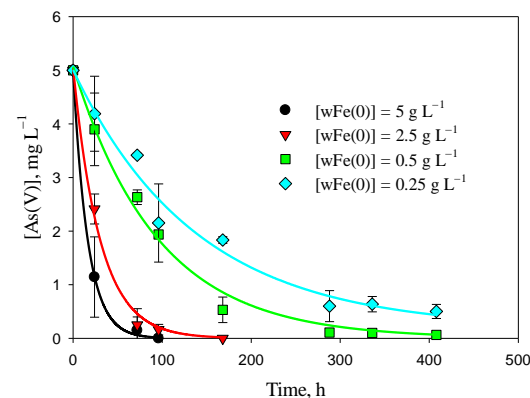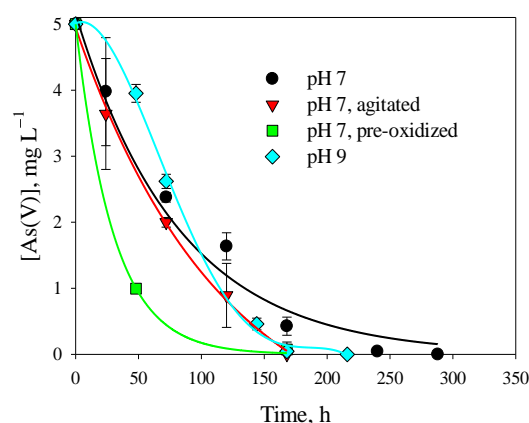
Figure 3. Temporal profiles of As(V) concentration using μFe(0). Conditions: $[As(V)]_0 = 5$ mg L^{-1}, $[μFe(0)] = 0.25$ g L^{-1}, RT, EC = 0.03 mS cm^{-1}, pH 7 or 0.25 mS cm^{-1}, pH 9, no agitation unless indicated. Error bars represent the standard deviation between duplicates. The black and green lines are fittings to Equation (3), while red and cyan lines are only for visualization and do not correspond to any fitting model.

The absence or presence of stirring is without any doubt an important factor influencing the As(V) removal rate with Fe(0), although, as other anions treated by the Fe(0)/H$_2$O system, it has been scarcely studied [56]. As shown in Figure 3, the stirring increases the rate of As(V) removal at pH 7, especially at long reaction times, allowing a complete removal in 168 h (7 days), while, as said, 288 h (12 days) were necessary without agitation. This result is similar to that found by Roy and Bose [68], who reported an increase in the removal rate under stirring due to an enhanced mass transfer. However, Fe(0) applications in filters imply diffusion transport of contaminants in the vicinity of Fe(0). In other words, agitation is relevant for fluidized bed reactors while quiescent experiments reproduce filtration systems [30].

Regarding the effect of pH, the removal of As(V) at pH 9 under stirring was slower than at pH 7, being necessary 216 h (9 days) to achieve an $[As(V)] < 10$ μg L^{-1}, despite the higher EC, which should increase the corrosion rate [48]. However, the removal capacity of μFe(0) is not significantly affected as the same MR was necessary at both pH, contrarily to other reports in the literature [34,48,54].

The use of partially corroded Fe(0) (pre-oxidized), obtained by leaving μFe(0) in water for 120 h, caused a significant increase in the As(V) removal rate.

The removal kinetics of As(V) with both Fe(0) materials could be adjusted to a pseudo-first-order kinetics using Equation (3), indicated in Figures 1–3 by the solid lines:

$$[As(V)] = A \times \exp^{-k \times t} + [As(V)]_\infty \tag{3}$$

where A is the concentration of As(V) removed, k is the pseudo-first order kinetic constant, and $[As(V)]_\infty$ is the As that remains in solution at the end of the run. This kinetic behavior for the removal of As(V) with Fe(0) has been previously reported [29,34,39,40,43,44,48]. Other kinetic models were tested, e.g., a saturation kinetics as proposed in [38], a pseudo-second-order kinetic model as proposed in [54,69], or a mixed pseudo-first and pseudo-second model as proposed in [68]. However, for the present experiments, all fittings were poorer than the one obtained with the simple Equation (3). The values of the kinetic parameters for the experiments extracted from Figures 1–3 are shown in Table 1.

Table 1. Kinetic parameters of the experimental results of As(V) removal extracted from in Figures 1–3 with Equation (3).

Experiment		A, mg L^{-1}	$k \times 10^3$, h^{-1}	$[As(V)]_\infty$, mg L^{-1}	R^2
μFe(0)	0.25 g L^{-1}	5.0 ± 0.2	12 ± 1	0	0.98
	0.50 g L^{-1}	5.00 ± 0.05	17 ± 0.3	0	1
	2.5 g L^{-1}	5.0 ± 0.2	37 ± 3	0	0.99
	5.0 g L^{-1}	5.0 ± 0.1	40 ± 2	0	1
	0.25 g L^{-1} [a]	5.00 ± 0.05	34 ± 1	0	1
wFe(0)	0.25 g L^{-1}	4.8 ± 0.3	7.2 ± 1.5	0.2 ± 0.3	0.97
	0.50 g L^{-1}	5.00 ± 0.05	10.6 ± 0.7	0	0.99
	2.5 g L^{-1}	5.0 ± 0.1	33 ± 2	0	1
	5.0 g L^{-1}	5.0 ± 0.1	60 ± 2	0	1

Note: [a] μFe(0) pre-oxidized by contact with water for 120 h (5 days) before use.

The results of Table 1 show that the pseudo-first order rate constants increase with the increasing Fe(0) dose. With μFe(0), the saturation seems to be reached at the highest Fe(0) dose (5 g L^{-1}). It can also be seen that, except for the highest dose, μFe(0) presents higher removal rates than wFe(0). If the surface area of both materials is estimated assuming that μFe(0) are spheres of an average diameter of 0.4 mm, and wFe(0) is a cylinder of 0.2 mm in diameter and employing 7.86 g cm^{-3} as the iron density [70], the exposed surface of μFe(0) can be calculated as 12.7 cm^2 g^{-1}, while that of wFe(0) would be 25.4 cm^2 g^{-1}. Thus, the somewhat higher rate cannot be assigned to a larger exposed surface area in μFe(0), but to a higher reactivity ([39,48] and references therein), or to a better dispersion of the material in the system. At [Fe(0)] = 5 g L^{-1}, the powdered μFe(0) may be partially occluded at the bottom of the reaction flask limiting O_2 diffusion, and thus Fe(II) oxidation (Equation (S5)), while for wFe(0), this effect may be less important due to its wool structure.

In Table 2, k values of the present work and other results reported in the literature for As(V) removal with Fe(0) under oxic conditions are presented, together with the initial As(V) removal rates (r_i), calculated as the derivate of Equation (3) at $t = 0$ ($r_i = k \times [As(V)]_0$) or from other data reported in the literature. In addition, t_R, the time required to achieve $[As(V)] \leq 10$ μg L^{-1} (the limit recommended by the WHO [12]) was included.

Table 2. Comparison of kinetic parameters k, r_i, and t_R for As(V) removal with Fe(0) under oxic conditions at circumneutral pH extracted from Figures 1–3 with Equation (3), and data from other authors.

Fe(0) Size (mm)	$[As(V)]_0$ (mg L^{-1})	MR As:Fe	pH	EC (mS cm^{-1})[a]	Stirring	$k \times 10^3$ (h^{-1})	r_i (mg L^{-1} h^{-1})	t_R (h)	Ref.
0.074–0.84(μFe(0))	5	1:67	7	0.03	No	12	0.06	288	This work
0.20(wFe(0))	5	1:1342	7	0.03	No	60	0.30	96	This work
<0.149	100	1:13.4	7	0.05-0.8	Magnetic	79.5	7.95	NR	[43]
<0.074	0.5	1:6708	8.28	≈3 [a]	NR	348	0.174	8	[48]
0.125–0.177	5	1:134	7	≈2.7 [a]	Orbital, 180 rpm	330	1.65	NR	[29]
0.149	2	1:16,109	6.4	≈0.9 [a]	Orbital, 50 rpm	77.8	0.1556	72	[39]
NR [b]	2	1:16,109	6.4	≈0.9 [a]	Orbital, 50 rpm	34.9	0.0698	<96	[39]
NR [c]	2	1:16,109	6.4	≈0.9 [a]	Orbital, 50 rpm	24.6	0.0492	<96	[39]
0.045	2	1:16,109	6.4	≈0.9 [a]	Orbital, 50 rpm	5.31	0.0106	NR	[39]
0.125–0.177	10	1:134	7	≈3.6 [a]	NR	—	10.5	NR	[45]
0–2–0.25	5	1:5366	9	NR	Orbital, 100 rpm	—	2.8	>120	[69]
<0.044	0.2	1:13,416	7	NR (no salt added)	Orbital	—	0.48	3	[71]
<0.212	5	1:537	7	≈2.6 [a]	NR	—	3.2	>50	[54]
NR [d]	0.1	1:40,247	7.1	1.50	Magnetic, 300 rpm	—	0.12	2.7	[49]

Notes: [a] When not provided, EC was calculated from the total dissolved solids (TDS) content using the following Equation: TDS (mg L^{-1}) = 0.65 × EC (μS cm^{-1}) [72]. NR: not reported; [b] powdered Fe(0), BET: 2.53 m^2 g^{-1}; [c] powdered Fe(0), BET: 2.33 m^2 g^{-1}; [d] identical to the wFe(0) used here, BET: 2.02 m^2 g^{-1}.

As can be appreciated in Table 2, the values of k obtained here are similar to those reported by Su and Puls [39], and smaller than those reported by Dou et al. [29], Wang et al. [34], Bang et al. [43], and Sun et al. [48]. The differences can be attributed to a smaller Fe(0) size, a lower EC, and the absence of agitation. It should be pointed out that only quiescent and/or slowly shaken system are considered adequate conditions to study removal of pollutants by Fe(0)/H_2O filtration systems ([56] and references therein)

A change in the kinetic regime takes place under stirring, with the system behaving with a mixed zero and pseudo-first order [38] (R^2 = 0.99, k_0 = 0.012 mg L^{-1} h^{-1}, k = 0.009 h^{-1}), with r_i almost equal to the one obtained without agitation. The use of partially corroded Fe(0) obtained by leaving μFe(0) in water for 120 h caused a significant increase in the As(V) removal rate, with k being almost three times higher than the one obtained with bare μFe(0) (k = 34 and 12 $\times$ 10^{-3} h^{-1}, respectively, Table 1), reinforcing the concept that the dominant process is Fe(0) corrosion.

The initial As(V) removal rates (r_i = k $\times$ [As(V)]$_0$) are among the smallest values reported in the literature, especially when comparing with reports that used identical or higher [As(V)]$_0$ values. The differences can be attributed to the lower particle size of the materials used there [34]. Other factors can be the use of stirring and/or the higher EC [71], and the pretreatment of Fe(0) with 6 M HCl that produces a highly porous surface [54,68]. For μFe(0), r_i is very similar to that reported by Su and Puls [39], while for wFe(0) = 2.5 g L^{-1}, r_i is almost the same to the one reported by Triszcz et al. [49], who used a material identical to wFe(0). Interestingly, these similar r_i values were obtained despite significant differences in [As(V)]$_0$ and EC values, and despite stirring was used by Triszcz et al. [49]. It should be emphasized that although 288 h were necessary to achieve [As(V)] $\leq$ 0.01 mg L^{-1} with 0.25 g L^{-1} of μFe(0), a low As:Fe MR (1:67) is used, which is among the smallest ratios reported in the literature (see Table 2 and [37]) and in the order of other more costly and/or complex materials, such as nZVI [27,34]. This makes this material very promising for the development of simple and low-cost household filters. In general, r_i values are dependent on [As(V)]$_0$, with a Pearson correlation factor r of 0.593 (p = 0.025), while no significant correlation was found for MR (r = -0.464, p = 0.095).

The t_R values obtained in this work are similar to others obtained with [As(V)]$_0$, = 5 mg L^{-1} [54,69], but up to 100 times higher than those starting from lower [As(V)]$_0$ and higher MR. A positive correlation could be obtained with [As(V)]$_0$ (r = 0.663, p = 0.052), while for MR the correlation was poor and negative (r = -0.447, p = 0.198). From this analysis, it can be concluded that with [As(V)]$_0$ $\leq$ 0.5 mg L^{-1} (commonly found in Argentine groundwaters) and with high MR ($\approx$1:10,000), the final recommended value of As(V) $\leq$ 0.01 mg L^{-1} could be obtained within a few hours of treatment.

3.2. Removal of As(III) with Fe(0)

One experiment of removal of As(III) with μFe(0) under similar conditions of the experiments starting from As(V) ([As(III)]$_0$ = 5 mg L^{-1}, pH 7, RT, EC = 0.03 mS cm^{-1}, without stirring) was performed to study the behavior of the species and for comparison with As(V). The experiment was made with a lower Fe(0) concentration ([μFe(0)] = 1 g L^{-1}), a slightly higher dose than that used for As(V) considering that 0.25 g L^{-1} of μFe(0) was enough for the complete As(V) removal (Figure 1), and that the As(III) removal rate would be slower. Figure 4 shows the evolution of As(III) decay and As(V) formation and decay.
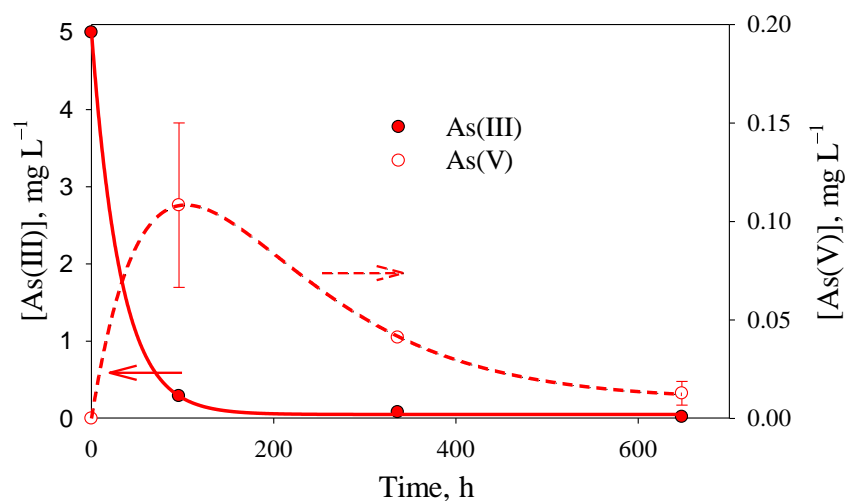
Figure 4. Temporal profiles of As(III) and As(V) concentrations in contact with $\mu Fe(0)$. Conditions: $[As(III)]_0 = 5 \text{ mg L}^{-1}$, $[\mu Fe(0)] = 1 \text{ g L}^{-1}$, pH 7, RT, EC = 0.03 mS cm^{-1}, without stirring. Error bars represent the standard deviation between duplicates, while the full line is the adjustment to Equation (3). The dashed line is only for visualization and does not correspond to any adjustment equation.

Figure 4 shows a fast initial As(III) disappearance followed by a slow subsequent removal, with a proper fitting to a pseudo-first order kinetics (Equation (3)). A comparison with k, r_i, and t_R values reported or calculated from the literature is shown in Table S2. As indicated in Table S2, a pseudo-first order kinetics was already reported for As(III) removal by Fe(0) under oxic conditions at pH 6–8.25 (e.g., [34,39,43,48,73,74]). In general, higher k values were obtained with smaller ZVI particles and higher MR (except for the work of Bang et al. [43]) or other experimental conditions (i.e., lower pH [43], EC, type of stirring, etc.). The same trend is followed by r_i, although for these parameters $[As(III)]_0$ is also a key condition. When comparing k and r_i values obtained for As(V) under identical conditions (Table 2), As(III) removal is generally slower, as previously reported [43,45,48], although other authors report the opposite behavior [39]. Regarding t_R, the value here obtained (648 h) was more than twice higher than that for As(V), despite a fourfold higher Fe(0) dose was used with As(III), in agreement with a slower removal kinetics with Fe(0) for this As species; besides, t_R is almost one order of magnitude higher than others reported in the literature, the difference being attributed to the lack of stirring, reflecting that this condition may be more critical for As(III) than for As(V).

Regarding the removal mechanism, from Figure 4 it is seen that As(III) is first oxidized to As(V), which is then removed by Fe(0) corrosion products. This is a slow process where 0.021 mg L^{-1} As(III) and 0.013 mg L^{-1} As(V) are reached after 648 h, indicating that, contrarily to the case of As(V) with = 0.25 g L^{-1}, the final As value recommended by the WHO is not reached despite the fourfold higher dose of $\mu Fe(0)$ used.

3.3. Removal of As(V) and As(III) by Coagulation-Flocculation

For the experiments of As(V) and As(III) removal using coagulation-flocculation, it was first required to determine the minimum dose of coagulant necessary to remove both species up to concentrations ≤ 0.01 mg L^{-1}. As Ca(OH)$_2$ is the common reagent to correct pH in water treatment plants, it was used here to adjust the pH to 7 after the addition of the coagulants. This pH was selected according to previous studies where the efficiency of As(V) removal was observed to decrease at and above pH 8 [58]. Reactions were performed, as said, in a Jar Test equipment with stirring, in contrast with most experiments with Fe(0). Samples were taken after 15, 30, and 60 min of reaction and, after 24 h, they did not show significant differences, indicating that the reaction is rapid and practically complete within 15 min. Table 3 shows the results of the treatment of solutions containing As(V) or As(III) using Al$_2$(SO$_4$)$_3$ and FeCl$_3$ as coagulants-flocculants after 15 min reaction time. No temporal

profiles could be taken because the reaction was very fast, and samples would have to be taken at very short times. As Fe(III) can oxidize As(III) [21], $[As_T]$ (i.e., $[As(V)]$ + $[As(III)]$) was evaluated in this case.

Table 3. Removal of As(V) and As(III) with coagulants-flocculants. Conditions: $[As(V)]_0$ or $[As(III)]_0$ = 5 mg L^{-1}, pH 7, RT, EC = 0.03 mS cm^{-1} (before adding the coagulant), mechanical agitation, reaction time: 15 min.

Coagulant	Dose (g L^{-1})	$[As_T]$ Remaining Starting from As(V) (mg L^{-1})	$[As_T]$ Remaining Starting from As(III) (mg L^{-1})
Al$_2$(SO$_4$)$_3$	0.25 g L^{-1}	<LD	5.00
	0.50 g L^{-1}	<LD	—
	2.5 g L^{-1}	<LD	3.91
	5.0 g L^{-1}	<LD	3.60
FeCl$_3$	0.25 g L^{-1}	<LD	0.06
	0.50 g L^{-1}	<LD	<LD
	2.5 g L^{-1}	<LD	<LD
	5.0 g L^{-1}	<LD	—

Table 3 indicates that, at pH 7, FeCl$_3$ and Al$_2$(SO$_4$)$_3$ are equally efficient to remove As(V), being necessary 0.25 g L^{-1} of both coagulants to obtain a final As$_T$ concentration $\leq$ 0.01 mg L^{-1}. This implies that an Al:As MR = 22:1 and an Fe:As MR = 23:1 were necessary to achieve an adequate removal of the contaminant, in agreement with the range reported by other authors for the removal of As(V) with FeCl$_3$ [75,76].

Although other iron-bearing coagulants, such as FeSO$_4$ or Fe$_2$(SO$_4$)$_3$, may be used, literature reports indicate that, for the treatment of As(V), ferric sulfate is as efficient as FeCl$_3$ [75]. Regarding Fe(II) compounds, there are discrepancies between the authors [75,77]. On the other hand, the study of the effect of pH indicates that the removal of As(V) with FeCl$_3$ is more efficient at pH between 7 and 8 [75]. Basically, no difference is expected at pH > 4.7. The kinetics of Fe(II) oxidation to Fe(III) by O$_2$ is very fast [78].

Regarding the removal of As(III), Table 3 shows that Al$_2$(SO$_4$)$_3$ is not efficient, as previously reported by other authors (e.g., [76]). On the other hand, FeCl$_3$ was efficient in removing As(III), although the dose required is at least twice the used for As(V), as reported before [76,79,80]. It can be concluded that FeCl$_3$ is a more efficient coagulant than Al$_2$(SO$_4$)$_3$ for removing As [58,76,81–83].

3.4. Removal of As(V) and As(III) with Clay

Results of experiments of As(V) removal with the Misiones natural clay in batch are shown in Figures 5 and 6.
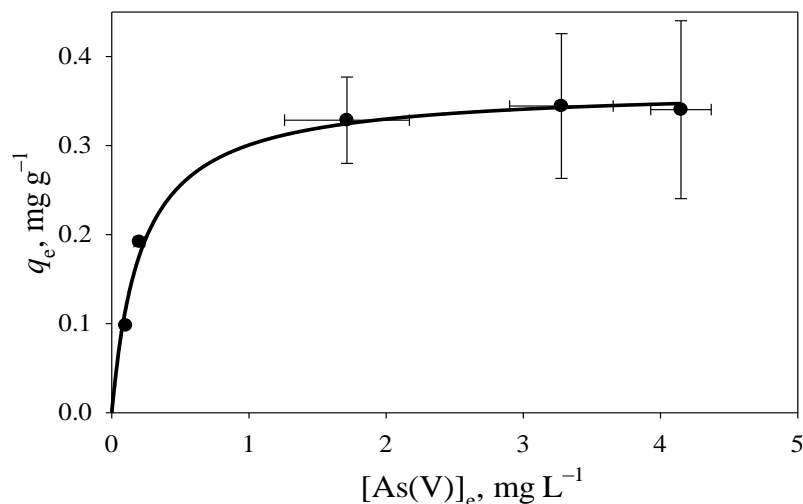
Figure 5. Adsorption equilibrium of As(V) on the clay. Conditions: [As(V)] = 5 mg L^{-1}, pH 7, [clay] = 2.5–50 g L^{-1}, RT, EC = 0.03 mS cm^{-1}. Error bars represent the standard deviation between duplicates, while the full line is the adjustment to Equation (5).
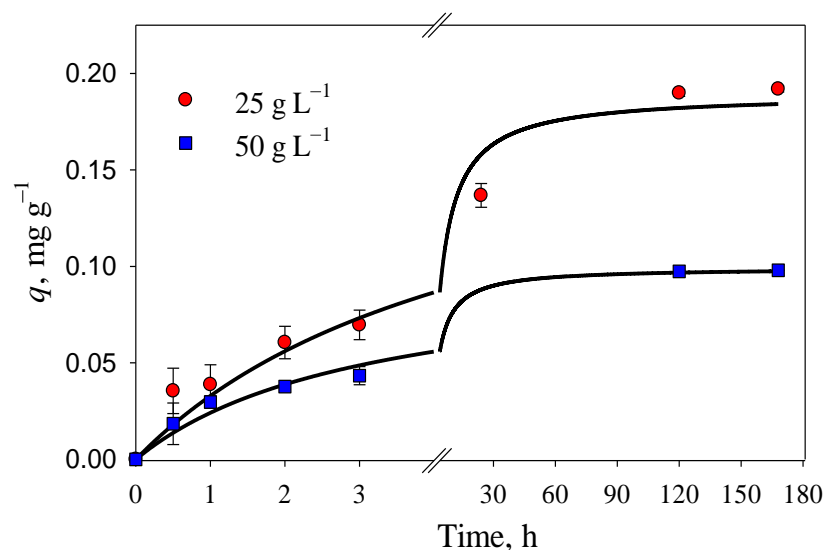

Figure 6. Adsorption kinetics of As(V) on the clay. Conditions: [As(V)] = 5 mg L^{-1}, pH 7, [clay] = 25 or 50 g L^{-1}, RT, EC = 0.03 mS cm^{-1}. Error bars represent the standard deviation between duplicates, while the full line is the adjustment to Equation (6).

In Figure 5, [As(V)]$_e$ is the equilibrium concentration of As(V) in solution, and q_e is the equilibrium surface concentration of As(V) over the clay. Both values were obtained from Equation (4), where q is the As(V) surface concentration, m is the mass of the clay, and V is the reaction volume. As usually found for As removal with Fe-based adsorbents [27], the relationship between [As(V)]$_e$ and q_e fits rather well in the Langmuir model (Equation (5), $R^2 = 0.98$), where the maximum adsorption capacity q_{max} (0.37 $\pm$ 0.01 mg As g^{-1}), and the equilibrium constant K (4.7 $\pm$ 0.7 mg^{-1} L) are in the same order of the values reported for the adsorption of As(V) on another clay from Misiones (q_{max} = 2.0 mg As g^{-1}, K = 0.54 mg^{-1} L) [65]. The values of q_{max} are similar to other values reported for the adsorption of As(V) in clays [59].

$$q = \frac{([As(V)]_0 - [As(V)]_t) \times V}{m} \tag{4}$$

$$q_e = q_{max} \frac{K \times [\text{As(V)}]_e}{1 + K \times [\text{As(V)}]_e} \tag{5}$$

$$q = \frac{k_c \times q_e^2 \times t}{1 + k_c \times q_e \times t} \tag{6}$$

The kinetic analysis was only performed for the two highest concentrations, 25 g L^{-1} and 50 g L^{-1}, because these doses allowed to reach the lowest As(V) final concentrations. The results are shown in Figure 6.

As in other similar studies [60], a good fit to a pseudo-second-order model (Equation (6), $R^2 \geq 0.97$) was obtained. The corresponding parameters were $q_e = 0.19 \pm 0.01$ mg As g^{-1} and k_c (kinetic constant) $= 1.14 \pm 0.18$ mg g^{-1} h^{-1}, and 0.100 ± 0.001 mg As g^{-1} and 3.24 ± 0.36 mg g^{-1} h^{-1} for [clay] = 25 g L^{-1} and 50 g L^{-1}, respectively. The values of k_c indicate a low rate of adsorption of As(V) on the clay [59–61].

Figure 7 shows the results of the adsorption kinetics of As(III) on the clay under the same conditions of As(V) (Figure 6).
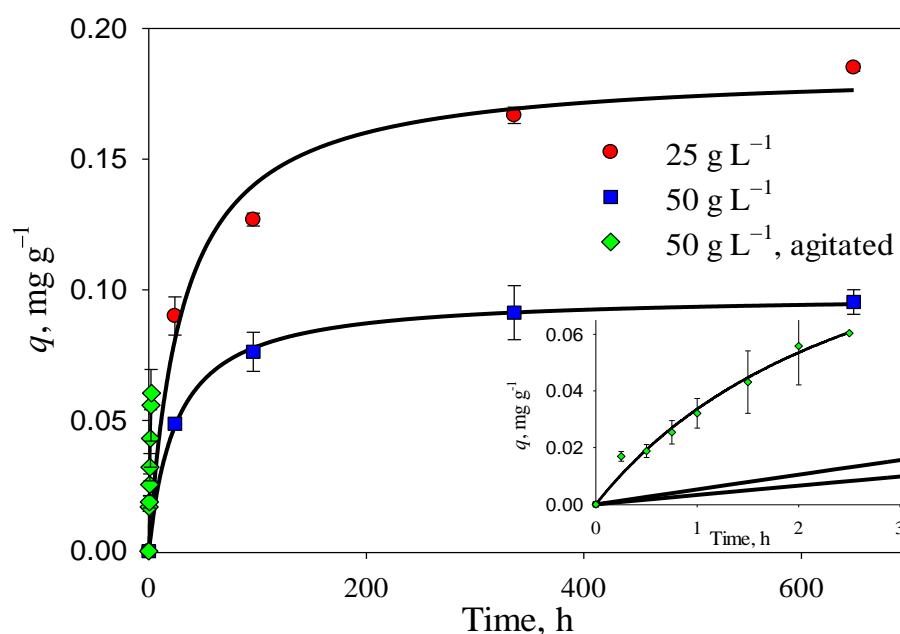

Figure 7. Kinetics of adsorption of As(III) on the clay, with and without orbital agitation. Conditions: [As(III)] = 5 mg L^{-1}, pH 7, [clay] = 25 g L^{-1} or 50 g L^{-1}, RT, EC = 0.03 mS cm^{-1}, agitation 0 rpm or 100 rpm. Full lines: adjustment to Equation (6). Inset: zoom-in to the first 3 h of reaction.

The adsorption kinetics also fits Equation (6) very well ($R^2 \geq 0.98$), with $q_e = 0.18 \pm 0.01$ mg As g^{-1} and $k_c = 0.174 \pm 0.018$ mg g^{-1} h^{-1} for [clay] = 25 g L^{-1}, and $q_e = 0.098 \pm 0.001$ mg As g^{-1} and $k_c = 0.40 \pm 0.02$ mg As g^{-1} h^{-1} for [clay] = 50 g L^{-1}; for the calculation of q, [As(V)] was replaced by [As$_T$] in Equation (4). The values of q_e are practically identical for As(V) and As(III), but the rate is noticeably slower for As(III). Under agitation, the speed increases markedly, as shown in the inset of Figure 7 (only for 50 g L^{-1}), and the adsorption kinetics also fits very well Equation (6), with $R^2 = 0.98$, $q_e = 0.13 \pm 0.03$ mg As g^{-1} and $k_c = 2.64 \pm 0.3$ mg g^{-1} h^{-1}. The stirring produces a 33% increase in q_e and 660% in k_c, indicating that this factor causes a higher impact on the removal rate rather than on the capacity of the material; in fact, the value of q_{max} obtained at 150 min of reaction (0.06 mg As g^{-1}) is less than half the value of q_e.

Figure S1 shows the evolution of the As(III) decay and the formation and decay of As(V) by treatment with the clay under the conditions of Figure 7. It is noticed that there is a partial oxidation to As(V), as its presence in solution was detected simultaneously with

As(III). The concentration of As(V) was, for both clay concentrations, 0.15 mg L^{-1} at 24 h, and between 0.05 g L^{-1} and 0.07 mg L^{-1} at longer times.

As a general conclusion, long times and a high amount of material are required for As(V) and As(III) removal with clay at these high As concentrations, being the adsorption process faster for As(V) than for As(III).

3.5. Comparison between the Technologies

Removal of As(III) using Fe(0), the clay and a mixture of both reagents were compared, and the results (as As$_T$) are presented in Figure 8. As(III) was chosen for the comparison because, as stated in the Introduction and observed in the previous sections, it is the most resilient As species to the treatments. As can be seen, 1 g L^{-1} of μFe(0) is enough to produce a very good removal in around 200 h of contact (ca. 8 days). The use of the clay is not appropriate, even in large amounts, and the total removal is achieved only after more than 600 h (ca. 25 days). The addition of the clay does not produce any significant improvements in the efficiency of μFe(0); in fact, the kinetic parameters of a pseudo-first-order kinetics are virtually identical with and without the clay (see Table S3). However, for a longer run, the clay will sustain the efficiency of the system by delaying material cementation as generated iron oxides cover the clay surface.
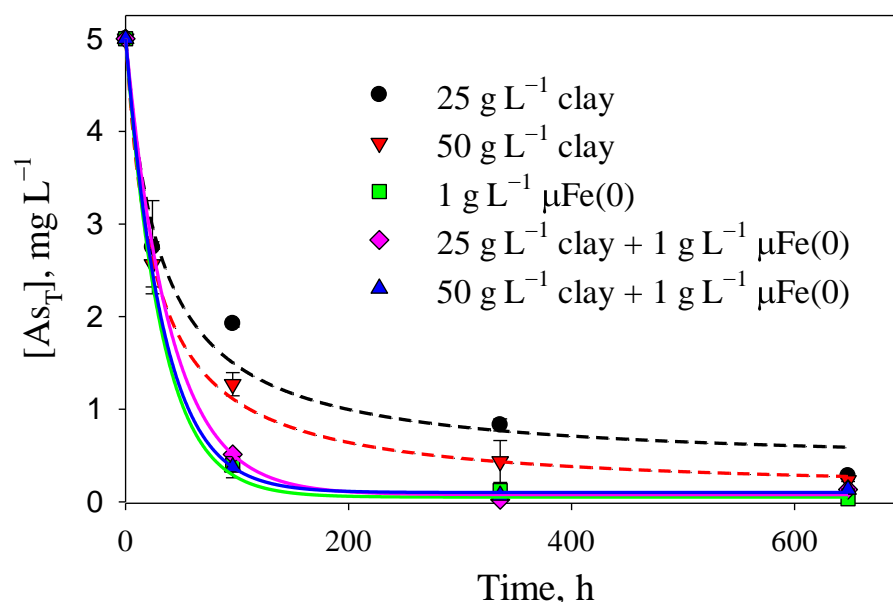

Figure 8. Total arsenic removal ([As$_T$]) with the clay, μFe(0) and the combination of the clay and μFe(0) starting from As(III) solutions. Conditions: [As(III)]$_0$ = 5 mg L^{-1}, pH 7, RT, EC = 0.03 mS cm^{-1}, no stirring. Error bars represent the standard deviation between duplicates, while the full lines are the adjustment to a pseudo-first-order kinetics with Equation (3), and the dashed lines are the fittings to Equation (6), with [As$_T$] values calculated from *q* using Equation (4).

Table 4 compares the different technologies studied in the present work according to the minimum dose of reagent, reaction time, and Fe:As or Al:As MR required to completely remove As(III) or As(V).

Table 4. Comparison between the different technologies studied for the removal of As(V) and As(III) from synthetic solutions. Conditions: [As(V)] or [As(III)] = 5 mg L^{-1}, pH 7 (constant), RT, EC = 0.03 mS cm^{-1}.

Experiment	Minimum Dose (g L^{-1})	t_R (h)	As:Fe or As:Al MR
As(V), μFe(0)	0.25	288	1:67
As(V), μFe(0) [a]	0.25	168	1:67
As(III), μFe(0)	1	>648	1:268
As(V), wFe(0)	2.50	168	1:670
As(V), $Al_2(SO_4)_3$	0.25	0.25	1:22
As(III), $Al_2(SO_4)_3$	>5.00	ND	>1:438
As(V), $FeCl_3$	0.25	0.25	1:23
As(III), $FeCl_3$	0.50	0.25	1:46
As(V), clay	50	>168	—
As(III), clay	50	>648	—

Note: [a]: under stirring; ND: not determined.

It can be seen that, for both μFe(0) and coagulants, the minimum dose needed to completely remove 5 mg L^{-1} of As(V) is 0.25 g L^{-1}, but the advantage of the use of coagulants is the shorter reaction time needed, and that they generate a smaller amount of residues because a low MR is used. However, the coagulants have the disadvantage that the counterions (chloride and sulfate, respectively) remain in the treated water, increasing the EC. Moreover, a continuous addition of the reagents to the solution and a sedimentation/filtration step is required, making the process too complex for simple household systems. Another reason for the use of Fe(0) immobilized in a reactive filter media over a $FeCl_3$-based coagulation system is that As(V)/As(III) adsorption/coprecipitation by Fe(0) and its corrosion products can retain a higher amount of As. This is because with Fe(0) the corrosion products are in equilibrium with the high As initial concentration, while coagulants would be in equilibrium with the lower As final concentration [76], as supported by Baker many years ago [84,85]. Indeed, Banerji and Chaudhari reported that MR as low as 1:20 can be used for efficient As removal with Fe(0) [86].

3.6. Stability of As Retained in the Clay and in Fe(0)

The stability of As retained in μFe(0) in the clay and in the μFe(0)/clay mixture at the end of the experiments, as shown in Figure 8, were studied according to the procedure described in Section 2.4. This is an aspect not often studied in the literature. The values of q were calculated using Equation (4) and, from these values, As_T concentration at the end of those experiments was obtained. Table 5 shows the percentage of As_T leached after the contact of the recovered solid with water.

Table 5. Percentage of leachate of As_T after the contact with water for 14 days of the solids recovered from experiments of As(III) removal with μFe(0), the clay, and their combination. Conditions of the initial experiments of Figure 8.

Material	Dose (g L^{-1})	q (mg As g^{-1})	[As(III)] In the Leachate (mg L^{-1})	[As(V)] In the Leachate (mg L^{-1})	% As_T Leached
μFe(0)	1	5	0.007	0.119	0.063
clay	25	0.2	0.028	0.091	1.49
clay	50	0.1	0.007	0.119	3.15
clay/μFe(0)	25/1	0.192	0.021	0.084	1.36
clay/μFe(0)	50/1	0.098	0.028	0.076	2.67

The leaching in water represents the fraction of As that is readily available [87], and correspondingly, the most dangerous from an environmental point of view. Although As(III) and As(V) concentrations in the leachate are similar when using 1 g L^{-1} μFe(0) and 50 g L^{-1} clay, the percentage of As in the residue is much higher in the case of μFe(0)

because the mass of μFe(0) used is much lower than the mass of clay with a corresponding lower leached fraction. Moreover, the addition of μFe(0) to the clay causes the percentage of the leachate to decrease. This is an additional reason to choose μFe(0) over clay as the adsorbent, as it presents a higher As removal capacity (*q*), and retains As more strongly (lower percentage of As leached). It should also be noted that, in all cases, As(III) is partially oxidized to As(V) in the removal process either with clay, μFe(0) or with the mixture. In contrast, Bretzler et al. [88] reported that As(V) retained in Fe(0)/sand columns did not leach out when water flowed through, and Kanel and Choi [73] also reported no As(III) leaching from ZVI after 14 days in contact with water. Nevertheless, the concentration of As_T in the leachate in the present work is well below the 1 mg L^{-1} of As_T limit set by the Argentine legislation for dangerous wastes [87].

3.7. Suitability of Fe(0) Technology

After testing several materials that include two Fe(0) materials under various experimental conditions (including mixing speeds), it has been concluded that a well-characterized ZVI can be the best material for decentralized solutions [86,89,90]. Coagulation and adsorption are rapid technologies, but Fe(0) implies both adsorption and local coagulation (coprecipitation). This obviously conciliates previous reports that have in principle disqualified ZVI evaluated under the same conditions of other materials (e.g., [91]). Other works recommend ZVI compared with other materials [92–97].

From the point of view of the authors of the present work, the solution is to consider ZVI as an independent variable in designing related systems, as suggested recently by Yang et al. [98,99].

4. Conclusions

Three methods for As removal (5 mg L^{-1} at pH 7) were compared: (1) Fe(0) in two forms, μFe(0) and wFe(0); (2) coagulation-flocculation with $Al_2(SO_4)_3$ or $FeCl_3$; and (3) treatment by adsorption on a natural clay. The results indicate that the removal of As(V) using the Fe(0) materials without stirring is relatively slow and 288 h (12 days) were needed for a complete removal ([As] < 10 μg L^{-1}) when using 0.25 g L^{-1} of μFe(0), the minimal dose of this material. By stirring or using pre-oxidized μFe(0), the removal is improved, allowing a complete removal in 168 h (7 days). At pH 9 with agitation, the removal of As(V) was slower than at pH 7, being necessary 9 days to achieve an [As(V)] < 10 μg L^{-1}.

The removal kinetics of As(V) with both Fe(0) materials could be adjusted to a pseudo-first-order kinetics. When starting from As(III) (5 mg L^{-1}, pH 7), despite with the use of a μFe(0) dose four times higher than the minimal one determined for As(V), complete As removal could not be obtained even after 648 h (27 days); partial As(III) oxidation to As(V) was also observed.

Regarding experiments with coagulants-flocculants at pH 7, 0.25 g L^{-1} of $Al_2(SO_4)_3$ or $FeCl_3$ was required to remove As(V) to a final concentration $\leq$ 10 μg L^{-1}. For As(III), 0.5 g L^{-1} $FeCl_3$ were needed for the complete removal and the removal was poor with $Al_2(SO_4)_3$.

In the experiments with the natural clay, a dose higher than 50 g L^{-1} was needed to achieve a complete As(V) or As(III) removal; the adsorption equilibrium of As(V) fitted the Langmuir model, and both As(V) and As(III) removal responded to a pseudo-second-order model, with a similar capacity for both As species; however, As(V) adsorption process was much faster than that of As(III).

The combination of μFe(0) and clay did not improve the As(III) removal capacity or removal rate in comparison with μFe(0) alone. The small percentage of As leached in the solution from either μFe(0), clay or μFe(0) + clay when starting from As(III) indicates that As is strongly retained in these materials, especially on μFe(0), and that As(III) is in all cases partially oxidized to As(V).

Although doses below 0.25 g L^{-1} for As(V) with both $Al_2(SO_4)_3$ and $FeCl_3$ can be used for As removal, as stated before, coagulation-flocculation was used mainly as a comparison for Fe(0) efficiency. It is important to say that ref. [24] indicates that doses

between 45 mg L^{-1} and 56 mg L^{-1} of Al$_2$(SO$_4$)$_3$ were necessary for a complete As(V) removal when starting from [As(V)]$_0$ = 0.5–1 mg L^{-1}, being the Al:As molar ratios similar to the one used here.

As identical doses are required for the complete As(V) removal, it can be concluded that μFe(0), FeCl$_3$, and Al$_2$(SO$_4$)$_3$ are equally efficient for the treatment of this As species, while for As(III) the lower dose corresponds to FeCl$_3$, followed by μFe(0). On the other hand, the natural clay used proved to be a poor material either for As(V) or As(III) removal. Although the use of Fe(0) has the disadvantage of requiring long reaction times, it does not generate changes on the EC of the treated water. Therefore, Fe(0) can be chosen as the best alternative for low-cost, small-scale applications for As removal.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15081481/s1. Section S1. Mechanism for As removal by Fe(0), Equations (S1)–(S12); Section S2. Characterization of the natural clay, Table S1. Chemical composition of natural clay; Section S3. Comparison of kinetic parameters extracted from Figure 4 from the main text, Table S2. Comparison of the kinetic parameters k, r_i, and t_R for As(III) removal with Fe(0) under oxic conditions at circumneutral pH extracted from Figure 4 with Equation (3) of the main text and data from other authors; Section S4. Kinetics of adsorption of As(III) and formation of As(V) by treatment with the clay, Figure S1: Kinetics of adsorption of As(III) and formation and adsorption of As(V) in the clay system. Conditions: [As(III)] = 5 mg L^{-1}, pH 7, [clay] = 25 g L^{-1} or 50 g L^{-1}, RT, EC = 0.03 mS cm^{-1}. Full lines correspond to the adjustment to Equation (6) of the main text, with [As(III)] calculated from Equation (4) of the main text. Dashed lines are only for better visualization and do not correspond to any fitting equation; Section S5. Comparison of technologies, Table S3. Kinetic parameters of the experimental results of As(III) removal extracted from Figure 8 with Equation (3) of the main text, with μFe(0) and with or without the addition of clay. Reference [100] is citied in the Supplementary Materials.

Author Contributions: Conceptualization: M.I.L., G.E.D.S. and J.M.M.; methodology: L.E.L., G.E.D.S., F.D.R. and J.M.M.; writing—original draft: G.E.D.S., F.D.R. and J.M.M.; writing—review and editing: M.I.L. and J.M.M.; supervision: M.I.L., G.E.D.S. and J.M.M. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data presented in this study are available on request from J.M.M. (jmeichtry@frba.utn.edu.ar).

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

References

1. Mandal, B.K.; Suzuki, K.T. Arsenic round the world: A review. *Talanta* **2002**, *58*, 201–235. [CrossRef]
2. Sharma, V.K.; Sohn, M. Aquatic arsenic: Toxicity, speciation, transformations, and remediation. *Environ. Int.* **2009**, *35*, 743–759. [CrossRef] [PubMed]
3. Ng, J.C. Environmental Contamination of arsenic and its toxicological impact on humans. *Environ. Chem.* **2005**, *2*, 146–160. [CrossRef]
4. Sen, P.; Biswas, T. Arsenic: The largest mass poisoning of a population in history. *BMJ* **2013**, *346*, f3625. [CrossRef]
5. Hughes, M.F.; Beck, B.D.; Chen, Y.; Lewis, A.S.; Thomas, D.J. Arsenic Exposure and Toxicology: A Historical Perspective. *Toxicol. Sci.* **2011**, *123*, 305–332. [CrossRef]
6. Mandal, P. An insight of environmental contamination of arsenic on animal health. *Emerg. Contam.* **2017**, *3*, 17–22. [CrossRef]
7. Kim, S.; Ryu, D.-Y. A short review of arsenic-induced toxicity. *J. Prev. Vet. Med.* **2016**, *40*, 46–52. [CrossRef]
8. ATSDR. 2022 Priority List of Hazardous Substances. Available online: https://www.atsdr.cdc.gov/SPL/index.html (accessed on 22 February 2023).
9. Litter, M.I.; Morgada, M.E.; Bundschuh, J. Possible treatments for arsenic removal in Latin American waters for human consumption. *Environ. Pollut.* **2010**, *158*, 1105–1118. [CrossRef]

10. Smedley, P.L.; Kinniburgh, D.G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568. [CrossRef]

11. Shakoor, M.B.; Nawaz, R.; Hussain, F.; Raza, M.; Ali, S.; Rizwan, M.; Oh, S.-E.; Ahmad, S. Human health implications, risk assessment and remediation of As-contaminated water: A critical review. *Sci. Total Environ.* **2017**, *601–602*, 756–769. [CrossRef] [PubMed]

12. WHO (World Health Organization). *Guidelines for Drinking-Water Quality*, 4th ed.; WHO: Geneva, Switzerland, 2011; Available online: http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf (accessed on 28 February 2023).

13. Nicolli, H.B.; Bundschuh, J.; Blanco, M.D.C.; Tujchneider, O.C.; Panarello, H.O.; Dapeña, C.; Rusansky, J.E. Arsenic and associated trace-elements in groundwater from the Chaco-Pampean plain, Argentina: Results from 100 years of research. *Sci. Total Environ.* **2012**, *429*, 36–56. [CrossRef]

14. Murcott, S. *Arsenic Contamination in the World—An International Sourcebook*; IWA Publishing: London, UK, 2012.

15. WHO. Available online: http://www.who.int/news-room/fact-sheets/detail/arsenic (accessed on 28 February 2023).

16. Bundschuh, J.; Litter, M.I.; Parvez, F.; Román-Ross, G.; Nicolli, H.B.; Jean, J.-S.; Liu, C.-W.; López, D.; Armienta, M.A.; Guilherme, L.R.; et al. One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* **2012**, *429*, 2–35. [CrossRef]

17. Goyenechea, M. Sobre la nueva enfermedad descubierta en Bell-Ville. *Rev. Med. Rosario* **1917**, *7*, 485.

18. Bardach, A.E.; Ciapponi, A.; Soto, N.; Chaparro, M.R.; Calderon, M.; Briatore, A.; Cadoppi, N.; Tassara, R.; Litter, M.I. Epidemiology of chronic disease related to arsenic in Argentina: A systematic review. *Sci. Total Environ.* **2015**, *538*, 802–816. [CrossRef] [PubMed]

19. Litter, M.I.; Ingallinella, A.M.; Olmos, V.; Savio, M.; Difeo, G.; Botto, L.; Torres, E.M.F.; Taylor, S.; Frangie, S.; Herkovits, J.; et al. Arsenic in Argentina: Occurrence, human health, legislation and determination. *Sci. Total Environ.* **2019**, *676*, 756–766. [CrossRef] [PubMed]

20. Hering, J.G.; Chen, P.-Y.; Wilkie, J.A.; Elimelech, M.; Liang, S. Arsenic removal by ferric chloride. *J. Am. Water Works Assoc.* **1996**, *88*, 155–167. [CrossRef]

21. Lenoble, V. Arsenite oxidation and arsenate determination by the molybdene blue method. *Talanta* **2003**, *61*, 267–276. [CrossRef]

22. Mohan, D.; Pittman, C.U., Jr. Arsenic removal from water/wastewater using adsorbents—A critical review. *J. Hazard. Mater.* **2007**, *142*, 1–53. [CrossRef]

23. Litter, M.I.; Sancha, A.M.; Ingallinella, A.M. *Tecnologías Económicas para el Abatimiento de Arsénico en Aguas*; CYTED Editorial: Buenos Aires, Argentina, 2010.

24. Mondal, P.; Bhowmick, S.; Chatterjee, D.; Figoli, A.; Van der Bruggen, B. Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions. *Chemosphere* **2013**, *92*, 157–170. [CrossRef]

25. Hering, J.G.; Katsoyiannis, I.A.; Theoduloz, G.A.; Berg, M.; Hug, S.J. Arsenic Removal from Drinking Water: Experiences with Technologies and Constraints in Practice. *J. Environ. Eng.* **2017**, *143*. [CrossRef]

26. Litter, M.I.; Ingallinella, A.M.; Olmos, V.; Savio, M.; Difeo, G.; Botto, L.; Torres, E.M.F.; Taylor, S.; Frangie, S.; Herkovits, J.; et al. Arsenic in Argentina: Technologies for arsenic removal from groundwater sources, investment costs and waste management practices. *Sci. Total Environ.* **2019**, *690*, 778–789. [CrossRef] [PubMed]

27. Hao, L.; Liu, M.; Wang, N.; Li, G. A critical review on arsenic removal from water using iron-based adsorbents. *RSC Adv.* **2018**, *8*, 39545–39560. [CrossRef] [PubMed]

28. Hassan, H.R. A review on different arsenic removal techniques used for decontamination of drinking water. *Environ. Pollut. Bioavailab.* **2023**, *35*, 2165964. [CrossRef]

29. Dou, X.; Li, R.; Zhao, B.; Liang, W. Arsenate removal from water by zero-valent iron/activated carbon galvanic couples. *J. Hazard. Mater.* **2010**, *182*, 108–114. [CrossRef] [PubMed]

30. Noubactep, C. *Metallic Iron for Safe Drinking Water Production*; Freiberg Online Geoscience: Freiberg, Germany, 2011; Volume 27, ISSN 1434-7512.

31. Ghauch, A. *Iron-Based Metallic Systems: An Excellent Choice for Sustainable Water Treatment*; Freiberg Online Geoscience: Freiberg, Germany, 2015; Volume 38, ISSN 1434-7512.

32. Noubactep, C. Metallic iron for environmental remediation: A review of reviews. *Water Res.* **2015**, *85*, 114–123. [CrossRef]

33. Noubactep, C.; Makota, S.; Bandyopadhyay, A. Rescuing Fe0 remediation research from its systemic flaws. *Res. Rev. Insights* **2017**, *1*, 1–8. [CrossRef]

34. Wang, X.; Zhang, Y.; Wang, Z.; Xu, C.; Tratnyek, P.G. Advances in metal(loid) oxyanion removal by zerovalent iron: Kinetics, pathways, and mechanisms. *Chemosphere* **2021**, *280*, 130766. [CrossRef]

35. Liang, F.; Wang, L.; Zhu, H.; Dong, Q.; Zhang, Y.; Liu, J.; Zhang, S.; Ye, Z.; Zhang, Y.; Zhang, X.; et al. Study on the Arsenate Removal from Raw As(V)-Rich Wastewater Using Zero-Valent Iron. *Water* **2022**, *14*, 1118. [CrossRef]

36. Mamindy-Pajany, Y.; Hurel, C.; Marmier, N.; Roméo, M. Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. *Desalination* **2011**, *281*, 93–99. [CrossRef]

37. Lackovic, J.A.; Nikolaidis, N.P.; Dobbs, G.M. Inorganic Arsenic Removal by Zero-Valent Iron. *Environ. Eng. Sci.* **2000**, *17*, 29–39. [CrossRef]

38. Farrell, J.; Wang, J.; O'Day, P.; Conklin, M. Electrochemical and Spectroscopic Study of Arsenate Removal from Water Using Zero-Valent Iron Media. *Environ. Sci. Technol.* **2001**, *35*, 2026–2032. [CrossRef]

39. Su, C.; Puls, R.W. Arsenate and arsenite removal by zerovalent iron: Kinetics, redox transformation, and implications for in situ groundwater remediation. *Environ. Sci. Technol.* **2001**, *35*, 1487–1492. [CrossRef]
40. Su, C.; Puls, R.W. Arsenate and Arsenite Removal by Zerovalent Iron: Effects of Phosphate, Silicate, Carbonate, Borate, Sulfate, Chromate, Molybdate, and Nitrate, Relative to Chloride. *Environ. Sci. Technol.* **2001**, *35*, 4562–4568. [CrossRef]
41. Melitas, N.; Wang, J.; Conklin, M.; O'Day, P.; Farrell, J. Understanding Soluble Arsenate Removal Kinetics by Zerovalent Iron Media. *Environ. Sci. Technol.* **2002**, *36*, 2074–2081. [CrossRef] [PubMed]
42. Nikolaidis, N.P.; Dobbs, G.M.; Lackovic, J.A. Arsenic removal by zero-valent iron: Field, laboratory and modeling studies. *Water Res.* **2003**, *37*, 1417–1425. [CrossRef] [PubMed]
43. Bang, S.; Korfiatis, G.P.; Meng, X. Removal of arsenic from water by zero-valent iron. *J. Hazard. Mater.* **2005**, *121*, 61–67. [CrossRef] [PubMed]
44. Lien, H.-L.; Wilkin, R.T. High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **2005**, *59*, 377–386. [CrossRef]
45. Bang, S.; Johnson, M.D.; Korfiatis, G.P.; Meng, X. Chemical reactions between arsenic and zero-valent iron in water. *Water Res.* **2005**, *39*, 763–770. [CrossRef]
46. Leupin, O.X.; Hug, S.J. Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* **2005**, *39*, 1729–1740. [CrossRef]
47. Leupin, O.X.; Hug, S.J.; Badruzzaman, A.B.M. Arsenic Removal from Bangladesh Tube Well Water with Filter Columns Containing Zerovalent Iron Filings and Sand. *Environ. Sci. Technol.* **2005**, *39*, 8032–8037. [CrossRef]
48. Sun, H.; Wang, L.; Zhang, R.; Sui, J.; Xu, G. Treatment of groundwater polluted by arsenic compounds by zero valent iron. *J. Hazard. Mater.* **2006**, *129*, 297–303. [CrossRef] [PubMed]
49. Triszcz, J.M.; Porta, A.; Einschlag, F.S.G. Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal. *Chem. Eng. J.* **2009**, *150*, 431–439. [CrossRef]
50. Giles, D.E.; Mohapatra, M.; Issa, T.B.; Anand, S.; Singh, P. Iron and aluminium based adsorption strategies for removing arsenic from water. *J. Environ. Manag.* **2011**, *92*, 3011–3022. [CrossRef] [PubMed]
51. Katsoyiannis, I.A.; Ruettimann, T.; Hug, S.J. pH Dependence of Fenton Reagent Generation and As(III) Oxidation and Removal by Corrosion of Zero Valent Iron in Aerated Water. *Environ. Sci. Technol.* **2008**, *42*, 7424–7430. [CrossRef]
52. Kanel, S.R.; Manning, B.; Charlet, L.; Choi, H. Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron. *Environ. Sci. Technol.* **2005**, *39*, 1291–1298. [CrossRef]
53. Noubactep, C. Investigating the processes of contaminant removal in Fe^0/H_2O systems. *Korean J. Chem. Eng.* **2012**, *29*, 1050–1056. [CrossRef]
54. Mondal, P.; Bhowmick, S.; Jullok, N.; Ye, W.; Van Renterghem, W.; Berghe, S.V.D.; Van der Bruggen, B. Behavior of As(V) with $ZVI–H_2O$ System and the Reduction to As(0). *J. Phys. Chem. C* **2014**, *118*, 21614–21621. [CrossRef]
55. Voegelin, A.; Kaegi, R.; Frommer, J.; Vantelon, D.; Hug, S.J. Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **2010**, *74*, 164–186. [CrossRef]
56. Gheju, M.; Balcu, I. Effect of Sand Co-Presence on Cr^{VI} Removal in Fe^0-H_2O System. *Water* **2023**, *15*, 777. [CrossRef]
57. Song, P.; Yang, Z.; Zeng, G.; Yang, X.; Xu, H.; Wang, L.; Xu, R.; Xiong, W.; Ahmad, K. Electrocoagulation treatment of arsenic in wastewaters: A comprehensive review. *Chem. Eng. J.* **2017**, *317*, 707–725. [CrossRef]
58. Hering, J.G.; Chen, P.-Y.; Wilkie, J.A.; Elimelech, M. Arsenic Removal from Drinking Water during Coagulation. *J. Environ. Eng.* **1997**, *123*, 800–807. [CrossRef]
59. Bentahar, Y.; Hurel, C.; Draoui, K.; Khairoun, S.; Marmier, N. Adsorptive properties of Moroccan clays for the removal of arsenic(V) from aqueous solution. *Appl. Clay Sci.* **2016**, *119*, 385–392. [CrossRef]
60. Mudzielwana, R.; Gitari, M.W.; Ndungu, P. Performance evaluation of surfactant modified kaolin clay in As(III) and As(V) adsorption from groundwater: Adsorption kinetics, isotherms and thermodynamics. *Heliyon* **2019**, *5*, e02756. [CrossRef]
61. Bundschuh, J.; Litter, M.; Ciminelli, V.S.; Morgada, M.E.; Cornejo, L.; Hoyos, S.G.; Hoinkis, J.; Alarcón-Herrera, M.T.; Armienta, M.A.; Bhattacharya, P. Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Latin America—A critical analysis. *Water Res.* **2010**, *44*, 5828–5845. [CrossRef] [PubMed]
62. Claesson, M.; Fagerberg, J. Arsenic in Groundwater of Santiago del Estero—Sources, Mobility Patterns and Remediation with Natural Materials. MScThesisTRITA-LWREX-03-05. Master's Thesis, Department of Land and Water Research Engineering, KTH, Stockholm, Sweden, 2003.
63. Bundschuh, J.; Bhattacharya, P.; Sracek, O.; Mellano, M.F.; Ramírez, A.E.; Storniolo, A.D.R.; Martín, R.A.; Cortés, J.; Litter, M.; Jean, J.-S. Arsenic removal from groundwater of the Chaco-Pampean Plain (Argentina) using natural geological materials as adsorbents. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2011**, *46*, 1297–1310. [CrossRef] [PubMed]
64. Hergenreder, M.B.; Pereyra, F.N. Estudios Preliminares para la Remoción de Arsénico en Aguas Subterráneas Utilizando Mé-todos de Adsorción. *Rev. Tecnol. Cienc.* **2018**, *32*, 219–224.
65. Boglione, R.; Griffa, C.; Panigatti, M.C.; Keller, S.; Schierano, M.C.; Asforno, M. Arsenic adsorption by soil from Misiones province, Argentina. *Environ. Technol. Innov.* **2018**, *13*, 30–36. [CrossRef]
66. Meichtry, J.M.; Castiglia, M.D.; Mugrabi, F.; Lan, L.E.; Reina, F.D.; De Seta, G.E.; López, A.R.; Domingo, E. Removal of arsenic in water by low-cost materials and safe final disposal. *Proyecciones* **2015**, *13*, 47–58.

67. Levy, I.K.; Mizrahi, M.; Ruano, G.; Zampieri, G.; Requejo, F.G.; Litter, M.I. TiO$_2$-Photocatalytic Reduction of Pentavalent and Trivalent Arsenic: Production of Elemental Arsenic and Arsine. *Environ. Sci. Technol.* **2012**, *46*, 2299–2308. [CrossRef]

68. Roy, S.; Bose, P. Modeling Arsenite Adsorption on Rusting Metallic Iron. *J. Environ. Eng.* **2010**, *136*, 405–411. [CrossRef]

69. Eljamal, O.; Sasaki, K.; Tsuruyama, S.; Hirajima, T. Kinetic Model of Arsenic Sorption onto Zero-Valent Iron (ZVI). *Water Qual. Expo. Health* **2010**, *2*, 125–132. [CrossRef]

70. Liley, P.E.; Thomson, G.H.; Friend, D.G.; Daubert, T.E.; Buck, E. *Physical and Chemical Data, Perry's Chemical Engineering Handbook*, 7th ed.; Perry, R.H., Green, D.W., Maloney, J.O., Eds.; McGraw-Hill: New York, NY, USA, 1997; ISBN 0-07-115448-5.

71. Biterna, M.; Arditsoglou, A.; Tsikouras, E.; Voutsa, D. Arsenate removal by zero valent iron: Batch and column tests. *J. Hazard. Mater.* **2007**, *149*, 548–552. [CrossRef]

72. Rusydi, A.F. Correlation between conductivity and total dissolved solid in various type of water: A review. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *118*, 012019. [CrossRef]

73. Kanel, S.R.; Choi, H. Removal of Arsenic from Groundwater by Industrial Byproducts and Its Comparison with Zero-Valent Iron. *J. Hazard. Toxic Radioact. Waste* **2017**, *21*, 04016028. [CrossRef]

74. Trois, C.; Cibati, A. South African sands as an alternative to zero valent iron for arsenic removal from an industrial effluent: Batch experiments. *J. Environ. Chem. Eng.* **2015**, *3*, 488–498. [CrossRef]

75. Baskan, M.B.; Pala, A. Determination of arsenic removal efficiency by ferric ions using response surface methodology. *J. Hazard. Mater.* **2009**, *166*, 796–801. [CrossRef] [PubMed]

76. Lakshmanan, D.; Clifford, D.; Samanta, G. Arsenic Removal by Coagulation With Aluminum, Iron, Titanium, and Zirconium. *J. Am. Water Work. Assoc.* **2008**, *100*, 76–88. [CrossRef]

77. Roberts, L.C.; Hug, S.J.; Ruettimann, T.; Billah, M.; Khan, A.W.; Rahman, M.T. Arsenic Removal with Iron(II) and Iron(III) in Waters with High Silicate and Phosphate Concentrations. *Environ. Sci. Technol.* **2003**, *38*, 307–315. [CrossRef]

78. King, D.W.; Lounsbury, H.A.; Millero, F.J. Rates and Mechanism of Fe(II) Oxidation at Nanomolar Total Iron Concentrations. *Environ. Sci. Technol.* **1995**, *29*, 818–824. [CrossRef]

79. Kumar, P.R.; Chaudhari, S.; Khilar, K.C.; Mahajan, S. Removal of arsenic from water by electrocoagulation. *Chemosphere* **2004**, *55*, 1245–1252. [CrossRef]

80. Meng, X.; Bang, S.; Korfiatis, G.P. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Water Res.* **2000**, *34*, 1255–1261. [CrossRef]

81. Abejón, R.; Garea, A. A bibliometric analysis of research on arsenic in drinking water during the 1992–2012 period: An outlook to treatment alternatives for arsenic removal. *J. Water Process. Eng.* **2015**, *6*, 105–119. [CrossRef]

82. Scott, K.N.; Green, J.F.; Do, H.D.; McLean, S.J. Arsenic removal by coagulation. *J. Am. Water Works Assoc.* **1995**, *87*, 114–126. [CrossRef]

83. Ouzounis, K.; Katsoyiannis, I.; Zouboulis, A.; Mitrakas, M. Is the Coagulation-Filtration Process with Fe(III) Efficient for As(III) Removal from Groundwaters? *Sep. Sci. Technol.* **2015**, *50*, 1587–1592. [CrossRef]

84. Baker, M.N. Sketch of the History of Water Treatment. *J. AWWA* **1934**, *26*, 902–938. [CrossRef]

85. Baker, M.N. Ch. 13: Coagulation: Ancient and Modern. In *The Quest For Pure Water: The History of Water Purification from the Earliest Records to the Twentieth Century*, 2nd ed.; Ch. 13: Coagulation: Ancient and Modern; American Water Works Association: New York, NY, USA, 1949; pp. 299–320.

86. Banerji, T.; Chaudhari, S. A cost-effective technology for arsenic removal: Case study of zerovalent iron-based IIT Bombay arsenic filter in West Bengal. In *Water and Sanitation in the New Millennium*; Nath, K., Sharma, V., Eds.; Springer: New Delhi, India, 2017. [CrossRef]

87. De Seta, E.G.; Reina, F.D.; Mugrabi, F.I.; Lan, L.E.; Guerra, J.P.; Laburu, A.P.; Domingo, E.J.; Meichtry, J.M. Safe disposal of solid wastes generated during arsenic removal in drinking water. *Int. J. Environ. Health* **2018**, *9*, 50–65. [CrossRef]

88. Bretzler, A.; Nikiema, J.; Lalanne, F.; Hoffmann, L.; Biswakarma, J.; Siebenaller, L.; Demange, D.; Schirmer, M.; Hug, S.J. Arsenic removal with zero-valent iron filters in Burkina Faso: Field and laboratory insights. *Sci. Total Environ.* **2020**, *737*, 139466. [CrossRef]

89. Hussam, A.; Munir, A.K.M. A simple and effective arsenic filter based on composite iron matrix: Development and deployment studies for groundwater of Bangladesh. *J. Environ. Sci. Health A* **2007**, *42*, 1869–1878. [CrossRef]

90. Ndé-Tchoupé, A.I.; Konadu-Amoah, B.; Gatcha-Bandjun, N.; Hu, R.; Gwenzi, W.; Noubactep, C. Kanchan Arsenic Filters for Household Water Treatment: Unsuitable or Unsustainable? *Water* **2022**, *14*, 2318. [CrossRef]

91. Indelicato, B.M. Comparison of Zerovalent Iron and Activated Carbon for Treating Chlorinated Contaminants in Groundwater. Master's Thesis, Massachusetts Institute of Technology, Cambridge, MA, USA, 1998.

92. Morrison, S.J.; Metzler, D.R.; Dwyer, B.P. Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: Reaction progress modeling. *J. Contam. Hydrol.* **2001**, *56*, 99–116. [CrossRef] [PubMed]

93. Morrison, S.J.; Mushovic, P.S.; Niesen, P.L. Early Breakthrough of Molybdenum and Uranium in a Permeable Reactive Barrier. *Environ. Sci. Technol.* **2006**, *40*, 2018–2024. [CrossRef]

94. Allred, B.J.; Martinez, L.R.; Gamble, D.L. Phosphate Removal from Agricultural Drainage Water Using an Iron Oxyhydroxide Filter Material. *Water Air Soil Pollut.* **2017**, *228*, 240. [CrossRef]

95. Allred, B.J.; Tost, B. Laboratory comparison of four iron-based filter materials for water treatment of trace element contaminants. *Water Environ. Res.* **2014**, *86*, 2221–2232. [CrossRef] [PubMed]

96. Khan, A.H.; Rasul, S.B.; Munir, A.K.M.; Habibuddowla, M.; Alauddin, M.; Newaz, S.; Hussam, A. Appraisal of a simple arsenic removal method for ground water of Bangladesh. *J. Environ. Sci. Health A* **2000**, *35*, 1021–1041. [CrossRef]

97. Morrison, S.J.; Spangler, R.R. Chemical barriers for controlling groundwater contamination. *Environ. Prog.* **1993**, *12*, 175–181. [CrossRef]

98. Yang, H.; Hu, R.; Ndé-Tchoupé, A.I.; Gwenzi, W.; Ruppert, H.; Noubactep, C. Designing the Next Generation of Fe^0-Based Filters for Decentralized Safe Drinking Water Treatment. *Processes* **2020**, *8*, 745. [CrossRef]

99. Yang, H.; Hu, R.; Ruppert, H.; Noubactep, C. Modeling porosity loss in Fe^0-based permeable reactive barriers with Faraday's law. *Sci. Rep.* **2021**, *11*, 16998. [CrossRef] [PubMed]

100. Agazzi, A.; Pirola, C. Fundamentals method and future trends of environmental microwave sample preparation. *Microchem. J.* **2000**, *67*, 337–341. [CrossRef]