Metallic iron for environmental remediation: Learning from Electrocoagulation

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Abstract

The interpretation of processes yielding aqueous contaminant removal in the presence of elemental iron (e.g., in Fe^0/H_2O systems) is subject to numerous complications. Reductive transformations by Fe^0 and its primary corrosion products (Fe^{II} and H/H_2) as well as adsorption onto and co-precipitation with secondary and tertiary iron corrosion products (iron hydroxides, oxyhydroxides, and mixed valence Fe^{II}/Fe^{III} green rusts) are considered the main removal mechanisms on a case-to-case basis. Recent progress involving adsorption and co-precipitation as fundamental contaminant removal mechanisms have faced a certain scepticism. This work shows that results from electrocoagulation (EC), using iron as sacrificial electrode, support the adsorption/co-precipitation concept. It is reiterated that despite a century of commercial use of EC, the scientific understanding of the complex chemical and physical processes involved is still incomplete.

Key words: Adsorption; Co-precipitation; Electrocoagulation; Flocculation; Zerovalent iron.

Capsule: Mistakes made by users of electrocoagulation should be avoided for passive remediation Fe^0/H_2O systems.

1 Introduction

Groundwater contamination is an environmental concern of worldwide relevance [1-4]. The conventional method to treat contaminated aquifers involves pumping groundwater up from the aquifer, treating it above-ground, and either re-injecting it back into the aquifer or discharging it elsewhere (pump-and-treat method) [2]. The involved energy-intensive processes (pumping and operating systems) were shown to be expensive [3]. In many cases, the subsurface residual contaminant levels are undesirably high. Therefore, the pump-and-treat method is cost-intensive and ineffective as a rule. As an alternative, permeable reactive barriers (PRB) were introduced to treat contaminated groundwater below ground [1, 3] and the PRB technology is currently under development [5-7]. A PRB transforms the contaminations into less harmful substances or immobilizes them while allowing groundwater to pass through. The contaminant is either biologically or chemically transformed and/or physically removed [4, 5, 8-10]. Several reactive materials have been used including activated carbon, compost, clays, Fe^{II}-bearing minerals, metallic iron, wood chip or zeolites. Two of the most common designs are 'funnel and gate' and 'continuous walls' [3] and metallic iron (Fe^0) represents the most commonly used reactive material [5, 11].

The PRB technology using metallic iron (Fe^0) has gained acceptance as an effective passive remediation strategy for the treatment of a variety of organic and inorganic contaminants in groundwater [5, 8-14]. Even pathogens are efficiently removed in Fe^0/H_2O systems [15, 16]. Presently, around 120 Fe^0-PRBs have been installed worldwide and are mostly achieving their remediation goals. Theoretically, barrier performance failure can be related to three issues: (i) continual build-up of mineral precipitates on the Fe^0 surface (surface passivation or reactivity loss), (ii) loss of pore space (porosity loss and/or loss of hydraulic permeability), and (iii) development of preferential flow paths or complete bypass of the Fe^0 barrier resulting in the loss of hydraulic control [8, 17].

Despite two decades of extensive research, the mechanisms of contaminant removal in Fe^0/H_2O systems are not fully understood [10, 18-20]. In fact, Fe^0 was primarily used as reducing agent. Accordingly, mostly reductive transformations (degradation or precipitation) were considered and adsorption and co-precipitation were regarded as side effects for organic contaminants [21-23] or main removal mechanism for some inorganic contaminants [12, 14, 24]. For example, Lackovic et al. [25] reported that the removal mechanism for arsenic contrasted with that of chlorinated hydrocarbons (reductive dechlorination) and hexavalent chromium (reductive precipitation), and involved either adsorption or co-precipitation on the iron surface. However, two important facts challenge the universal validity of the reductive transformation concept: (i) a quantitative removal of redox-insensitive compounds as triazoles [26], methylene blue [27, 28], or zinc [24] were reported, and (ii) Fe^0/H_2O systems have been reported to function as a Fenton-like system for the oxidation of several contaminants [29].

A survey of the spectrum of efficiently removed species (oxidable, reducible and redox-insensitive) suggests that some removal mechanisms may be universal while others are specific. Universal mechanisms are necessarily those involved in the removal of redox-insensitive species: adsorption and co-precipitation. Therefore, as a rule, oxidable and reducible species may first be adsorbed and co-precipitated before redox transformations occur. Some species may be transformed in the aqueous phase (e.g. Cr^{VI} by Fe^{II} at pH < 4), but they will be adsorbed and/or co-precipitated when pH increases. This is the idea behind the adsorption/co-precipitation concept [19, 20]. According to this concept, a Fe^0/H_2O system should be regarded as a domain of precipitating iron oxide. All species (including contaminants, Fe^{II}, H_2/H) entering this domain can be regarded as foreign species in an "ocean" of iron oxides [30]. The papers cited [19, 20, 30] did not manage to convince authors of current publications dealing with contaminant removal in Fe^0/H_2O systems [31-33]. For example, Kang and Choi [33] stated that questioning the premise of reductive transformation is "hardly acceptable since the role of the direct electron transfer in Fe^0-mediated reactions is

well established and generally accepted among the research community." However, the validity of the reductive transformation concept was challenged, both theoretically [19, 20, 30] and experimentally [27, 28]. Furthermore, O'Hannesin and Gillham [13] reported that abiotic contaminant reduction coupled with metallic iron oxidation was a "broad consensus".

The purpose of this work is to corroborate the universality of the adsorption/co-precipitation concept of electrocoagulation (EC) using iron electrodes. Two major conclusions can be drawn from the Fe^0 EC: (i) in-situ produced iron hydroxides can effectively removed a variety of dissolved particles and suspended matter from aqueous solution, and (ii) a technology can be successfully used without fully understanding the fundamental chemical and physical mechanisms governing their functionality (e.g., the know why). However, a proper understanding of the fundamental physico-chemical principles will allow accurate model development for the design of improved systems, process control and process optimization. For the sake of clarity, the processes of electrochemical iron dissolution will be recalled before the EC technology is described.

2. Aqueous iron dissolution: the background

Aqueous iron corrosion is essentially an electrochemical process involving the anodic dissolution of iron and an appropriated cathodic reduction. For natural waters the two main cathodic reduction reactions are H^+ reduction (or "H_2 evolution") and O_2 reduction ("O_2 adsorption"), depending on the pH value [34, 35] (Fig. 1). Figure 1 shows clearly that the rate of Fe^0 dissolution decreases linearly with increasing pH for pH < 4. For the pH range 4 to 10, the rate of Fe^0 dissolution remains low and is almost constant. At pH > 10 a very slow linear decrease of iron dissolution with increasing pH is observed.

The major feature from Fig. 1 is that in the pH range of natural waters ($4 \leq pH \leq 10$), which is exactly the area of passive remediation Fe^0/H_2O systems, the kinetics of iron dissolution is very low. This is not surprising given the low solubility of Fe in this pH range [36, 37] (Fig.

2). Therefore, the most important effect of pH on the rate of Fe dissolution is indirect and relates to how pH changes conditions for the formation of iron oxide scales. Accordingly, at lower pH values (lower supersaturation, slower precipitation) relatively porous, detached and unprotective oxide scales are formed. At higher pH values (higher supersaturation, faster precipitation), more protective scales are formed. This behaviour is reflected by the observed decrease of the corrosion rate at pH > 10 (Fig. 1).

In natural waters, the electrochemical reactions are always accompanied by the formation of scales of mixed oxides including FeOOH, Fe_2O_3, Fe_3O_4 or green rusts [38-40], which are mostly non-protective [38-41]. Therefore, Fe^0 for environmental remediation ideally corrodes until material depletion. It is important to note that any experiment starting at pH < 4 and ending at pH > 4 is accompanied by more or less intensive iron precipitation with the possibility of contaminant co-precipitation. The conventional treatment of Cr^{VI} in waste waters is based on this principle. For example, Cr^{VI} is first reduced by Fe^{II} species to Cr^{III} at pH 3 and then the pH is raised to value between pH 8 and 10 to precipitate Cr^{III}, e.g. as $Cr(OH)_3$ [42-44]. Clearly, Cr^{III} and other metals are precipitated or co-precipitated as hydroxides and separated from solution by sedimentation or filtration. In Fe^0/H_2O, on the other hand, no supplementary addition of chemicals is required.

2.1 Anodic reaction

The anodic iron dissolution after Eq. 1 (Tab. 1) is rigorously valid for strong acidic solutions. For neutral and near neutral waters (4 ≤ pH ≤ 10, Fig. 1), iron dissolution is characterized by "oxygen adsorption" and has been reported to be a two-step scheme [35]. The transfer of the first electron across the interface involves water molecules that dissociate during the adsorption (Eq. 2); the transfer of the second electron limits the process under steady-state conditions. In parallel, adsorbed oxygen is formed via a similar scheme. The adsorbed oxygen is removed from the surface due to its chemical reaction with hydroxonium ions (H_3O^+ - Eq.

3), water molecules (H_2O - Eq. 4), or hydroxide ions (HO^- - Eq. 5). In natural systems, the anodic iron dissolution is affected by the presence of various ubiquitous species, e.g. Cl^-, HCO_3^-/CO_2, MnO_2, NO_3^-, PO_4^{3-} or SO_4^{2-}. Some species, like HCO_3^-/CO_2, favour iron dissolution and others (NO_3^-, PO_4^{3-}) inhibit iron corrosion [40, 45].

2.2 Cathodic reactions

At pH < 4 "H_2 evolution" (Eq. 6) is the major cathodic reaction (Fig. 1). It is well established that the presence of O_2 and CO_2 increases the rate of aqueous iron corrosion by increasing the rate of the "H_2 evolution" reaction [34, 40]. In particular, for CO_2-rich solutions the domain of H_2 evolution is extended to pH 4.5. However, additional H_2 is produced by carbonate reduction (Eq. 7). For pH > 4 the importance of H_2 evolution decreases progressively with increasing pH for two reasons: (i) the Fe^0 surface is (at least partially) shielded by oxide scales and (ii) O_2 reduction (Eq. 8) is spatially more favourable. It is important to note that O_2 is also used for Fe^{II} oxidation (Eq. 9) and that due to the presence of oxide scales, O_2 is mostly reduced by Fe^{II} species [46].

2.3 Oxide scale on Fe^0

The extent of iron dissolution from a Fe^0 material depends primarily on the solubility of iron (hydroxides or salts), which is a function of pH (Fig. 2). The semblance between Fig. 1 and Fig. 2 attests this. Accordingly, the solubility of iron (Fe^{II} or Fe^{III}) is a decreasing function of increasing pH for pH ≤ 5. For 5 ≤ pH ≤ 10, the solubility of iron is almost constant and less than 10^{-5} M.

At a given pH value, whenever the solubility of an hydroxide ($Fe(OH)_n$) is exceeded it precipitates (Eq. 10 and 11). This precipitation could lead to the formation of an oxide scale. The scale formation can be regarded as dehydration of precipitated hydroxides (Eq. 12 to 15). The oxide scale formation is a dynamic process which continues after the initial film building

because of its non-protective nature [38-40]. However, the kinetics of Fe^0 corrosion is slowed down because: (i) the film represents a diffusion barrier for the species involved in the corrosion process (including eventual contaminants), and (ii) the film covers a portion of the reactive Fe^0 surface. Accordingly, ways to sustain corrosion include [47] (i) avoiding or delaying scale formation (e.g. acidification), (ii) destroying or removing formed oxide scales (ultrasound vibration), and (iii) sustaining iron corrosion by an external source of energy. The latter coincides with the principle of electrocoagulation.

3. Electrocoagulation using iron electrodes

3-.1 Background

Electrocoagulation (EC) is an electrochemical technology for the treatment of water and wastewater. A current with a potential (U_0) passes through an electrochemical reactor and must overcome: (i) the equilibrium potential difference (E_{eq}), (ii) the anode overpotential (η_a), (iii) the cathode overpotential (η_c) and (iv) the ohmic potential drop (d/k*j – d is distance between the electrodes, k is a constant and j the current density) of the solution [35, 48, 49]. The anode overpotential (η_a) includes the activation overpotential ($\eta_{a,a}$) and concentration overpotential ($|\eta_{c,a}|$), as well as the possible passive overpotential resulting from the passive film at the anode surface, while the cathode overpotential (η_c) is principally composed of the activation overpotential ($\eta_{a,c}$) and the concentration overpotential ($|\eta_{c,c}|$). Therefore,

$$U_0 = E_{eq} + \eta_{a,a} + \eta_{a,c} + |\eta_{c,a}| + |\eta_{c,c}| + \frac{d}{k} * j \qquad (22)$$

When iron is used as electrode material, there are three major types of reactions in the electrochemical reactor (see Tab. 2 for more details):

(i) oxidation reaction at the anode (iron dissolution):

$$Fe^0 \Rightarrow Fe^{2+} + 2\ e^- \qquad (23)$$

$$E_{(Fe^{II}/Fe^{0})} = E^{0}_{(Fe^{II}/Fe^{0})} + \frac{R * T}{2F * \ln[Fe^{2+}]} \quad (24)$$

(ii) reduction reaction at the cathode:

$$2\ H^{+} + 2\ e^{-} \Rightarrow H_2\uparrow \quad (25)$$

$$E_{(H^{+}/H_2)} = E^{0}_{(H^{+}/H_2)} + \frac{R * T}{2F * \ln\left[\frac{[H^{+}]^2}{P_{H2}}\right]} \quad (26)$$

(iii) hydrolysis reaction:

$$Fe^{2+} + 2\ H_2O \Rightarrow Fe(OH)_2 + 2\ H^{+} \quad (27)$$

$$K = \frac{[H^{+}]^2}{[Fe^{2+}]} \quad (28)$$

The equilibrium potential difference between the anode and the cathode is:

$$E_{eq} = E^{0}_{(Fe^{II}/Fe^{0})} - E^{0}_{(H^{+}/H_2)} + \frac{R * T}{2F * \ln\left[\frac{P_{H2}}{K}\right]} \quad (29)$$

Eq. (29) suggests that E_{eq} is not a function of pH. Although the discussed system is very simplified, this suggestion reveals that the electrical potential ($U_0 \neq 0$) minimizes the importance of pH compared to passive Fe^0/H_2O discussed in section 2. In addition, no oxide scales are formed on the Fe^0 surface since iron oxides cause the contaminants to flocculate. The activation overpotential ($\eta_{a,a}$ and $|\eta_{c,a}|$) can be calculated from Tafel equation [48] when the current density is relatively large. Discussing this issue is beyond the scope of this communication. More details on reactions occurring in a Fe^0 EC are given in Tab. 2 (Eq. 30 to 41).

3.2 Principle of Fe^0 electrocoagulation

The EC process is based on the continuous in-situ production of coagulants in the contaminated water. Coagulants result from anodic Fe^0 dissolution with simultaneous formation of hydroxyl ions (HO^-) and hydrogen gas (H_2) at the cathode. This process produces iron hydroxides ($Fe(OH)_2$, $Fe(OH)_3$) and/or polyhydroxides, with the added benefit

that the generated gas assists in bringing the flocculated particles to the surface while providing them additional buoyancy to float at the water surface. To purify water, the hydroxide flocculates and coagulates the suspended solids (Eq. 36, 37, 40, 41 - Tab. 2). Additionally, there is the possibility of removing substances at anode and cathode respectively. (Eq. 34, 35 - Tab. 2). However, contaminant removal at electrodes concerns only redox-sensitive species. All other species are removed mainly in the bulk solution by flocculation. Even reducible species are flocculated after reduction.

3.3 Efficiency of Fe^0 EC for water treatment

EC has been demonstrated to be effective in the treatment of water and wastewater to remove metals such as Pb^{II}, Cd^{II}, Cr^{VI}, As^{III}/As^{V}, Mn^{II}, Cu^{II}, Zn^{II}, Ni^{II}, Al^{III}, Fe^{II}/Fe^{III}, Co^{II}, Mg^{II}, Mo^{II}, and Pt^{II}. It has also been employed in removing anions such as AsO_4^{3-}, CN^-, MoO_4^{2-}, PO_4^{3-}, SeO_4^{2-}, SO_4^{2-}, NO_3^-, F^-, and Cl^-, organic compounds such as total petroleum hydrocarbons (TPH), toluene, benzene and xylenes (TBX), methyl tert-butyl ether (MTBE), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids, clay minerals, organic dyes, oil, and greases from a variety of industrial effluents [50-53]. Table 3 summarises some standard electrode potentials of water constituents and contaminants relevant for passive Fe^0/H_2O systems and Fe^0 EC. On the other hand, EC has been reported to be very effective in the removal of inorganic compounds and pathogens [50, 54, 55]. The large spectrum of contaminants that can be removed in passive Fe^0/H_2O systems and by electrocoagulation is the primary reason for this communication. With EC, contaminants are mostly flocculated and coagulated in the bulk solution while in passive subsurface Fe^0/H_2O systems contaminants are adsorbed and co-precipitated in the vicinity of Fe^0 (Tab. 4). In both cases contaminants and suspended particles are sequestered (or enmeshed) into in-situ formed flocs. In the case of Fe^0 EC, contaminant removal has been mostly attributed to flocculation for more than a century, even though a quantitative reduction of some contaminants (e.g.

Cr^{VI}) cannot be ruled out [44, 56]. In fact, Cr^{VI} can be reduced to Cr^{III} by dissolved Fe^{II}, adsorbed Fe^{II} and the surface of Fe^0 electrode [44]. The mechanisms of Fe^0 EC is presented in the next section in detail.

3.4 Fe^0 EC mechanisms: state-of-the-art

Electrocoagulation can be considered as an electrochemically ($U_0 \neq 0$) driven accelerated corrosion process. For a particular electrical current flow in an electrolytic cell, the mass (m) of iron, theoretically dissolved from the sacrificial anode, is quantified by Faraday's law [m = f(I,t) - I = current (A), t = electrolysis time (s)]. Fe^0 EC is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from water (Tab. 2, Tab. 3). A systematic holistic approach is required to understand Fe^0 EC and its controlling parameters [44, 52, 57-59]. Most studies have focused on the removal efficiency of a specific pollutant, manipulating parameters such as conductivity, pH, current density (applied current), and electrode materials without exploring the fundamental mechanisms involved in the EC process (Tab. 4). The mechanisms involved are yet not clearly understood [48-52, 60]. However, these physico-chemical mechanisms have to be understood to optimize and control the process, to allow modelling of the method and to improve the design of the system [44, 51, 52, 57, 61-63], The sole merit of the majority of studies on water treatment using Fe^0 EC available is to demonstrate the effectiveness of EC for water treatment. In order words, "…the fact that electrocoagulation is being successfully applied to contaminated water is testament to its potential which is yet to be fully realized." [20]. This statement can be applied to passive subsurface Fe^0/H_2O systems without restriction and is the second reason for this communication. Clearly more fundamental information is needed on the physical chemistry involved in both processes. This information should be gained under the specific conditions relevant to each system. It should be acknowledged that for Fe^0 EC or EC in general, purposeful mechanistic investigations are progressively becoming available [44, 57, 58]. For

example Heidmann and Calmano [44] showed differential Cr^{VI} removal mechanisms at higher (1.0–3.0 A) and lower (0.05–0.1 A) current densities. Accordingly, at higher currents Cr^{VI} is reduced directly at the cathode and precipitated afterwards as $Cr(OH)_3$. At lower currents (0.05–0.1 A) Cr^{VI} removal resulted from reduction through Fe^{2+} from iron corrosion. Their investigation demonstrated that currents below 0.1 A were efficient in removing Cr^{VI} and cost effective (low current for long retention time).

4. Concluding remarks

The permeable reactive barrier (PRB) technology (the passive remediation Fe^0/H_2O system) is a technology lying at the intersection of at least two fundamental technologies: (i) electrochemistry (aqueous iron oxidative dissolution) and (ii) precipitation/co-precipitation. Each of these fields has been studied and possesses a great deal of individual understanding [64]. However, published literature lacks a quantitative appreciation of the way in which these technologies interact to provide optimal passive Fe^0/H_2O systems. Research is required that focuses on explaining and quantifying the key interactions and relationships between electrochemistry, precipitation/co-precipitation, and contaminant removal (by adsorption, co-precipitation, oxidation or reduction). The electrocoagulation teaches that a technique can be efficiently used for one century without proper understanding of key processes [44, 50, 51]. The PRB technology is only 20 years old and should avoid the mistakes made by practitioners of EC. Even though existing PRBs mostly work properly, it is essential to know about the details on a micro-scale when designing and operating new treatment walls. The first step in the future is to investigate the well-established premise of reductive transformation of contaminants by Fe^0 or in Fe^0/H_2O systems. This premise was already shown to be inconsistent with many conceptual models for iron corrosion used in other branches of science including synthetic organic chemistry [65], hydrometallurgy [66,67] and iron corrosion produced in the petroleum [66]. Furthermore, newest mechanistic investigations

with carbon tetrachloride (CT) using steady-state polarization curves and electrochemical impedance spectroscopy corroborate the fact iron corrosion is "helpful" for the reductive dechlorination of CT [10].

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Table 1: Relevant reactions for the process of aqueous Fe^0 dissolution, oxide scale formation and contaminant (Ox) removal in a passive remediation Fe^0/H_2O system. FeOOH is a proxy of corrosion products and $Fe_x(OH)_y^{(3x-y)}$ is an iron hydroxide.

Process	Reaction	Eq.
Fe^0 dissolution	$Fe^0 \Leftrightarrow Fe^{2+} + 2\ e^-$	1
Fe^0 passivation	$Fe^0 + H_2O \Rightarrow Fe(O)_{ads} + 2\ H^+ + 2e^-$	2
Fe^0 depassivation	$Fe(O)_{ads} + 2H^+ \Rightarrow Fe^{2+} + H_2O$	3
	$Fe(O)_{ads} + H_2O \Rightarrow Fe(OH)_2$	4
	$Fe(O)_{ads} + OH^- \Rightarrow HFeO_2^-$	5
H_2 evolution	$2\ H^+ + 2e^- \Rightarrow H_2\uparrow$	6
H_2CO_3 reduction	$2\ H_2CO_3 + 2e^- \Rightarrow H_2\uparrow + H_2CO_3^-$	7
O_2 reduction	$O_2 + 2\ H_2O + 4\ e^- \Rightarrow 4\ OH^-$	8
Fe^{2+} oxidation	$Fe^{2+} \Rightarrow Fe^{3+} + e^-$	9
	$Fe^{2+} + 2\ OH^- \Rightarrow Fe(OH)_2$	10
	$Fe^{3+} + 3\ OH^- \Rightarrow Fe(OH)3$	11
Scale formation	$Fe(OH)_2 \Rightarrow FeO + H_2O$	12
	$2\ Fe(OH)_3 \Rightarrow Fe_2O_3 + 3\ H_2O$	13
	$4\ Fe(OH)_3 \Rightarrow Fe(OH)_2 + Fe_3O_4 + 5\ H_2O + ½\ O_2$	14
	$Fe(OH)_3 \Rightarrow FeOOH + H_2O$	15
Fe^0 reduction	$Fe^0 + Ox_{(aq)} \Rightarrow Fe^{2+} + Red_{(s\ or\ aq)}$	16
adsorption	$FeOOH + Ox_{(aq)} \Leftrightarrow FeOOH\text{-}Ox$	17
co-precipitation	$Ox_{(aq)} + n\ Fe_x(OH)_y^{(3x-y)} \Leftrightarrow Ox[Fe_x(OH)_y^{(3x-y)}]_n$	18
$Fe^{II}_{(aq)}$ reduction	$Fe^{II}_{(aq)} + Ox_{(aq)} \Rightarrow Fe^{III} + Red_{(s\ or\ aq)}$	19
$Fe^{II}_{(s)}$ reduction	$Fe^{II}_{(s)} + Ox_{(aq\ or\ aq)} \Rightarrow Fe^{III} + Red_{(s\ or\ aq)}$	20
H_2 reduction	$H_2 + Ox_{(aq\ or\ aq)} \Rightarrow H^+ + Red_{(s\ or\ aq)}$	21

Table 2: Relevant reactions for the process of aqueous Fe^0 dissolution, coagulant production and contaminant (Ox) removal by electrocoagulation using iron electrodes.

Process	Reaction	Eq.
	Reactions at the electrodes	
Fe^0 dissolution	$Fe^0 \Leftrightarrow Fe^{2+} + 2\ e^-$ (anode)	23
	$Fe^0 \Leftrightarrow Fe^{3+} + 3\ e^-$ (anode)	30
H_2O electrolysis	$2\ H_2O \Rightarrow 4\ H^+ + O_2 + 4\ e^-$ (anode)	31
Fe^{2+} oxidation	$4\ Fe^{2+} + O_2 + 2\ H_2O \Rightarrow 4\ Fe^{3+} + 4OH^-$ (anode)	32
H_2O electrolysis	$2\ H_2O + 2\ e^- \Rightarrow H_2\uparrow + 2\ OH^-$ (cathode)	33
Ox reduction	$H_2 + Ox_{(aq\ or\ aq)} \Rightarrow H^+ + Red_{(s\ or\ aq)}$	34
	$Fe^0 + Ox_{(aq)} \Rightarrow Fe^{2+} + Red_{(s\ or\ aq)}$	35
	$Fe^{II}_{(aq)} + Ox_{(aq)} \Rightarrow Fe^{III} + Red_{(s\ or\ aq)}$	36
	$H_2 + Ox_{(aq\ or\ aq)} \Rightarrow H^+ + Red_{(s\ or\ aq)}$	37
	Reactions occurring in the bulk solution	
Ox reduction	$Fe^{II}_{(aq)} + Ox_{(aq)} \Rightarrow Fe^{III} + Red_{(s\ or\ aq)}$	36
	$H_2 + Ox_{(aq\ or\ aq)} \Rightarrow H^+ + Red_{(s\ or\ aq)}$	37
Fe precipitation	$Fe_{(aq)}^{2+} + 2\ OH^{- -} \Rightarrow Fe(OH)_{2(s)}$	38
	$Fe_{(aq)}^{3+} + 3\ OH^{- -} \Rightarrow Fe(OH)_{3(s)}$	39
Ox adsorption	$FeOOH + Ox_{(aq)} \Leftrightarrow FeOOH\text{-}Ox$	40
Ox coagulation	$Ox_{(aq)} + n\ Fe_x(OH)_y^{(3x-y)} \Leftrightarrow Ox[Fe_x(OH)_y^{(3x-y)}]_n$	41
Further reactions	**Destabilization of the contaminants**: particulate suspension, breaking of emulsions, and aggregation of the destabilized phases to form flocs through compression of the diffuse double layer and charge neutralization of the ionic species present occurs. Suspended solids and colloids in small quantities are easily removed.	
	Physicochemical Reactions: chemical reaction and precipitation of metal hydroxides with pollutants, electrophoretic migration of ions, oxidation of pollutants to less toxic species.	

Table 3: Standard electrode potentials of some water constituents and contaminants relevant for passive Fe^0/H_2O systems and electrocoagulation using iron electrodes (Fe^0 EC). Apart from alkyl halides (RX) all others are arranged in increasing order of E°. The higher the E° value, the stronger the reducing capacity of Fe^0 for the oxidant of a couple. Note that, Li^+, Rb^+, Al^{3+} and Zn^{2+} can not be reduced in passive Fe^0/H_2O systems whereas aqueous Fe^{II} species can reduce molecular O_2 and CrO_4^{2-}. Due to the external potential more reduction reactions are possible in Fe^0 EC but contaminant reduction is not the primary goal. Modified after ref. [20].

Reaction			E° (V)	Eq.
Li^0	⇔	$Li^+ + e^-$	-3.05	(i)
Rb^0	⇔	$Rb^+ + e^-$	-2.93	(ii)
Al^0	⇔	$Al^{3+} + 3\ e^-$	-1.66	(iii)
Zn^0	⇔	$Zn^{2+} + 2\ e^-$	-0.76	(iv)
Fe^0	⇔	$Fe^{2+} + 2\ e^-$	-0.44	(v)
$Fe^{2+}_{(s)}$	⇔	$Fe^{3+}_{(s)} + e^-$	-0.36 to -0.65	(vi)
Cd^0	⇔	$Cd^{2+} + 2\ e^-$	-0.403	(vii)
Ni^0	⇔	$Ni^{2+} + 2\ e^-$	-0.25	(viii)
Pb^0	⇔	$Pb^{2+} + 2\ e^-$	-0.13	(ix)
$H^+ + e^-$	⇔	½ H_2 (g)	0.00	(x)
$UO_2^{2+}{}_{(aq)} + 2\ e^-$	⇔	$UO_{2\ (s)}$	0.27	(xi)
Cu^0	⇔	$Cu^{2+} + 2\ e^-$	0.34	(xii)
$NO_3^- + 10\ H^+ + 8\ e^-$	⇔	$NH_4^+ + 3\ H_2O$	0.36	(xiii)
$RX + e^-$	⇔	$R^\bullet + X^-$	0.41 to 0.59	(xiv)
$H_3AsO_4 + 2\ H^+ + 2\ e^-$	⇔	$H_3AsO_3 + 2\ H_2O$	0.56	(xv)
Fe^{2+}	⇔	$Fe^{3+} + e^-$	0.77	(xvi)
Ag^0	⇔	$Ag^{2+} + 2\ e^-$	0.80	(xvii)
$O_2 + 2\ H_2O + 4\ e^-$	⇔	$4\ OH^-$	0.81	(xviii)
Hg^0	⇔	$Hg^{2+} + 2\ e^-$	0.85	(xix)
$2\ Cl^-$	⇔	$Cl_2 + 2\ e^-$	1.34	(xx)
$CrO_4^{2-} + 8\ H+ + 3\ e^-$	⇔	$Cr^{3+} + 4\ H_2O$	1.51[a]	(xxi)

Table 4: Comparative overview of some relevant facts on remediation Fe^0/H_2O systems and electrocoagulation with Fe^0 electrode. In investigating remediation Fe^0/H_2O systems, the lack of a systematic approach is yet to be realized.

Process	**Fe^0/H_2O systems**	**Electrocoagulation using Fe^0 electrode**
Basic reaction	Fe^0 dissolution (corrosion)	electrochemically accelerated Fe^0 corrosion
Nature	Passive (no energy input)	Active (electrolysis)
Discoverer	Gillham (1990)	Dieterich (1906)
Applicability	Groundwater, surface water and wastewater remediation	Groundwater, surface water and wastewater remediation
Operating mode	Adsorption onto Fe^0 and Fe-oxides Co-precipitation with Fe-hydroxides Reduction by Fe^0, Fe^{II} or H/H_2 Oxidation by Fenton reagents	In situ generation of coagulants by dissolution of Fe^0 from the anode Production of Fe polyhydroxides (flocs) Flocculation of contaminant and particles
Removed species	Metals, anions, non-metals, organic and inorganic compounds, pathogens	Metals, anions, non-metals, organic and inorganic compounds, pathogens
Removal site	In the vicinity of Fe^0	In the bulk solution
Operating parameters	Reactivity of used Fe^0 Used amount of Fe^0 pH value, nature of contaminant Initial contaminant concentration	Nature of used Fe^0 (electrode) Initial contaminant concentration Nature of the contaminant, pH value Current density and electrolysis time
State-of-the-art	A broad consensus on reductive transformation and case-by-case relevance of other mechanisms	Lack of systematic approach acknowledged Need of studies directed at a broad-based understanding of EC technology

Figure 1: Relative corrosion rate of iron as a function of pH (modified after Wilson, 1923). It is arbitrarily assumed that at pH 4 iron corrodes with 12 % of its rate at pH 0.

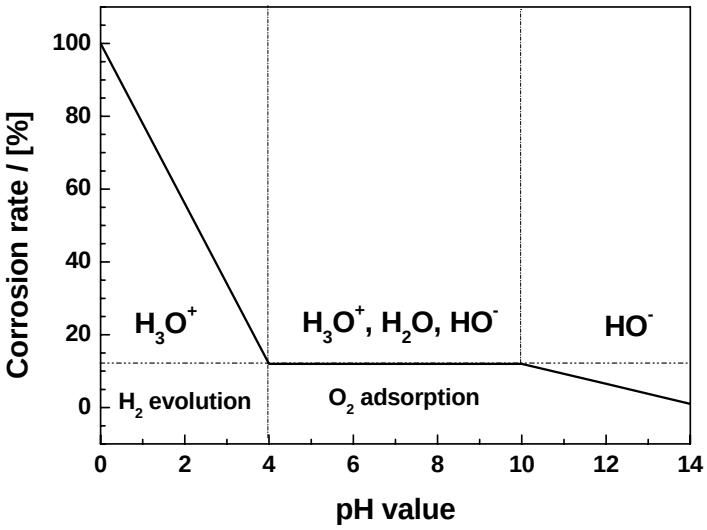
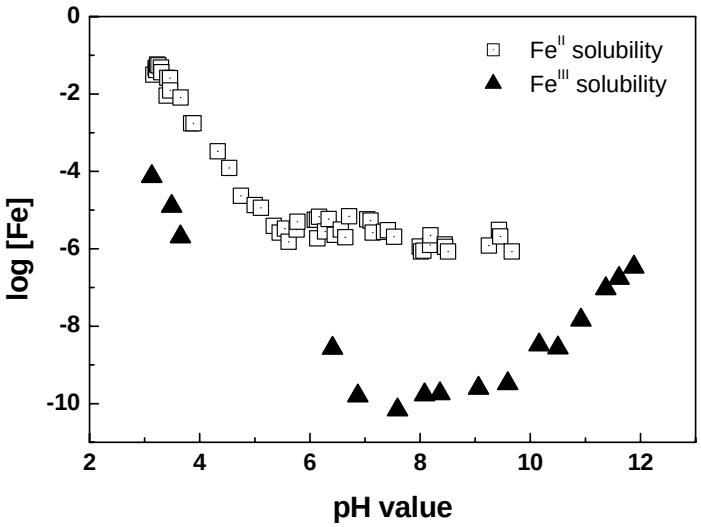
Figure 2: Solubility data of Fe^{II} in 0.1 M NaCl (25 °C) and Fe^{III} in 0.01 M NaCl (25 °C) as a function of pH. Data for Fe^{II} are from ref. [37] and data for Fe^{III} from ref. [36].