

Opinion

Conceptualizing the Fe⁰/H₂O System: A Call for Collaboration to Mark the 30th Anniversary of the Fe⁰-Based Permeable Reactive Barrier Technology

Viet Cao ¹, Omari Bakari ², Joseline Flore Kenmogne-Tchidjo ³, Nadège Gatcha-Bandjun ⁴, Arnaud Igor Ndé-Tchoupé ⁵, Willis Gwenzi ⁶, Karoli N. Njau ² and Chicgoua Noubactep ^{2,5,7,8,9,*}

¹ Faculty of Natural Sciences, Hung Vuong University, Nguyen Tat Thanh Street, Viet Tri 35120, Phu Tho, Vietnam

² Department of Water and Environmental Science and Engineering, Nelson Mandela African Institution of Science and Technology, Arusha P.O. Box 447, Tanzania

³ Department of Chemistry, Faculty of Sciences, University of Yaoundé I, Yaoundé P.O. Box 812, Cameroon

⁴ Faculty of Science, Department of Chemistry, University of Maroua, Maroua P.O. Box 46, Cameroon

⁵ School of Earth Science and Engineering, Hohai University, Fo Cheng Xi Road 8, Nanjing 211100, China

⁶ Grassland Science and Renewable Plant Resources, Faculty of Organic Agricultural Science, University of Kassel, Steinstrasse 19, D-37213 Witzenhausen, Germany

⁷ Centre for Modern Indian Studies (CeMIS), Universität Göttingen, Waldweg 26, D-37073 Göttingen, Germany

⁸ Department of Applied Geology, University of Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany

⁹ Faculty of Science and Technology, Campus of Banekane, Université des Montagnes, Bangangté P.O. Box 208, Cameroon

* Correspondence: cnoubac@gwdg.de; Tel.: +49-0049-551-3933191



Citation: Cao, V.; Bakari, O.;

Kenmogne-Tchidjo, J.F.;

Gatcha-Bandjun, N.; Ndé-Tchoupé,

A.I.; Gwenzi, W.; Njau, K.N.;

Noubactep, C. Conceptualizing the

Fe⁰/H₂O System: A Call for

Collaboration to Mark the 30th

Anniversary of the Fe⁰-Based

Permeable Reactive Barrier

Technology. *Water* **2022**, *14*, 3120.

<https://doi.org/10.3390/w14193120>

Academic Editor: Alexandre

T. Paulino

Received: 4 September 2022

Accepted: 27 September 2022

Published: 3 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: Science denial relates to rejecting well-established views that are no longer questioned by scientists within a given community. This expression is frequently connected with climate change and evolution. In such cases, prevailing views are built on historical facts and consensus. For water remediation using metallic iron (Fe⁰), also known as the remediation Fe⁰/H₂O system, a consensus on electro-chemical contaminant reduction was established during the 1990s and still prevails. Arguments against the reductive transformation concept have been regarded for more than a decade as ‘science denial’. However, is it the prevailing concept that denies the science of aqueous iron corrosion? This article retraces the path taken by our research group to question the reductive transformation concept. It is shown that the validity of the following has been questioned: (i) analytical applications of the arsenazo III method for the determination of uranium, (ii) molecular diffusion as sole relevant mass-transport process in the vicinity of the Fe⁰ surface in filtration systems, and (iii) the volumetric expansive nature of iron corrosion at pH > 4.5. Item (i) questions the capability of Fe⁰ to serve as an electron donor for U^{VI} reduction under environmental conditions. Items (ii) and (iii) are inter-related, as the Fe⁰ surface is permanently shielded by a non-conductive oxide scale acting as a diffusion barrier to dissolved species and a barrier to electrons from Fe⁰. The net result is that no electron transfer from Fe⁰ to contaminants is possible under environmental conditions. This conclusion refutes the validity of the reductive transformation concept and calls for alternative theories.

Keywords: disinformation; interdisciplinarity; science denial; scientific evidence; water treatment; zero-valent iron

“In the sciences, people quickly come to regard as their own personal property that which they have learned and had passed on to them at the universities and academies. If someone else comes along with new ideas that contradict the Credo and in fact even threaten to overturn it, then all passions are raised against this threat and no method is left untried to suppress it. People resist it in every way possible: pretending not to have heard about it; speaking disparagingly of it, as if it were not even worth the effort of looking into

the matter. And so a new truth can have a long wait before finally being accepted.” Johann Wolfgang von Goethe (28 August 1749–22 March 1832).

1. Introduction

Water pollution has become a serious concern worldwide, as various discharges from agricultural, domestic, and industrial activities are sources and vectors of pollutants [1,2]. The quest for safe drinking water and a clean environment has motivated the use of metallic iron (Fe^0) in water remediation [3,4]. Although Fe^0 has been industrially used for water treatment for some 170 years [5–11], research on using Fe^0 for water treatment boomed only after 1990, and following the advent of Fe^0 -based subsurface permeable reactive barriers (Fe^0 PRBs) for groundwater remediation [12–14]. In particular, in 1990, Reynolds et al. [15] fortuitously found that Fe^0 -based sampling vessels eliminated trichloroethylene and other halogenated hydrocarbons from polluted groundwater [16–18]. This observation coincided with an active search for appropriate materials to realize the concept of subsurface reactive walls presented during the 1980s [18,19]. After some five years (1994–1998) of controversial discussion on the mechanisms of the reductive degradation of organics and reductive precipitation of inorganics in $\text{Fe}^0/\text{H}_2\text{O}$ systems [13,20–29], a consensus was reached on the electro-chemical nature of these reductive transformations [14] (Table 1).

Table 1. Outline of relevant arguments given to justify the process of contaminant removal using $\text{Fe}^0/\text{H}_2\text{O}$ systems up to the “broad consensus” in 1998 [14].

Article	Objectives	Contaminants of Concern	Conclusion	Important Remarks
Gillham and O’Hannesin [12]	Assess the suitability of Fe^0 for the dehalogenation of 14 chlorinated methanes, ethanes, and ethenes (RCl).	CT; TCM; DCM; TBM; HCA; PCE; TCE; trans-DCE; cis-DCE; DCE; VC; 1,1,2,2-TECA; 1,1,1,2-TECA; and 1,1,1-TCA	Dehalogenation of RCl by Fe^0 occurs probably via direct reduction.	Study focused on contaminant removal. Little attention was paid to the actual mechanisms.
Lipczynska-Kochany et al. [27]	Investigate of the effect of acidification on the dehalogenation kinetics of carbon tetrachloride (RCl) by Fe^0 , and contribute to understanding the mechanisms of these processes.	CCl_4	Acidification enhances RCl dehalogenation by Fe^0 .	Study questioned the sustainability of direct reduction by increasing pH values.
Matheson and Tratnyek [13]	Contribute to understanding the mechanism (and kinetics) of chlorinated methanes (RCl) transformations in the presence of granular Fe^0 .	CCl_4 ; CH_3Cl ; and TCE	Dehalogenation of RCl by Fe^0 occurs mostly via direct reduction.	Reductive transformation of RCl by Fe^0 was favored.
Schreier and Reinhard [28]	Investigate the ability of Fe and Mn powders to transform some chlorinated organic compounds (RCl) under anaerobic conditions.	PCE; 1,1,1-TCA; 1,1-DCE; DCM; 1,1-DCA; and 1,4-DCB	Dehalogenation of RCl by Fe^0 occurs via direct reduction.	Study reported on a time lag prior to quantitative contaminant reduction.
Burris et al. [20]	Determine the sorption and reduction kinetics of trichloroethylene and tetrachloroethylene (RCl) with Fe^0 under anaerobic conditions.	TCE and PCE	Reduction rates are first-order, thereby indicating that the bulk of sorption occurs on non-reactive sites.	Study seeking to confirm the reductive transformation paradigm.

Table 1. Cont.

Article	Objectives	Contaminants of Concern	Conclusion	Important Remarks
Cantrell et al. [29]	Assess the suitability of Fe ⁰ to remove some selected metals from groundwater, while characterizing the reaction kinetics and relating the findings to the thermodynamics of involved redox couples.	UO ₂ ²⁺ ; MoO ₄ ²⁻ ; TcO ₄ ⁻ ; and CrO ₄ ²⁻	Metals removal by Fe ⁰ occurs partly via direct reductive precipitation.	Study conducted in analogy to Matheson and Tratnyek [13].
Warren et al. [21]	Contribute to understanding the mechanism (and kinetics) of carbon tetrachloride (RCl) dehalogenation using Fe ⁰ .	CCl ₄	Reductive dehalogenation of RCl by Fe ⁰ is mediated by hydrogen at the metal surface.	The reductive transformation paradigm was questioned.
Roberts et al. [22]	Assess whether β-elimination reactions of chlorinated ethylenes (RCl) occur in the presence of Fe ⁰ and Zn ⁰ .	DCE; trans-DCE; Cis-DCE; 1,1-DCE and VC	Dehalogenation of RCl by Fe ⁰ occurs via direct reduction.	Study conducted in analogy to Matheson and Tratnyek [13].
Weber [23]	Study the reduction of 4-aminoazobenzene by Fe ⁰ to determine whether the process is surface-mediated.	4-aminoazobenzene (4-AAB)	Reductive transformation by Fe ⁰ is a surface-mediated process with direct electron transfer from Fe ⁰ to the substrate.	Study seeking to confirm the reductive transformation paradigm.
Burris et al. [24]	Examine the sorption of chlorinated ethenes (RCl) to cast iron (Fe ⁰) surfaces to: (i) assess the generality of non-reactive sorption behavior for cast irons; (ii) determine the predominant non-reactive sorbent on the cast iron surface; (iii) determine whether sorption to cast iron adheres to Traube's rule (sorption proportional to hydrophobicity); and (iv) evaluate rate-limited sorption/desorption for the non-reactive sites.	TCE and PCE	Significant mass transfer limitations to non-reactive sorption sites exist for PCE but not for TCE.	Study seeking to confirm the reductive transformation paradigm.
Fiedor et al. [25]	Investigate the removal mechanism of soluble uranium from groundwater by Fe ⁰ .	UO ₂ ²⁺ (i.e., U ⁶⁺)	Reduction of U ⁶⁺ to U ⁴⁺ by Fe ⁰ is mediated by Fe ²⁺ or H ₂ , but the reaction is kinetically slow.	The reductive transformation paradigm was questioned.
Gu et al. [26]	Determine the effectiveness of Fe ⁰ and several adsorbent materials in removing uranium (U) from contaminated groundwater, and to investigate the rates and mechanisms that are involved in the reactions.	UO ₂ ²⁺	Uranium removal by Fe ⁰ occurs via direct reductive precipitation.	Study conducted in analogy to Matheson and Tratnyek [13].
O'Hannesin and Gillham [14]	Long-term field investigation of the suitability of granular Fe ⁰ for the in-situ degradation of dissolved chlorinated organic compounds (RCl).	TCE and PCE	Dehalogenation of RCl by Fe ⁰ is quantitative and occurs via direct reduction.	Reductive transformation of RCl by Fe ⁰ was favored and explicitly recognized as a "broad consensus".

Table 1 is by no means a 'pros and cons' list to assist any decision-making process. A pros and cons list is conventionally used to help understand both sides of an argument.

Pros are listed as arguments in favor of making a particular decision, while the cons are counter-arguments against the same decision. In Table 1, however, arguments are listed to recall the genesis of the reductive transformation concept, arguing that contaminant reduction is the cathodic reaction simultaneous to the oxidative dissolution of metallic iron (reductive transformation paradigm). In other words, the reductive transformation paradigm regards Fe^0 as a relevant reducing agent under environmental conditions [13,18]. In this context, Fe^0 is often regarded as ‘a fixed source of electrons’ for the reductive transformation of aqueous inorganic and organic contaminants [18]. Factually, this concept fails to justify the quantitative removal of microorganisms [30,31].

Sustained by the reductive transformation paradigm, the past 30 years have witnessed the application of Fe^0 -based systems for groundwater remediation [32–37]. Efficient systems for wastewater treatment [38–41] and safe drinking water supply [42–45] were also presented. Despite such an impressive record, with more than 5000 peer-reviewed articles [46,47], the Fe^0 remediation technology is still an innovative one [37,48–50]. Nonetheless, the large majority of active researchers and practitioners regard Fe^0 remediation as an established technology [33,34,51,52]. The main point of the discrepancy between the two groups is about the role of Fe^0 in removing contaminants in $\text{Fe}^0/\text{H}_2\text{O}$ systems [37,50]. Since 2007, our research group has strongly refuted the view that any electron from Fe^0 can be transferred to dissolved contaminants under field or environmentally relevant conditions. Noubactep has been considered for more than a decade as a leading “science denier”: (i) questioning scientific milestones and spreading misinformation, and (ii) “contradicting decades of scientific endeavor” just like scientists denying climate change, pandemic issues, or the theory of evolution [53–56]. Our arguments have been mostly considered as “contrarian claims” [57] as opposed to sound scientific data supporting the view that contaminant reduction is the cathodic reaction simultaneous to Fe^0 oxidation (Table 1). The following statement of a potential reviewer recently (2022) declining a manuscript submitted by Noubactep et al. at a “reputed” journal supports this negative view of the alternative concept: “You should not be sending these diatribes by Noubactep out for review. He submits variations on this paper all over the place. They mostly get rejected without review, but occasionally one slips through. They are an impenetrable mixture of about 1/3 creative critical reviewing and about 2/3 paranoid delusional nonsense. I stopped agreeing to review them almost 10 years ago” (Statement 1). This statement is just opposed to the opening quote by the German writer, pictorial artist, biologist, theoretical physicist, and polymath Johann Wolfgang von Goethe [58]. In particular, Statement 1 can be regarded as a dissuasive demonstration that it is “not even worth the effort of looking into” science denial by the submitting authors. Table 2 gives an overview of some of these ‘datribes’ from 2007 to 2022. It is seen from the titles that the prevailing concept has been constantly challenged.

Table 2. A selection of 34 articles of our research group refuting the view that Fe^0 oxidative dissolution is the anodic half-reaction coupled to contaminant reduction in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Citations stands for the number of references according to Google Scholar (Accessed on 31 August 2022).

Year	Title	Journal	Citations	Reference
2022	Metallic iron for water remediation: Plenty of room for collaboration and convergence to advance the science	Water/MDPI	2	[37]
2022	Should the term ‘metallic iron’ appear in the title of a research paper?	Chemosphere	9	[59]
2021	Metallic iron for environmental remediation: The fallacy of the electron efficiency concept	Front. Environ. Chem.	10	[50]
2021	The mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems: The burden of a poor literature review	Chemosphere	9	[60]

Table 2. Cont.

Year	Title	Journal	Citations	Reference
2020	Tracing the scientific history of Fe ⁰ -based environmental remediation prior to the advent of permeable reactive barriers	Processes/MDPI	17	[61]
2020	Metallic iron for environmental remediation: Starting an overdue progress in knowledge	Water/MDPI	23	[62]
2019	Redirecting research on Fe ⁰ for environmental remediation: The search for synergy	Int. J. Environ. Res. Public Health	13	[63]
2019	The operating mode of Fe ⁰ /H ₂ O systems: Hidden truth or repeated nonsense?	Fresenius Environ. Bull.	12	[64]
2019	Metallic iron and the dialogue of the deaf	Fresenius Environ. Bull.	19	[65]
2018	Fe ⁰ /H ₂ O systems for environmental remediation: The scientific history and future research directions	Water/MDPI	16	[66]
2018	Iron corrosion: Scientific heritage in jeopardy	Sustainability/MDPI	6	[67]
2018	Metallic iron for environmental remediation: How experts maintain a comfortable status quo	Fresenius Environ. Bull.	5	[68]
2017	Metallic iron for water treatment: Leaving the valley of confusion	Appl. Water Sci.	44	[69]
2017	Rescuing Fe ⁰ remediation research from its systemic flaws	Res. Rev. Insights	23	[70]
2016	Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray	Water/MDPI	36	[71]
2016	Research on metallic iron for environmental remediation: Stopping growing sloppy science	Chemosphere	38	[72]
2016	No scientific debate in the zero-valent iron literature	Fresenius Environ. Bull.	17	[73]
2015	Metallic iron for environmental remediation: A review of reviews	Water Res.	140	[74]
2014	Water remediation by metallic iron: Much ado about nothing—As profitless as water in a sieve?	CLEAN-Soil, Air, Water	8	[75]
2014	Flaws in the design of Fe ⁰ -based filtration systems?	Chemosphere	46	[76]
2013	Metallic iron for water treatment: Prevailing paradigm hinders progress	Fresenius Environ. Bull.	12	[77]
2013	Metallic iron for environmental remediation: Missing the ‘valley of death’	Fresenius Environ. Bull.	10	[78]
2013	Metallic iron for environmental remediation: the long walk to evidence	Corros. Rev.	19	[79]
2012	Metallic iron for environmental remediation: Back to textbooks	Fresenius Environ. Bull.	19	[80]
2011	Metallic iron for water treatment: A knowledge system challenges mainstream science	Fresenius Environ. Bull.	30	[81]
2011	Aqueous contaminant removal by metallic iron: Is the paradigm shifting?	Water SA	76	[82]
2010	On nanoscale metallic iron for groundwater remediation	J. Hazard. Mater.	70	[83]
2010	The suitability of metallic iron for environmental remediation	Environ. Progr.	78	[84]

Table 2. Cont.

Year	Title	Journal	Citations	Reference
2009	An analysis of the evolution of reactive species in Fe ⁰ /H ₂ O systems	J. Hazard. Mater.	144	[85]
2009	Fe ⁰ -based alloys for environmental remediation: Thinking outside the box	J. Hazard. Mater.	34	[86]
2009	On the validity of specific rate constants (k _{SA}) in Fe ⁰ /H ₂ O systems	J. Hazard. Mater.	18	[87]
2009	On the operating mode of bimetallic systems for environmental remediation	J. Hazard. Mater.	36	[88]
2008	A critical review on the mechanism of contaminant removal in Fe ⁰ -H ₂ O systems	Environ. Technol.	396	[89]
2007	Processes of contaminant removal in “Fe ⁰ -H ₂ O” systems revisited. The importance of co-precipitation	Open Environ. Sci.	170	[90]

Statement 1 and the relatively low attention received by our published articles (Table 2) suggest that there is a communication problem. From our perspective, the contributions were well-conceived and timely. The often claimed ‘paucity of experimental support’ for our views is not acceptable (Section 3). Our efforts to promote the hypothesis that aqueous contaminant removal in the presence of Fe⁰ occurred primarily by adsorption and co-precipitation within the oxide scale even started earlier than 2007. Table 3 presents five articles written by the corresponding author in German on the same topic. The main feature from Table 3 is that the alternative concept was known to active German researchers on Fe⁰ for water remediation, even before 2007. Moreover, one of the papers at TerraTech has even been referenced by a research group from Bern, Switzerland [91], attesting that “German papers” were internationally known. It is also surprising that even German PhD candidates have not really considered the core of our work in their literature review. To the best of our knowledge, Burghardt [92] is the sole exception, explicitly basing some reasoning on Noubactep’s PhD and related articles. From the English language papers in Table 2, the most cited, with 396 counts, is a 15-year-old critical review. Two comparative review articles from the same year have received more attention as evidenced by their number of citations: (i) Cundy et al. [93] with 722 counts, and (ii) Thiruvengkatachari et al. [94] with 422 counts. The additional burden in getting some few articles published (statement 1) suggests that the research community is not willing to test any alternative view. This sentiment was reinforced while publishing Hu et al. [50] at *Frontiers in Environmental Chemistry*. Despite the innovative open peer-review process at *Frontiers*, the initial submission was rejected twice after evaluation; only the second re-submission was positively evaluated by all invited reviewers, who accepted to endorse the publication. The whole procedure lasted for some 18 months. Two recent articles [37,50] extensively present the state-of-the-art knowledge on the view that Fe⁰ is a generator of contaminant scavengers and secondary reducing agents (e.g., Fe^{II} species, Fe^{II}/Fe^{III} species, H₂). Interested readers are referred to these open-access papers. As part of a special issue, having been invited to encourage the scientific community to pay more attention to the adsorption/co-precipitation concept, the present article retraces the path of our research group through the past 15 years. The aim is to demonstrate the relevance of the opening quote by Johann Wolfgang von Goethe [58] for the science of aqueous iron corrosion. The presentation starts with an elucidation of the Fe⁰/H₂O system and its aspects that have not been properly considered by pioneers of Fe⁰ remediation technology. Following this, the milestones of our research group are presented together with commentaries on how they were perceived, mostly by reviewers of journal articles and academic theses.

Table 3. The five articles in German (‘German papers’) refuting the reductive transformation concept and their citations according to Google Scholar (accessed on 31 August 2022). The original titles are given in the references.

Year	Title	Journal	Citations	Reference
2015	New concepts for designing experiments regarding the process of water treatment in Fe ⁰ /H ₂ O systems	Afrika and Wissenschaft	0	[95]
2007	Response to the comments by colleagues Ebert and co-authors on my articles “The end of a myth” (TerraTech 11–12/2006) and “On the operating mode of reactive walls” (TerraTech 3–4/2007)	TerraTech	1	[96]
2007	On the operating mode of reactive walls: The emergence of the view that contaminant reduction occurs at the surface of elemental iron	TerraTech	1	[97]
2006	The end of a myth: Contaminant reduction by electrons from elemental iron contradicts three centuries of corrosion research	TerraTech	4	[98]
2003	Investigations for the passive in-situ immobilization of U(VI) from water	Wissenschaftliche Mitteilungen	16	[99]

2. The Fe⁰/H₂O System

2.1. General Aspects

The treatment of polluted surface water and groundwater is a costly endeavor. The introduction of in-situ treatment technologies such as Fe⁰-based permeable reactive barriers (PRBs) has substantially reduced the costs of groundwater remediation [3]. Fe⁰ PRBs take advantage of the electro-chemical nature of aqueous iron corrosion to remove contaminants from the aqueous phase. In some cases, contaminants are transformed or degraded to less-toxic, non-toxic or immobilized chemical forms [12,13,29,100]. The current discrepancy in the Fe⁰ remediation literature stems from an insufficient analysis of the Fe⁰/H₂O systems and their related dynamics [37,50]. This section presents the Fe⁰/H₂O system and makes a holistic analysis of it.

Upon immersion in an aqueous environment, a piece of Fe⁰ is oxidized by water (H₂O or H⁺) following an electro-chemical mechanism (Equation (1)).



It is fundamental to state straight away that the reaction according to Equation (1) occurs both under anoxic (anaerobic) and oxic (aerobic) conditions. This phenomenon is published as an award-winning breakthrough which is a century old [101]. It was demonstrated by W.R. Whitney in 1903, and awarded the first Willis Rodney Whitney Award 44 years later in 1947. Even now, the Willis Rodney Whitney Award is given by the National Association of Corrosion Engineers (NACE—<https://www.corrosionpedia.com> (accessed on: 3 September 2022)) for “significant contributions to corrosion science, such as the development or improvement of a theory that provides a fundamental understanding of corrosion phenomena”. Clearly, the demonstration of W.R. Whitney advanced corrosion a century ago; it is thus strange that contrarian views have been introduced and supported for decades (Table 1) [37,50,59].

2.2. Fe^0 Corrosion under Anoxic Conditions

Under anoxic conditions (no dissolved O_2), Fe^0 is corroded by H^+ (Equation (1)) and traces of Fe^{3+} (Equation (2)).



The net result is a system with various species of Fe^{II} (e.g., FeO , $Fe(OH)_2$), Fe^{II}/Fe^{III} (e.g., Fe_3O_4), Fe^{III} (e.g., $FeOOH$) hydroxides/oxides, and H_2 . Fe^{II} species, Fe^{II}/Fe^{III} species, and H_2 are stand-alone reducing agents. There is a high density of reductive species but reduction of contaminants occurs according to a chemical mechanism, meaning that the reducing electrons are not from Fe^0 . This assertion refutes the discovery of Reynold et al. [15] and the whole consensus on which the reductive transformation concept is built (Table 1) [37,50]. Clearly, Fe^0 corrosion by water is an electro-chemical process, but contaminant-reductive transformation in the presence of iron metal (Fe^0) is a chemical reaction. This statement is indirectly supported by Burriss et al. [20,24], who arbitrarily segregated the Fe^0 surface into reactive and non-reactive sites. The same authors were the first to insist on the importance of adsorption processes for organics, beside reductive transformations. Their arguments were later supported by many other researchers, including Mantha et al. [102], Furukawa et al. [103], and Mielczarski et al. [104]. Our research group was the first to radically exclude Fe^0 from the relevant reducing agents, while regarding solid iron corrosion products as the main contaminant scavengers [82,84,89,90].

2.3. Fe^0 Corrosion under Oxidic Conditions

Under oxidic conditions (presence of O_2), Fe^0 is still corroded by H^+ (Equation (1)), but generated Fe^{2+} is instantaneously used for O_2 reduction (Equation (3)). In other words, corrosion is accelerated because Fe^{2+} (Equation (1)) is consumed for O_2 reduction (Le Chatelier's principle). Equation (3) considers the fact that, at circum-neutral pH, produced Fe^{III} species hydrolyze and precipitate [105].



Despite the abundance of O_2 , the Fe^0 surface is shielded by a non-conductive oxide scale (oxide film) acting as diffusion barrier to O_2 . The net result is that, in the vicinity of Fe^0 , the Fe^0 /oxide interface is still highly anoxic and on the exterior of the oxide scale, the oxide/water interface is highly oxidic. In other words, under external oxidic conditions, the oxide scale on Fe^0 is highly layered. The outer layers are highly oxidic, while the inner layers are highly anoxic comparable to the situation in Section 2.2. Under these conditions, redox transformations are possible, but electrons from Fe^0 are not involved. Clearly, the oxide scale is the site for contaminant redox transformations and their scavenging as well [48,81,104–106].

2.4. Dynamics of the Fe^0/H_2O System

From the pure thermodynamic perspective, Fe^0 corrosion results in Fe solid precipitates ($FeCPs$) that are contaminant scavengers. $FeCPs$ remove contaminants from the aqueous phase by two main mechanisms: (i) enmeshment during their precipitation (co-precipitation), and (ii) adsorption onto their surface. Depending on the contaminant/ $FeCP$ molar ratio, even species without affinity to $FeCPs$ can be quantitatively removed. Two particular examples are cationic methylene blue (MB) and Zn^{2+} [37,50]. Our research group has exploited these properties of MB and the simplicity of its analytical determination to develop a simple but efficient tool to characterize the reactivity of Fe^0/H_2O systems (the MB method). The MB method characterizes the extent of in-situ sand coating in a Fe^0 /sand system as iron corrodes [107,108]. In column experiments, the most reactive system is the one experiencing the earliest breakthrough [109].

The performance of a field Fe^0 PRB depends on local hydrogeochemical conditions and barrier composition (e.g., Fe^0 ratio). At the beginning of the implementation of Fe^0 PRBs during the 1990s, there was an agreement on that field performance monitoring of

contaminant level, Eh value, pH value, and permeability were needed to elucidate the operating mode and assess the potential limitations of the PRB technology. However, after two decades, published works on sustainable PRB systems still lack these before and after analyses [36,110,111]. Moreover, little or no effort was directed at characterizing the iron corrosion rate, that is, the rate at which a decrease in porosity in the reactive zone occurs, or the rate at which contaminant scavengers are generated. Clearly, the real problem of Fe⁰ PRBs resulting from the poor system analysis is that the rate at which FeCPs are produced is not known, and has even not been properly investigated [112–114]. Instead, the importance of foreign minerals (e.g., CaCO₃, MgCO₃) has been largely overemphasized, while the expansive nature of iron corrosion under aqueous conditions has been overlooked [112,114]. Even the Fe⁰ intrinsic reactivity has been poorly considered and experiments have rarely lasted for more than four months [115–117].

3. Arguments against the Reductive Transformation Concept

The reductive transformation concept was adopted by a consensual approach as discussed in Section 1 (Table 1). This is simply not acceptable in natural sciences, and in the era of advanced instrumental analysis [118–123]. Moreover, the concept has ignored many important results from mainstream corrosion science, including the seminal work of Whitney [101]. Whitney [101] was a continuation of investigations on the electro-chemical nature of metal corrosion as started in 1819 by Michael Faraday or in 1830 by Auguste de la Rive (www.icorr.org/world-corrosion-science; accessed on: 3 September 2022). More recently, the results of Whitney [101] have been independently rediscovered by several researchers, including Michael Boris Khudenko [124], who used Cu²⁺ cementation by Fe⁰ to generate Fe^{II} and H⁺ for the degradation of organics in wastewater. In other words, the reductive transformation concept is a clear distortion of the science of aqueous iron corrosion [37,50]. Clearly, it is over to the followers of this concept to demonstrate its validity. This section will present three tangible arguments against the aforementioned concept.

In the second half of the 1990s, the mechanism of U^{VI} removal by Fe⁰/H₂O systems was discussed controversially [25,26,125]. Research groups with expertise on U^{VI} interactions with iron oxides favored the view that U^{VI} could not be quantitatively reduced under field conditions [25,125]. However, somehow, “Reductive precipitation of uranium (VI) by zero-valent iron” by Gu et al. [26] has been favored by subsequent investigators and is still considered as the paper that has demonstrated the mechanism of U^{VI} removal in Fe⁰/H₂O systems. This opinion has been challenged by three articles by Noubactep et al. [126–128] who have clearly demonstrated that there is no quantitative U^{VI} removal under conditions where FeCP formation is hindered or delayed. A clear argument against the reductive precipitation concept comes from the arsenazo III method for U determination. In this method, U^{VI} is reduced to U^{IV} which forms stable complexes with arsenazo III. U^{VI} reduction occurs around pH 2.0 upon addition of HCl (6M) using granular Bi⁰ or Zn⁰ as a reducing agent [129,130]. In the early phase of the arsenazo III method, granular Fe⁰ was used as a reducing agent, but was abandoned because the reaction was not really quantitative. The question arises, why a reaction that is not quantitative at pH 2.0 (free UO₂²⁺ in solution) should become quantitative at pH values where UO₂²⁺ (U^{VI}) is not stable? At pH > 4.0, more than 90% of the initial U^{VI} concentration used by Gu et al. [26] precipitates as schoepite (UO₂(OH)₂) [126,131,132].

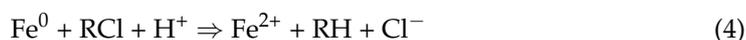
The second argument against the reductive transformation concept is physical in nature. The presentation in Section 2 has recalled that the Fe⁰ surface is permanently covered with a non-conductive layered oxide scale. It is reasoned that the oxide scale is the location of the contaminant removal and should never be altered or removed during experiments [87,90]. In the early phase of Fe⁰ investigations, these prerequisites were largely observed, for example by Matheson and Tratnyek [13] and Burris et al. [20] who just stirred their experimental vessels at 15 and 8 rpm, respectively (Table 3). However, soon after, experimental vessels were typically stirred or shaken at speeds exceeding 200 rpm (Table 4). Surprisingly, such high homogenization speeds were explicitly intended to keep

reactive particles in suspension to accelerate mass transfer. Results achieved under such conditions are inherently unrepresentative of practical or field environments. Thus, the large majority of data supporting the reductive transformation concept were obtained at mixing rates so high that no oxide scale could be generated in the vicinity of the Fe⁰ surface. The question arises, how can data obtained under undesirable conditions be used to support this concept.

Table 4. Experimental conditions of some selected studies investigating the operating mode of the Fe⁰/H₂O system in batch mode. It is seen that in the initial phase (here up to 1998) only low homogenization intensities were used; such conditions are representative of field situations.

Fe ⁰ Material		Contaminant	Volume (mL)	Homogenization		Reference
Size (mm)	Loading (g/L)			type	speed	
0.15	1.7	Chlorinated methanes	60	shaking	15	[13]
0.15	250	Halogenated aliphatics	40	Shaking	2	[12]
0.4	330	Trichloroethylene and tetrachloroethylene	15	stirring	8	[19]
<0.15	10	4-aminoazobenzene	50	shaking	-	[23]
0.01	2	Trichloromethane and trichloroethylene	2000	stirring	450 and 660	[133]
1.6–2.5	20	Uranium	20	quiescent	0	[126]
0.15	33	Nitrate	60	shaking	60	[134]
(5–8) × 10 ⁻⁵	2	Nitrate	500	stirring	200	[135]
0.315	13	Sulfate, chloride, nitrate, and bicarbonate	186	stirring	vigorous	[136]
0.6–0.425	25	Arsenite	2000	stirring	55	[137]
0.2–5	2.4	Total organic carbon	500	stirring	500 and 1000	[138]
0.25	2.5	Phosphorus	100	stirring	165	[139]

The third argument against the reductive transformation concept is also physical in nature. It is about the suitability of hybrid Fe⁰/aggregate systems. The view that Fe⁰ is at least partly oxidized by contaminants has resulted in the consideration of the stoichiometry of reactions similar to Equation (4) for the design of Fe⁰ PRBs [33,51,140,141].



Designing a PRB for the reductive transformation of RCl supposes that the more Fe⁰, the more efficient the system. Accordingly, a pure Fe⁰ filter (100% Fe⁰) should be more efficient than hybrid filters (e.g., Fe⁰/pyrite, Fe⁰/sand). Following this premise, hybrid pre-treatment zones have been tested, such that the pure filter works under perfect anoxic conditions [142–144]. However, pure Fe⁰ filters were proven efficient but not sustainable [109,145,146]. The reason for this is that columns packed with 100% Fe⁰ material left little room for solid phase expansion, because all particles are expansive. In fact, in-situ generated FeCPs that are useful for contaminant removal are equally undesirable, because they occupy the initial porosity, rendering the filter less and less permeable [112,113]. By establishing this, our research group has certainly reflected strong links between academic research and societal benefits. In particular, using this knowledge, we have presented the

most efficient household water filters and ways to improve them while extending their use to small communities [45,147].

4. Arguments against the Adsorption/Co-Precipitation Concept

The overarching goal for water remediation is to (detect and) remove toxic substances from water, where possible affordably and robustly. The adsorption/co-precipitation concept demonstrates that this objective is achieved for all biological and chemical pollutants in well-designed, case-specific Fe⁰-based treatment systems. This is because Fe⁰ acts as source of FeCPs, which are excellent contaminant scavengers. All contaminants are removed regardless of their redox reactivity [89,90,148,149]. This knowledge is very old because Fe⁰ has been used for water treatment before the advent of coagulation/filtration [1,9,11].

It may be surprising to read that no argument against the adsorption/co-precipitation concept has been presented, only skepticism, as already expressed in 2009: “Noubactep questioned the premise that Fe⁰-induced contaminant removal is initiated by the direct electron transfer from Fe⁰ to substrates and added that “the premise was already questioned and/or proven inconsistent” while citing only his own papers [80,90]. This argument is hardly acceptable, since the role of the direct electron transfer in Fe⁰-mediated reactions is well-established and generally accepted among the research community” (Statement 2) Kang and Choi [150]. The authors further blamed Noubactep for referencing only two of his papers to support the statement. It would have been better to state what is wrong with the statement. Today, reviewers still claim that we are using “non-standard, too high self-citation” while recognizing that we have been walking almost alone for more than a decade (Statement 1).

The sole pseudo-scientific argument against the adsorption/co-precipitation concept has been the quest for proofs. However, as demonstrated in the previous sections, no proofs are needed as any relevant experimental result could at best falsify the theory [151]. Yet our publications have sufficiently falsified the reductive transformation concept. With the volume of skepticism, our research group has not received any funding since 2008, that is, for 14 good years equivalent to five generations of PhD students. The lack of funding later turned to a blessing. This is because we had to work with what we could afford, and that were the conditions for the development of the low-cost methylene blue method (MB method, Section 5) [107,108].

5. Development of a New Research Tool for Fe⁰/H₂O Systems: The MB Method

The Fe⁰ PRB technology is definitively an innovative technology for groundwater remediation (Section 1) [152–155]. In innovation studies, it is crucial to properly derive the specific research methodology from the theory of the system [156,157]. In other words, it is crucial to assess how fit the methods used to answer the research question are. In our context, the common research question is: “What makes a Fe⁰-based remediation system efficient and sustainable?” The large majority of active researchers have coupled the answer to this question to the reductive potential of Fe⁰ for dissolved contaminants (e.g., chlorinated hydrocarbons, heavy metals). Accordingly, in the initial phase of the technology’s development, it was commonplace to compare the electrode potential of Fe⁰ ($E^0 = -0.44$ V) to that of dissolved species [22,158,159]. However, we are in a context where it was established long ago that no dissolved species can oxidize Fe⁰ [101,124]. These ancient works were not considered when introducing the reductive transformation theory. Not knowing these works, Noubactep argued from 2006 onwards that because so many classes of contaminants, including reducible ones (e.g., As^V, Cu^{II}, Cr^{VI}, RCl, Se^{VI}) are successfully treated in a Fe⁰/H₂O system, reduction cannot be the fundamental removal mechanism [89,90]. Results on Cr^{VI} removal in Fe⁰/H₂O systems have long falsified the reductive transformation concept [160].

In 2005, Song et al. [160] presented a mathematical model to explain why the presence of sand could enhance Cr^{VI} “reduction” by Fe⁰. The standard redox potential of the couple Cr^{VI}/Cr^{III} is 1.52 V, making Fe⁰ ($E^0 = -0.44$ V) a relevant reducing agent. However,

reduction of Cr^{VI} by Fe^{II} is also possible ($E^0 = 0.77$ V for the couple $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) and this is even well-documented [161,162]. In other words, Cr^{VI} reduction is possible by both Fe^0 and Fe^{II} . However, the question remains open, why adding sand, which was then largely considered as “ Fe^0 dilution” [143,144,163], rather than enhancing the “reduction” efficiency. The answer is given when considering that, in the Fe^0/sand system, the negatively charged sand surface is progressively coated with a positively charged oxide scale, which is good scavenger for negatively charged Cr^{VI} (chromate CrO_4^{2-}) [164]. In other words, regardless of whether Cr^{VI} is reduced to Cr^{III} or not, its quantitative removal in Fe^0/sand systems is justified by a larger adsorptive surface made available by coated sand.

Our research group has focused on ‘contaminant removal’ and not on ‘contaminant reduction’. One additional reason was that contaminant reduction is rarely a removal mechanism in the range of concentration relevant to natural waters [10,48,82]. In other words, while having the same target (efficient and sustainable $\text{Fe}^0/\text{H}_2\text{O}$ systems), the research community was not working on the same research question and that justifies the decade-old discrepancy [37,50,59]. Clearly, while using the same valid methodologies (e.g., batch tests, column experiments, structural analysis), the research question was not the same. Usually, the interested reader must assess whether the methodology used is suitable to answer the research question. The presentation herein demonstrates that the same research question was not asked, and even that it may not be worth insisting on results provided for the wrong research question (e.g., contaminant reduction by electrons from Fe^0).

As a matter of fact, different methods provide different results, and these complementary methods are used to understand the $\text{Fe}^0/\text{H}_2\text{O}$ system [118,120,164–166]. Moreover, there should be an openly explained reason for using each specific method [116,157,166]. What will each specific method reveal about the phenomenon that would otherwise remain hidden? Importantly, because the $\text{Fe}^0/\text{H}_2\text{O}$ system is a dynamic one, it should be kept in mind that all observations from the laboratory and the field are just “static snapshots” and their measurements are inaccurate [50,151]. Therefore, innovative methodologies for characterizing the dynamics of the system are highly needed [156].

The conventional approach to investigating the $\text{Fe}^0/\text{H}_2\text{O}$ system consists of characterizing the following at diverse timescales: (i) used Fe^0 materials, (ii) in-situ generated FeCPs and other mineral phases, (iii) contaminant concentration, (iv) nature and concentration of daughter products, (v) contact time, (vi) pH value, and for column experiments, (vi) changes of the hydraulic conductivity (permeability). Because of the dynamic nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system, each recorded observation is a real static snapshot and its magnitude depends on variables like Fe^0 intrinsic reactivity, proportion of Fe^0 in the reactive zone, solution chemistry and temperature. Clearly, from the measurements and observations performed, a reconstruction of the phenomena (reverse modelling) is difficult and even impossible.

To improve system characterization, our research group introduced the MB method to follow the extent of Fe^0 corrosion or the extent to which sand is coated in-situ by generated FeCPs. The MB method is rooted on the historical observation by Mitchell and colleagues that the efficiency of natural sand for MB discoloration depends on the extent to which its surface contains coated iron oxides [167]. Accordingly, if the same mass of two different Fe^0 materials is added to a given amount of sand, the more reactive system is the one producing more FeCPs (e.g., for Cr^{VI} removal, see [160]), or the one depicting the lower extent of MB discoloration. Using this simple experimental tool, impressive results have been achieved, as recently summarized by Konadu-Amoah et al. [108]. For this article, it suffices to recall that the MB method has clarified the importance of hybrid systems ($\text{Fe}^0/\text{aggregates}$) for sustainable Fe^0 filters [109]. This challenging issue has been controversially discussed in the literature for at least a decade [31,71,142,163,168,169]. The key issue has been using a small amount of Fe^0 (e.g., 100 g) and extending the contact time, for example, to more than 40 days in batch experiments and 4 months in column studies [109,170].

6. Concluding Remarks

This article is regarded as our contribution to the 30th anniversary of Fe⁰ PRB technology in 2022. It summarizes our perspective as requested by Special Issue invitation. It is certainly an expansion of some earlier ideas [37,50]. We hope to have delineated that the currently prevailing reductive transformation concept cannot enable the design of sustainable Fe⁰ filtration systems, because the issue of permeability loss cannot be solved by increasing the Fe⁰ ratio up to 100%. The way forward is to continue in the path of the adsorption/co-precipitation concept, a concept that has been around for 15 years, but has been largely ignored by active researchers. The adsorption/co-precipitation concept expresses a theory of how sustained permeability is achieved. It also advocates for a database of reactive Fe⁰ materials which, when complete, will simplify the design of non-site-specific Fe⁰/H₂O systems.

According to the viewpoints discussed in this article, the following key conclusions and perspectives are put forward:

1. operational reference Fe⁰ materials are needed to enable at least a semi-quantitative comparison of results achieved under independent conditions.
2. experiments regarding the operating mode of filtration Fe⁰/H₂O systems should be performed under diffusion-controlled conditions.
3. pure Fe⁰ filters (100% Fe⁰) are not sustainable. Thus, Fe⁰ should always be mixed with non-expansive aggregates like pumice or sand.
4. results based on the reductive transformation concept have been the cornerstone for the development of the adsorption/co-precipitation concept. Accordingly, observations and recommendations/suggestions anchored on the adsorption/co-precipitation concept should be acknowledged as valuable contributions in transferring scientific knowledge.
5. the entire environmental research community should question the validity of the view that Fe⁰ is a (strong) reducing agent under environmental conditions.
6. the MB method is a powerful tool for characterizing the dynamics of Fe⁰/H₂O systems.

Finally, we wish to thank the active Fe⁰ research community for their skepticism and some few editors/reviewers for being patient listeners to our proposal. The aforementioned skepticism has been a driving force encouraging us to mine the literature for proofs. Among the findings, the evidence that using iron filings for floc generation (e.g., flocculation) [1] was perhaps as important as the “discovery” of Whitney [101] demonstrating that H⁺ and H⁺ alone are reducing agents for Fe⁰ under environmental conditions. These two papers definitively falsified the reductive transformation concept, and thus breaking the last trace of skepticism. It is our conviction that rooting future research on the adsorption/co-precipitation concept will help provide cost-effective, robust, and sustainable Fe⁰-based water treatment systems.

Author Contributions: Conceptualization: V.C., J.F.K.-T., N.G.-B., O.B., A.I.N.-T. and C.N.; methodology: O.B., K.N.N., A.I.N.-T. and W.G.; writing—original draft: V.C., J.F.K.-T., N.G.-B., O.B., A.I.N.-T., W.G. and C.N.; writing—review and editing: V.C., J.F.K.-T., N.G.-B., A.I.N.-T., W.G. and C.N.; supervision: C.N., K.N.N. and W.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank the peer reviewers for their valuable suggestions and comments that improved this paper. Viet Cao is supported by Hung Vuong University through the project “Synthesis of Fe₃O₄/graphene oxide nanocomposite for the treatment of organic contami-

nants. The Germany Research Foundation and the Open Access Publication Funds of the Göttingen University are acknowledged for funding the open access publication.

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

References

- Baker, M.N. *The Quest for Pure Water: The History of Water Purification from the Earliest Records to the Twentieth Century*; American Water Works Assn: New York, NY, USA, 1948; p. 527.
- Howe, K.J.; Hand, D.W.; Crittenden, J.C.; Trussell, R.R.; Tchobanoglous, G. *Principles of Water Treatment*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2012; p. 674.
- Henderson, A.D.; Demond, A.H. Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environ. Eng. Sci.* **2007**, *24*, 401–423. [[CrossRef](#)]
- Guan, X.; Sun, Y.; Qin, H.; Li, J.; Lo, I.M.C.; He, D.; Dong, H. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades (1994–2014). *Water Res.* **2015**, *75*, 224–248. [[CrossRef](#)] [[PubMed](#)]
- Bischof, G. *The Purification of Water: Embracing the Action of Spongy Iron on Impure Water*; Bell and Bain: Glasgow, Scotland, 1873; p. 19.
- Devonshire, E. The purification of water by means of metallic iron. *J. Frankl. Inst.* **1890**, *129*, 449–461. [[CrossRef](#)]
- Baker, M.N. Sketch of the history of water treatment. *J. Am. Water Works Assoc.* **1934**, *26*, 902–938. [[CrossRef](#)]
- Crane, R.A.; Noubactep, C. Elemental metals for environmental remediation: Learning from hydrometallurgy. *Fresenius Environ. Bull.* **2012**, *21*, 1192–1196.
- Mwakabona, H.T.; Ndé-Tchoupé, A.I.; Njau, K.N.; Noubactep, C.; Wydra, K.D. Metallic iron for safe drinking water provision: Considering a lost knowledge. *Water Res.* **2017**, *117*, 127–142. [[CrossRef](#)]
- Gheju, M. Progress in understanding the mechanism of Cr^{VI} Removal in Fe⁰-based filtration systems. *Water* **2018**, *10*, 651. [[CrossRef](#)]
- Antia, D.D.J. Water treatment and desalination using the eco-materials n-Fe⁰ (ZVI), n-Fe₃O₄, n-Fe_xO_yH_z[mH₂O], and n-Fe_x[Cation]_nO_yH_z[Anion]_m [rH₂O]. In *Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications*; Kharissova, O.V., Ed.; Springer Nature: Basel, Switzerland, 2020; pp. 1–85. [[CrossRef](#)]
- Gillham, R.W.; O'Hannesin, S.F. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* **1994**, *32*, 958–967. [[CrossRef](#)]
- Matheson, L.J.; Tratnyek, P.G. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* **1994**, *28*, 2045–2053. [[CrossRef](#)]
- O'Hannesin, S.F.; Gillham, R.W. Long-term performance of an in situ “iron wall” for remediation of VOCs. *Ground Water* **1998**, *36*, 164–170. [[CrossRef](#)]
- Reynolds, G.W.; Hoff, J.T.; Gillham, R.W. Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.* **1990**, *24*, 135–142. [[CrossRef](#)]
- Lee, G.; Rho, S.; Jahng, D. Design considerations for groundwater remediation using reduced metals. *Korean J. Chem. Eng.* **2004**, *21*, 621–628. [[CrossRef](#)]
- Gillham, R.W. Development of the granular iron permeable reactive barrier technology (good science or good fortune). In *Advances in Environmental Geotechnics, Proceedings of the International Symposium on Geoenvironmental Engineering, Hangzhou, China, 8–10 September 2007*; Chen, Y., Tang, X., Zhan, L., Eds.; Springer: Berlin, Germany; London, UK, 2008; pp. 5–15.
- Totten, L.A.; Assaf-Anid, N.M. Abiotic Dehalogenation by Metals. In *Dehalogenation*; Häggblom, M.M., Bossert, I.D., Eds.; Springer: Boston, MA, USA, 2004. [[CrossRef](#)]
- McMurty, D.C.; Elton, R.O. New approach to in-situ treatment of contaminated groundwaters. *Environ. Progr.* **1985**, *4/3*, 168–170. [[CrossRef](#)]
- Burris, D.R.; Campbell, T.J.; Manoranjan, V.S. Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron-water system. *Environ. Sci. Technol.* **1995**, *29*, 2850–2855. [[CrossRef](#)]
- Warren, K.D.; Arnold, R.G.; Bishop, T.L.; Lindholm, L.C.; Betterton, E.A. Kinetics and mechanism of reductive dehalogenation of carbon tetrachloride using zero-valence metals. *J. Hazard. Mater.* **1995**, *41*, 217–227. [[CrossRef](#)]
- Roberts, A.L.; Totten, L.A.; Arnold, W.A.; Burris, D.R.; Campbell, T.J. Reductive elimination of chlorinated ethylenes by zero-valent metals. *Environ. Sci. Technol.* **1996**, *30*, 2654–2659. [[CrossRef](#)]
- Weber, E.J. Iron-mediated reductive transformations: Investigation of reaction mechanism. *Environ. Sci. Technol.* **1996**, *30*, 716–719. [[CrossRef](#)]
- Burris, D.R.; Allen-King, R.M.; Manoranjan, V.S.; Campbell, T.J.; Loraine, G.A.; Baolin, D. Chlorinated ethene reduction by cast iron: Sorption and mass transfer. *J. Environ. Eng.* **1998**, *124*, 1012–1019. [[CrossRef](#)]
- Fiedor, J.N.; Bostick, W.D.; Jarabek, R.J.; Farrel, J. Understanding the mechanism, of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy. *Environ. Sci. Technol.* **1998**, *32*, 1466–1473. [[CrossRef](#)]
- Gu, B.; Liang, L.; Dickey, M.J.; Yin, X.; Dai, S. Reductive precipitation of uranium (VI) by zero-valent iron. *Environ. Sci. Technol.* **1998**, *32*, 3366–3373. [[CrossRef](#)]

27. Lipczynska-Kochany, E.; Harms, S.; Milburn, R.; Sprah, G.; Nadarajah, N. Degradation of carbon tetrachloride in the presence of iron and sulphur containing compounds. *Chemosphere* **1994**, *29*, 1477–1489. [[CrossRef](#)]
28. Schreier, C.G.; Reinhard, M. Transformation of chlorinated organic compounds by iron and manganese powders in buffered water and in landfill leachate. *Chemosphere* **1994**, *29*, 1743–1753. [[CrossRef](#)]
29. Cantrell, K.J.; Kaplan, D.I.; Wietsma, T.W. Zero-valent iron for the in situ remediation of selected metals in groundwater. *J. Hazard. Mater.* **1995**, *42*, 201–212. [[CrossRef](#)]
30. You, Y.; Han, J.; Chiu, P.C.; Jin, Y. Removal and inactivation of waterborne viruses using zerovalent iron. *Environ. Sci. Technol.* **2005**, *39*, 9263–9269. [[CrossRef](#)]
31. Konadu-Amoah, B.; Hu, R.; Yang, H.; Cao, V.; Ndé-Tchoupé, A.I.; Gwenzi, W.; Ruppert, H.; Noubactep, C. Realizing the potential of metallic iron for environmental remediation: Flee or adapt? *Appl. Water Sci.* **2022**, *12*, 27. [[CrossRef](#)]
32. Warner, S.D. Two Decades of Application of Permeable Reactive Barriers to Groundwater Remediation. In *Permeable Reactive Barrier Sustainable Groundwater Remediation*; Naidu, R., Birke, V., Eds.; CRC Press: Boca Raton, FL, USA, 2015; pp. 25–39, ISBN 978-1-4822-2447-4.
33. Thakur, A.K.; Vithanage, M.; Das, D.B.; Kumar, M. A review on design, material selection, mechanism, and modelling of permeable reactive barrier for community-scale groundwater treatment. *Environ. Technol. Innov.* **2020**, *19*, 100917. [[CrossRef](#)]
34. Huang, J.; Jones, A.; Waite, T.D.; Chen, Y.; Huang, X.; Rosso, K.M.; Kappler, A.; Mansor, M.; Tratnyek, P.G.; Zhang, H. Fe(II) redox chemistry in the environment. *Chem. Rev.* **2021**, *121*, 8161–8233. [[CrossRef](#)]
35. Lanet, P.; Deluchat, V.; Baudu, M. Relevant design parameters for a reactor used in P removal with ZVI-based materials. *J. Ind. Eng. Chem.* **2021**, *104*, 8–21. [[CrossRef](#)]
36. Tao, R.; Yang, H.; Cui, X.; Xiao, M.; Gatcha-Bandjun, N.; Kenmogne-Tchidjo, J.F.; Lufingo, M.; Konadu-Amoah, B.; Tepong-Tsindé, R.; Ndé-Tchoupé, A.I.; et al. The suitability of hybrid Fe⁰/aggregate filtration systems for water treatment. *Water* **2022**, *14*, 260. [[CrossRef](#)]
37. Xiao, M.; Hu, R.; Ndé-Tchoupé, A.I.; Gwenzi, W.; Noubactep, C. Metallic iron for water remediation: Plenty of room for collaboration and convergence to advance the science. *Water* **2022**, *14*, 1492. [[CrossRef](#)]
38. Huang, Y.H.; Tang, C.; Zeng, H. Removing molybdate from water using a hybridized zero-valent iron/magnetite/Fe(II) treatment system. *Chem. Eng. J.* **2012**, *200–202*, 257–263. [[CrossRef](#)]
39. Ingram, D.T.; Callahan, M.T.; Ferguson, S.; Hoover, D.G.; Shelton, D.R.; Millner, P.D.; Camp, M.J.; Patel, J.R.; Kniel, K.E.; Sharma, M. Use of zero-valent iron biosand filters to reduce *E. coli* O157:H12 in irrigation water applied to spinach plants in a field setting. *J. Appl. Microbiol.* **2012**, *112*, 551–560. [[CrossRef](#)] [[PubMed](#)]
40. Kim, S.; Eckart, K.; Sabet, S.; Chiu, P.C.; Sapkota, A.R.; Handy, E.T.; East, C.L.; Kniel, K.E.; Sharma, M. Escherichia coli reduction in water by zero-valent iron–sand filtration is based on water quality parameters. *Water* **2021**, *13*, 2702. [[CrossRef](#)]
41. Kumar, A.; Ahammed, M.M.; Shaikh, I.N. Zero-valent iron-modified sand filters for greywater treatment. *Int. J. Environ. Sci. Technol.* **2022**. [[CrossRef](#)]
42. 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](#)]
43. 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; pp. 127–137.
44. George, D.; Ahammed, A.M. Effect of zero-valent iron amendment on the performance of biosand filters. *Water Supply* **2019**, *19*, 1612–1618. [[CrossRef](#)]
45. Tepong-Tsindé, R. Designing and piloting a household filter for the peri-urban population of Douala (Cameroon). *Freib. Online Geosci.* **2021**, *61*, 1–90.
46. Chen, Q.; Fan, G.; Na, W.; Liu, J.; Cui, J.; Li, H. Past, present, and future of groundwater remediation research: A scientometric analysis. *Int. J. Environ. Res. Public Health* **2019**, *16*, 3975. [[CrossRef](#)]
47. Li, X.; Li, Z.; Du, C.; Tian, Z.; Zhu, Q.; Li, G.; Shen, Q.; Li, C.; Li, J.; Li, W.; et al. Bibliometric analysis of zerovalent iron particles research for environmental remediation from 2000 to 2019. *Environ. Sci. Pollut. Res.* **2021**, *28*, 4200–4210. [[CrossRef](#)]
48. Ghauch, A. Iron-based metallic systems: An excellent choice for sustainable water treatment. *Freib. Online Geosci.* **2015**, *32*, 1–80.
49. Gheju, M.; Balcu, I. Sustaining the efficiency of the Fe(0)/H₂O system for Cr(VI) removal by MnO₂ amendment. *Chemosphere* **2019**, *214*, 389–398. [[CrossRef](#)] [[PubMed](#)]
50. Hu, R.; Ndé-Tchoupé, A.I.; Cao, V.; Gwenzi, W.; Noubactep, C. Metallic iron for environmental remediation: The fallacy of the electron efficiency concept. *Front. Environ. Chem.* **2021**, *2*, 677813. [[CrossRef](#)]
51. Obiri-Nyarko, F.; Grajales-Mesa, S.J.; Malina, G. An overview of permeable reactive barriers for in situ sustainable groundwater remediation. *Chemosphere* **2014**, *111*, 243–259. [[CrossRef](#)] [[PubMed](#)]
52. Naidu, R.; Birke, V. *Permeable Reactive Barrier: Sustainable Groundwater Remediation*; Taylor & Francis: Abingdon, UK; CRC Press: Boca Raton, FL, USA, 2015; p. 333, ISBN 978-1-4822-2447-4.
53. Lewandowsky, S.; Cook, J.; Lloyd, E. The ‘Alice in Wonderland’ mechanics of the rejection of (climate) science: Simulating coherence by conspiracism. *Synthese* **2018**, *195*, 175–196. [[CrossRef](#)]
54. Schmid, P.; Betsch, C. Effective strategies for rebutting science denialism in public discussions. *Nat. Hum. Behav.* **2019**, *3*, 931–939. [[CrossRef](#)]

55. Lewandowsky, S. Climate change disinformation and how to combat it. *Annu. Rev. Public Health* **2021**, *42*, 1–21. [[CrossRef](#)]
56. Houran, J. An introduction and mission of building bridges to reach the unknown. *J. Sci. Explor.* **2022**, *36*, 3–7. [[CrossRef](#)]
57. Lewandowsky, S.; Ballard, T.; Oberauer, K.; Benestad, R. A blind expert test of contrarian claims about climate data. *Glob. Environ. Chang.* **2016**, *39*, 91–97. [[CrossRef](#)]
58. Von Goethe, J.W. Conversations with Johann Peter Eckermann, 30 December 1823. Available online: www.aphorismen.de (accessed on 26 September 2022).
59. Noubactep, C. Should the term ‘metallic iron’ appear in the title of a research paper? *Chemosphere* **2022**, *287*, 132314. [[CrossRef](#)]
60. Cao, V.; Ndé-Tchoupé, A.I.; Hu, R.; Gwenzi, W.; Noubactep, C. The mechanism of contaminant removal in Fe(0)/H₂O systems: The burden of a poor literature review. *Chemosphere* **2021**, *280*, 130614. [[CrossRef](#)]
61. Cao, V.; Yang, H.; Ndé-Tchoupé, A.I.; Hu, R.; Gwenzi, W.; Noubactep, C. Tracing the Scientific History of Fe⁰-Based Environmental Remediation Prior to the Advent of Permeable Reactive Barriers. *Processes* **2020**, *8*, 977. [[CrossRef](#)]
62. Hu, R.; Yang, H.; Tao, R.; Cui, X.; Xiao, M.; Amoah, B.K.; Cao, V.; Lufingo, M.; Soppa-Sangue, N.P.; Ndé-Tchoupé, A.I.; et al. Metallic Iron for Environmental Remediation: Starting an Overdue Progress in Knowledge. *Water* **2020**, *12*, 641. [[CrossRef](#)]
63. Hu, R.; Noubactep, C. Redirecting research on Fe⁰ for environmental remediation: The search for synergy. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4465. [[CrossRef](#)] [[PubMed](#)]
64. Noubactep, C. The operating mode of Fe⁰/H₂O systems: Hidden truth or repeated nonsense? *Fresenius Environ. Bull.* **2019**, *28*, 8328–8330.
65. Ebelle, T.C.; Makota, S.; Tepong-Tsindé, R.; Nassi, A.; Noubactep, C. Metallic iron and the dialogue of the deaf. *Fresenius Environ. Bull.* **2019**, *28*, 8331–8340.
66. Hu, R.; Cui, X.; Gwenzi, W.; Wu, S.; Noubactep, C. Fe⁰/H₂O systems for environmental remediation: The scientific history and future research directions. *Water* **2018**, *10*, 1739. [[CrossRef](#)]
67. Hu, R.; Noubactep, C. Iron corrosion: Scientific heritage in jeopardy. *Sustainability* **2018**, *10*, 4138. [[CrossRef](#)]
68. Noubactep, C. Metallic iron for environmental remediation: How experts maintain a comfortable status quo. *Fresenius Environ. Bull.* **2018**, *27*, 1379–1393.
69. Makota, S.; Nde-Tchoupe, A.I.; Mwakabona, H.T.; Tepong-Tsindé, R.; Noubactep, C.; Nassi, A.; Njau, K.N. Metallic iron for water treatment: Leaving the valley of confusion. *Appl. Water Sci.* **2017**, *7*, 4177–4196. [[CrossRef](#)]
70. Noubactep, C.; Makota, S.; Bandyopadhyay, A. Rescuing Fe⁰ remediation research from its systemic flaws. *Res. Rev. Insights* **2017**, *1*, 1–8. [[CrossRef](#)]
71. Noubactep, C. Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray. *Water* **2016**, *8*, 162. [[CrossRef](#)]
72. Noubactep, C. Research on metallic iron for environmental remediation: Stopping growing sloppy science. *Chemosphere* **2016**, *153*, 528–530. [[CrossRef](#)] [[PubMed](#)]
73. Noubactep, C. No scientific debate in the zero-valent iron literature. *CLEAN Soil Air Water* **2016**, *44*, 330–332. [[CrossRef](#)]
74. Noubactep, C. Metallic iron for environmental remediation: A review of reviews. *Water Res.* **2015**, *85*, 114–123. [[CrossRef](#)] [[PubMed](#)]
75. Noubactep, C. Water remediation by metallic iron: Much ado about nothing—As profitless as water in a sieve? *CLEAN Soil Air Water* **2014**, *42*, 1177–1178. [[CrossRef](#)]
76. Noubactep, C. Flaws in the design of Fe⁰-based filtration systems? *Chemosphere* **2014**, *117*, 104–107. [[CrossRef](#)]
77. Kobbe-Dama, N.; Noubactep, C.; Tchatchueng, J.B. Metallic iron for water treatment: Prevailing paradigm hinders progress. *Fresenius Environ. Bull.* **2013**, *22*, 2953–2957.
78. Gatcha-Bandjun, N.; Noubactep, C. Metallic iron for environmental remediation: Missing the ‘valley of death’. *Fresenius Environ. Bull.* **2013**, *22*, 2632–2639.
79. Noubactep, C. Metallic iron for environmental remediation: The long walk to evidence. *Corros. Rev.* **2013**, *31*, 51–59. [[CrossRef](#)]
80. Togue-Kamga, F.; Btatkeu, K.B.D.; Noubactep, C.; Wofo, P. Metallic iron for environmental remediation: Back to textbooks. *Fresenius Environ. Bull.* **2012**, *21*, 1992–1997.
81. Noubactep, C. Metallic iron for water treatment: A knowledge system challenges mainstream science. *Fresenius Environ. Bull.* **2011**, *20*, 2632–2637.
82. Noubactep, C. Aqueous contaminant removal by metallic iron: Is the paradigm shifting? *Water SA* **2011**, *37*, 419–426. [[CrossRef](#)]
83. Noubactep, C.; Caré, S. On nanoscale metallic iron for groundwater remediation. *J. Hazard. Mater.* **2010**, *182*, 923–927. [[CrossRef](#)] [[PubMed](#)]
84. Noubactep, C. The suitability of metallic iron for environmental remediation. *Environ. Prog.* **2010**, *29*, 286–291. [[CrossRef](#)]
85. Noubactep, C. An Analysis of the Evolution of Reactive Species in Fe⁰/H₂O Systems. *J. Hazard. Mater.* **2009**, *168*, 1626. [[CrossRef](#)]
86. Noubactep, C.; Schöner, A. Fe⁰-based alloys for environmental remediation: Thinking outside the box. *J. Hazard. Mater.* **2009**, *165*, 1210–1214. [[CrossRef](#)]
87. Noubactep, C. On the validity of specific rate constants (k_{SA}) in Fe⁰/H₂O systems. *J. Hazard. Mater.* **2009**, *164*, 835–837. [[CrossRef](#)]
88. Noubactep, C. On the operating mode of bimetallic systems for environmental remediation. *J. Hazard. Mater.* **2009**, *164*, 394–395. [[CrossRef](#)]
89. Noubactep, C. A critical review on the mechanism of contaminant removal in Fe⁰-H₂O systems. *Environ. Technol.* **2008**, *29*, 909–920. [[CrossRef](#)]

90. Noubactep, C. Processes of contaminant removal in “Fe⁰–H₂O” systems revisited. The importance of co-precipitation. *Open Environ. Sci.* **2007**, *1*, 9–13. [[CrossRef](#)]
91. Flury, B.; Eggenberger, U.; Mäder, U. First results of operating and monitoring an innovative design of a permeable reactive barrier for the remediation of chromate contaminated groundwater. *Appl. Geochem.* **2009**, *24*, 687–696. [[CrossRef](#)]
92. Burghardt, D. Ermittlung Geochemischer, Geomikrobiologischer und Geotechnischer Grundlagen zur In-Situ-Immobilisierung von Arsen, Uran und Radium durch eine ‘Reaktive-Zonen’-Technologie. Ph.D. Dissertation, BTU Cottbus, Cottbus, Germany, 2006.
93. Cundy, A.B.; Hopkinson, L.; Whitby, R.L.D. Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Sci. Tot. Environ.* **2008**, *400*, 42–51. [[CrossRef](#)] [[PubMed](#)]
94. Thiruvengkatachari, R.; Vigneswaran, S.; Naidu, R. Permeable reactive barrier for groundwater remediation. *J. Ind. Eng. Chem.* **2008**, *14*, 145–156. [[CrossRef](#)]
95. Noubactep, C. Neue Konzepte zur Entwicklung einer Versuchsanordnung zur Prozessuntersuchung in Fe⁰/H₂O-Systemen. Afrika & Wissenschaft, NS2-August. 2015. Available online: <https://africa-and-science.com/?p=7323> (accessed on 3 September 2022).
96. Noubactep, C. Stellungnahme zum kommentar der kollegen Ebert und koautoren in TerraTech 7-8/07 zu meinen Beiträgen “das ende eines mythos” und “zur funktion reaktiver wände”. *TerraTech* **2007**, *9*, TT3-4.
97. Noubactep, C. Zur Funktion reaktiver Wände: Die Entstehung der Ansicht der Schadstoffreduktion an der Oberfläche des elementaren Eisens (Fe⁰). wlb Wasser, Luft und Boden, 50 (3/4). *TerraTech* **2007**, *3–4*, TT10-14.
98. Noubactep, C. Das Ende eines Mythos: Direkte Schadstoffreduktion durch elementares Eisen (Fe⁰) widerspricht drei Jahrhunderten Korrosionsforschung. *TerraTech* **2006**, *11–12*, TT11-14.
99. Noubactep, C. Untersuchungen zur Passiven In-Situ-Immobilisierung von U(VI) aus Wasser. Ph.D. Thesis, TU Bergakademie Freiberg, Freiberg, Germany, 2002. Available online: <https://katalog.ub.tu-freiberg.de/Record/0-233517979/HierarchyTree?recordID=0-233517979> (accessed on 3 September 2022).
100. Puls, R.W.; Paul, C.J.; Powell, R.M. The application of in situ permeable reactive (zero valent iron) barrier technology for the remediation of chromate-contaminated groundwater: A field test. *Appl. Geochem.* **1999**, *14*, 989–1000. [[CrossRef](#)]
101. Whitney, W.R. The corrosion of iron. *J. Am. Chem. Soc.* **1903**, *25*, 4, 394–406. [[CrossRef](#)]
102. Mantha, R.; Taylor, K.E.; Biswas, N.; Bewtra, J.K. A continuous system for Fe⁰ reduction of nitrobenzene in synthetic wastewater. *Environ. Sci. Technol.* **2001**, *35*, 3231–3236. [[CrossRef](#)]
103. Furukawa, Y.; Kim, J.-W.; Watkins, J.; Wilkin, R.T. Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron. *Environ. Sci. Technol.* **2002**, *36*, 5469–5475. [[CrossRef](#)]
104. Mielczarski, J.A.; Atenas, G.M.; Mielczarski, E. Role of iron surface oxidation layers in decomposition of azo-dye water pollutants in weak acidic solutions. *Appl. Catal. B* **2005**, *56*, 289–303. [[CrossRef](#)]
105. Roden, E.; Sobolev, D.; Glazer, B.; Luther, G.W., III. Potential for microscale bacterial Fe redox cycling at the aerobic-anaerobic interface. *Geomicrobiol. J.* **2004**, *21*, 379–391. [[CrossRef](#)]
106. Gheju, M. Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water Air Soil Pollut.* **2011**, *222*, 103–148. [[CrossRef](#)]
107. Bhatke-K., B.D.; Tchatchueng, J.B.; Noubactep, C.; Caré, S. Designing metallic iron based water filters: Light from methylene blue discoloration. *J. Environ. Manag.* **2016**, *166*, 567–573. [[CrossRef](#)] [[PubMed](#)]
108. Konadu-Amoah, B.; Ndé-Tchoupé, A.I.; Hu, R.; Gwenzi, W.; Noubactep, C. Investigating the Fe⁰/H₂O systems using the methylene blue method: Validity, applications and future directions. *Chemosphere* **2022**, *291*, 132913. [[CrossRef](#)] [[PubMed](#)]
109. Miyajima, K. Optimizing the design of metallic iron filters for water treatment. *Freib. Online Geosci.* **2012**, *32*, 1–60.
110. Wilkin, R.T.; Acree, S.D.; Ross, R.R.; Puls, R.W.; Lee, T.R.; Woods, L.L. Fifteen-year assessment of a permeable reactive barrier for treatment of chromate and trichloroethylene in groundwater. *Sci. Tot. Environ.* **2014**, *468–469*, 186–194. [[CrossRef](#)]
111. Wilkin, R.T.; Lee, T.R.; Sexton, M.R.; Acree, S.D.; Puls, R.W.; Blowes, D.W.; Kalinowski, C.; Tilton, J.M.; Woods, L.L. Geochemical and isotope study of trichloroethene degradation in a zero-valent iron permeable reactive barrier: A twenty-two-year performance evaluation. *Environ. Sci. Technol.* **2019**, *53*, 296–306. [[CrossRef](#)]
112. Caré, S.; Crane, R.; Calabrò, P.S.; Ghauch, A.; Temgoua, E.; Noubactep, C. Modeling the permeability loss of metallic iron water filtration systems. *CLEAN Soil Air Water* **2013**, *41*, 275–282. [[CrossRef](#)]
113. Domga, R.; Togue-Kamga, F.; Noubactep, C.; Tchatchueng, J.B. Discussing porosity loss of Fe⁰ packed water filters at ground level. *Chem. Eng. J.* **2015**, *263*, 127–134. [[CrossRef](#)]
114. Yang, H.; Hu, R.; Ruppert, H.; Noubactep, C. Modeling porosity loss in Fe⁰-based permeable reactive barriers with Faraday’s law. *Sci. Rep.* **2021**, *11*, 16998. [[CrossRef](#)]
115. Birke, V.; Schuett, C.; Burmeier, H.; Friedrich, H.-J. Impact of trace elements and impurities in technical zero-valent iron brands on reductive dechlorination of chlorinated ethenes in groundwater. In *Permeable Reactive Barrier Sustainable Groundwater Remediation*; Naidu, R., Birke, V., Eds.; CRC Press: Boca Raton, FL, USA, 2015; pp. 87–98. ISBN 978-1-4822-2447-4.
116. Li, J.; Dou, X.; Qin, H.; Sun, Y.; Yin, D.; Guan, X. Characterization methods of zerovalent iron for water treatment and remediation. *Water Res.* **2019**, *148*, 70–85. [[CrossRef](#)] [[PubMed](#)]
117. Lufingo, M.; Ndé-Tchoupé, A.I.; Hu, R.; Njau, K.N.; Noubactep, C. A novel and facile method to characterize the suitability of metallic iron for water treatment. *Water* **2019**, *11*, 2465. [[CrossRef](#)]

118. McGuire, M.M.; Carlson, D.L.; Vikesland, P.J.; Kohn, T.; Grenier, A.C.; Langley, L.A.; Roberts, A.L.; Fairbrother, D.H. Applications of surface analysis in the environmental sciences: Dehalogenation of chlorocarbons with zero-valent iron and iron-containing mineral surfaces. *Anal. Chim. Acta* **2003**, *496*, 301–313. [[CrossRef](#)]
119. Sadik, O.A.; Wanekaya, A.K.; Andreescu, S. Advances in analytical technologies for environmental protection and public safety. *J. Environ. Monit.* **2004**, *6*, 513–522. [[CrossRef](#)] [[PubMed](#)]
120. Halada, G.P. Complementary spectroscopic techniques to model the association of contaminant uranium with structural surfaces. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *150*, 185–194. [[CrossRef](#)]
121. Kelly, D.G.; Bennett, L.G.I.; Fill, M.M.; Mattson, K.M.; Nielsen, K.S.; White, S.D.; Allen, J.F. Analytical methods for the environmental quantification of uranium isotopes: Method of validation and environmental application. *J. Radioanal. Nucl. Chem.* **2008**, *278*, 807–811. [[CrossRef](#)]
122. Celiz, M.D.; Tso, J.; Aga, D.S. Pharmaceutical metabolites in the environment: Analytical challenges and ecological risks. *Environ. Toxicol. Chem.* **2009**, *28*, 2473–2484. [[CrossRef](#)]
123. Nödler, K.; Licha, T.; Bester, K.; Sauter, M. Development of a multi-residue analytical method, based on liquid chromatography–tandem mass spectrometry, for the simultaneous determination of 46 micro-contaminants in aqueous samples. *J. Chromat. A* **2010**, *1217*, 6511–6521. [[CrossRef](#)]
124. Khudenko, B.M. Feasibility evaluation of a novel method for destruction of organics. *Water Sci. Technol.* **1991**, *23*, 1873–1881. [[CrossRef](#)]
125. Farrell, J.; Bostick, W.D.; Jarabeck, R.J.; Fiedor, J.N. Uranium removal from ground water using zero valent iron media. *Ground Water* **1999**, *34*, 618–624. [[CrossRef](#)]
126. Noubactep, C.; Meinrath, G.; Dietrich, P.; Merkel, B. Mitigating uranium in groundwater: Prospects and limitations. *Environ. Sci. Technol.* **2003**, *37*, 4304–4308. [[CrossRef](#)] [[PubMed](#)]
127. Noubactep, C.; Meinrath, G.; Merkel, J.B. Investigating the mechanism of uranium removal by zerovalent iron materials. *Environ. Chem.* **2005**, *2*, 235–242. [[CrossRef](#)]
128. Noubactep, C.; Schöner, A.; Meinrath, G. Mechanism of uranium (VI) fixation by elemental iron. *J. Hazard Mater.* **2006**, *132*, 202–212. [[CrossRef](#)] [[PubMed](#)]
129. Savvin, S.B. Analytical use of arsenazo III: Determination of thorium, zirconium, uranium and rare earth elements. *Talanta* **1961**, *8*, 673–685. [[CrossRef](#)]
130. Savvin, S.B. Analytical applications of arsenazo III—III: The mechanism of complex formation between arsenazo III and certain elements. *Talanta* **1964**, *11*, 7–19. [[CrossRef](#)]
131. Kalin, M.; Wheeler, W.N.; Meinrath, G. The removal of uranium from mining waste water using algal/microbial biomass. *J. Environ. Radioact.* **2005**, *78*, 151–177. [[CrossRef](#)]
132. Jang, J.-H.; Dempsey, B.A.; Burgos, W.D. Solubility of Schoepite: Comparison and selection of complexation constants for U(VI). *Water Res.* **2006**, *40*, 2738–2746. [[CrossRef](#)]
133. Liao, C.-H.; Chen, I.-M.; Chang, Y.-F.; Lu, M.-C. Removal of dichloromethane and trichloroethylene by suspended zero valent iron and ultraviolet irradiation. *J. Environ. Sci. Health Part A* **2003**, *38*, 1717–1729. [[CrossRef](#)]
134. Choe, S.; Liljestrand, H.M.; Khim, J. Nitrate reduction by zero-valent iron under different pH regimes. *Appl. Geochem.* **2004**, *19*, 335–342. [[CrossRef](#)]
135. Yang, G.C.; Lee, H.-L. Chemical reduction of nitrate by nanosized iron: Kinetics and pathways. *Water Res.* **2005**, *39*, 884–894. [[CrossRef](#)] [[PubMed](#)]
136. Devlin, J.; Allin, K. Major anion effects on the kinetics and reactivity of granular iron in glass-encased magnet batch reactor experiments. *Environ. Sci. Technol.* **2005**, *39*, 1868–1874. [[CrossRef](#)] [[PubMed](#)]
137. Yu, X.; Amrhein, C.; Zhang, Y.; Matsumoto, M.R. Factors influencing arsenite removal by zero-valent iron. *J. Environ. Eng.* **2006**, *132*, 1459–1469. [[CrossRef](#)]
138. Segura, Y.; Martínez, F.; Melero, J.A. Pharmaceutical wastewater degradation: Effective and economical treatment using waste-metallic iron shavings. *Int. J. Environ. Stud.* **2014**, *71*, 200–208. [[CrossRef](#)]
139. Sleiman, N.; Deluchat, V.; Wazne, M.; Mallet, M.; Courtin-Nomade, A.; Kazpard, V.; Baudu, M. Phosphate removal from aqueous solutions using zero valent iron (ZVI): Influence of solution composition and ZVI aging. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *514*, 1–10. [[CrossRef](#)]
140. Sarr, D. Zero-valent-iron permeable reactive barriers—How long will they last? *Remediation* **2001**, *11*, 1–18.
141. Liu, H.; Wang, Q.; Wang, C.; Li, X.-z. Electron efficiency of zero-valent iron for groundwater remediation and wastewater treatment. *Chem. Eng. J.* **2013**, *215–216*, 90–95. [[CrossRef](#)]
142. Mackenzie, P.D.; Horney, D.P.; Sivavec, T.M. Mineral precipitation and porosity losses in granular iron columns. *J. Hazard. Mater.* **1999**, *68*, 1–17. [[CrossRef](#)]
143. Kenneke, J.F.; McCutcheon, S.C. Use of pretreatment zones and zero-valent iron for the remediation of chloroalkenes in an oxic aquifer. *Environ. Sci. Technol.* **2003**, *37*, 2829–2835. [[CrossRef](#)]
144. Westerhoff, P.; James, J. Nitrate removal in zero-valent iron packed columns. *Water Res.* **2003**, *37*, 1818–1830. [[CrossRef](#)]
145. Hussam, A. Contending with a development disaster: Sono filters remove arsenic from well water in Bangladesh. *Innovations* **2009**, *4*, 89–102. [[CrossRef](#)]

146. Miyajima, K.; Noubactep, C. Effects of mixing granular iron with sand on the efficiency of methylene blue discoloration. *Chem. Eng. J.* **2012**, *200–202*, 433–438. [[CrossRef](#)]
147. Tepong-Tsindé, R.; Ndé-Tchoupé, A.I.; Noubactep, C.; Nassi, A.; Ruppert, H. Characterizing a newly designed steel-wool-based household filter for safe drinking water provision: Hydraulic conductivity and efficiency for pathogen removal. *Processes* **2019**, *7*, 966. [[CrossRef](#)]
148. Phukan, M. Characterizing the Fe⁰/sand system by the extent of dye discoloration. *Freib. Online Geosci.* **2015**, *40*, 1–70.
149. Phukan, M.; Noubactep, C.; Licha, T. Characterizing the ion-selective nature of Fe⁰-based filters using azo dyes. *Chem. Eng. J.* **2015**, *259*, 481–491. [[CrossRef](#)]
150. Kang, S.-H.; Choi, W. Response to Comment on “Oxidative Degradation of Organic Compounds Using Zero-Valent Iron in the Presence of Natural Organic Matter Serving as an Electron Shuttle”. *Environ. Sci. Technol.* **2009**, *43*, 3966–3967. [[CrossRef](#)]
151. Brenner, S. Sequences and consequences. *Phil. Trans. R. Soc. B* **2010**, *365*, 207–212. [[CrossRef](#)]
152. Padervand, M.; Ghasemi, S.; Hajiahmadi, S.; Rhimi, B.; Nejad, Z.G.; Karima, S.; Shahsavari, Z.; Wang, S. Multifunctional Ag/AgCl/ZnTiO₃ structures as highly efficient photocatalysts for the removal of nitrophenols, CO₂ photoreduction, biomedical waste treatment, and bacteria inactivation. *Appl. Catal. A* **2022**, *643*, 118794. [[CrossRef](#)]
153. Heidarpour, H.; Padervand, M.; Soltanieh, M.; Vossoughi, M. Enhanced decolorization of rhodamine B solution through simultaneous photocatalysis and persulfate activation over Fe/C₃N₄ photocatalyst. *Chem. Eng. Res Design* **2020**, *153*, 709–720. [[CrossRef](#)]
154. Singh, R.; Chakma, S.; Birke, V. Performance of field-scale permeable reactive barriers: An overview on potentials and possible implications for in-situ groundwater remediation applications. *Sci. Tot. Environ.* **2022**. [[CrossRef](#)]
155. Plessl, K.; Russ, A.; Vollprecht, D. Application and development of zero-valent iron (ZVI) for groundwater and wastewater treatment. *Int. J. Environ. Sci. Technol.* **2022**. [[CrossRef](#)]
156. Noubactep, C. Investigating the processes of contaminant removal in Fe⁰/H₂O systems. *Korean J. Chem. Eng.* **2012**, *29*, 1050–1056. [[CrossRef](#)]
157. Raunio, M.; Pugh, R.; Sheikh, F.A.; Egbetokun, A. Importance of methodological diversity for innovation system studies. *Afr. J. Sci. Technol. Innov. Dev.* **2019**, *11*, 465–467. [[CrossRef](#)]
158. Johnson, T.L.; Scherer, M.M.; Tratnyek, P.G. Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.* **1996**, *30*, 2634–2640. [[CrossRef](#)]
159. Scherer, M.M.; Richter, S.; Valentine, R.L.; Alvarez, P.J.J. Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up. *Rev. Environ. Sci. Technol.* **2000**, *30*, 363–411. [[CrossRef](#)]
160. Song, D.-I.; Kim, Y.H.; Shin, W.S. A simple mathematical analysis on the effect of sand in Cr(VI) reduction using zero valent iron. *Korean J. Chem. Eng.* **2005**, *22*, 67–69. [[CrossRef](#)]
161. Gheju, M.; Balcu, I. Hexavalent chromium reduction with scrap iron in continuous-flow system. Part 2: Effect of scrap iron shape and size. *J. Hazard. Mater.* **2010**, *182*, 484–493. [[CrossRef](#)]
162. Gheju, M.; Balcu, I. Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations. *J. Hazard. Mater.* **2011**, *196*, 131–138. [[CrossRef](#)]
163. Bi, E.; Devlin, J.F.; Huang, B. Effects of mixing granular iron with sand on the kinetics of trichloroethylene reduction. *Ground Water Monit. Remed.* **2009**, *29*, 56–62. [[CrossRef](#)]
164. Kosmulski, M. Isoelectric points and points of zero charge of metal (hydr)oxides: 50 years after Parks’ review. *Adv. Colloid Interface Sci.* **2016**, *238*, 1–61. [[CrossRef](#)]
165. Neff, D.; Reguer, S.; Bellot-Gurlet, L.; Dillmann, P.; Bertholon, R. Structural characterization of corrosion products on archaeological iron: An integrated analytical approach to establish corrosion forms. *J. Ram. Spectr.* **2004**, *35*, 739–745. [[CrossRef](#)]
166. Tsukahara, S. Recent analytical methodologies on equilibrium, kinetics, and dynamics at liquid/liquid interface (Review). *Anal. Chim. Acta* **2006**, *556*, 16–25. [[CrossRef](#)] [[PubMed](#)]
167. Mitchell, G.; Poole, P.; Segrove, H.D. Adsorption of methylene blue by high-silica sands. *Nature* **1955**, *176*, 1025–1026. [[CrossRef](#)]
168. Moraci, N.; Lelo, D.; Bilardi, S.; Calabrò, P.S. Modelling long-term hydraulic conductivity behaviour of zero valent iron column tests for permeable reactive barrier design. *Can. Geotech. J.* **2016**, *53*, 946–961. [[CrossRef](#)]
169. Naseri, E.; Ndé-Tchoupé, A.I.; Mwakabona, H.T.; Nanseu-Njiki, C.P.; Noubactep, C.; Njau, K.N.; Wydra, K.D. Making Fe⁰-Based Filters a Universal Solution for Safe Drinking Water Provision. *Sustainability* **2017**, *9*, 1224. [[CrossRef](#)]
170. Yang, H.; Liu, Q.; Hu, R.; Ptak, T.; Taherdangkoo, R.; Liu, Y.; Noubactep, C. Numerical case studies on long-term effectiveness of metallic iron based permeable reactive barriers: Importance of porosity heterogeneity of the barrier. *J. Hydrol. Part B* **2022**, *612*, 128148. [[CrossRef](#)]