



Short communication

In situ microwave-enhanced electrochemical reactions at stainless steel: Nano-iron for aqueous pollutant degradation

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ABSTRACT

Iron nanoparticle deposition and stripping are observed from aqueous Fe^{2+} solution at pH 3 on stainless electrodes in the presence of focused microwave activation. The effects of Fe^{2+} concentration and microwave power are evaluated. It is shown that the resulting iron nanoparticle deposit (i) gives well-defined anodic stripping responses, (ii) is readily released into the solution phase, and (iii) is highly reactive towards chlorinated hydrocarbons such as trichloroacetate. The combined effects of increased mass transport and localized microwave heating improve pollutant degradation treatments.

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1. Introduction

Iron nanoparticles are highly reactive and elusive species in aqueous media. The size and properties of iron particles are highly dependent on the preparation conditions and electrochemical reducing methods seem to lead to high purity nanoparticles with specific size range controlled by the current [1,2]. Most work has been focused on the synthesis of iron oxide nanoparticles, but iron nanoparticles are much more reactive and useful, for example, as reducing agents or in pollutant treatment.

Direct electrochemical reduction methods have been applied for the degradation of aqueous chloroacetic acids [3–5] (often employed as model chlorinated hydrocarbons), with special attention to the use of iron, or iron-modified electrodes. The main source of chloroacetates is the oxidation of chlorine compounds during the disinfection of water supplies. Iron is the main component of pipes for water supply [6], and iron has been extensively used to dehalogenate compounds [7]. A remaining problem is that reductive dehalogenation of chloroacetic acids requires high overpotentials since the reaction takes place at potentials more negative than -1.0 V vs. SCE, concurrently with hydrogen evolution, which diminishes the efficiency of the process [5]. Stainless steel has previously been used as cathode material in environmental treatment processes [8,9] since it is a fairly robust material at negative potentials, resistant to adsorption of impurities, and relatively cheap.

Microwave radiation can be focused into the region close to the electrode surface to give locally enhanced temperatures (with superheating)

at the electrode/electrolyte interface [10,11]. A combination of heating (with inverted temperature gradient) and strong mass transport can be achieved in particular at microelectrodes. In this study, the behavior of stainless steel electrodes in aqueous solution and with self-focused microwave activation is investigated. It is shown that Fe^{2+} can lead to well-defined deposition at stripping reactions consistent with the Fe(0)/Fe(II) conversion [12]. Nanoparticle deposits are confirmed by microscopy. In situ microwave radiation is proposed to enhance the formation of iron nanoparticles and the electrocatalytic reduction of chloroacetic acids in aqueous media.

2. Experimental methods

2.1. Chemicals

All solutions were prepared using analytical-grade reagents (purchased from Aldrich in the purest commercially available grade) and demineralised and filtered water ($18.2\text{ M}\Omega\text{ cm}$) from an Elgastat water purification system (Elga, Bucks, UK). Solutions were partially degassed using a flow-through vacuum system (ca. 15 Torr achieved with a membrane pump) with electrolyte solution flux of typically 2 mL min^{-1} .

2.2. Instrumentation

Microwave-activated cyclic voltammetry experiments were performed on a Bio-Logic SP-300 electrochemical workstation (Bio-Logic, France). The working electrode was a $50\text{ }\mu\text{m}$ diameter stainless steel wire (AISI 316 L) from Advent, embedded in a glass tube with epoxy

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resin (SP 106, from Gurit). All potentials were measured using a KCl-saturated calomel electrode (SCE), and the auxiliary electrode was a platinum wire. The electrochemical cell (Fig. 1A) was placed inside a modified domestic multimode microwave oven (Panasonic NN-3456) with modified power supply (Oxford Electronics). Details of the cell design and application of microwaves have been described previously [13]. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM6480LV SEM system.

3. Results and discussion

3.1. Microwave effects on electrochemical processes at stainless steel I.: $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ calibration

Electrochemical processes in the presence of self-focused microwave radiation experience both faster mass transport and elevated temperatures. Therefore, a temperature calibration is required since the operating temperature is controlled by changing the anode current of the microwave magnetron. It is well known [13] that the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox system is a suitable system for quantifying the effect of thermal activation since an increase of the temperature at the electrode surface will provoke a linear shift of the equilibrium potential due to the reaction entropy associated with the redox process [14]. The shift in the equilibrium potential for a solution containing 10 mM $\text{Fe}(\text{CN})_6^{3-}$ and 10 mM $\text{Fe}(\text{CN})_6^{4-}$ in 1 M KCl, recorded with microwave pulses and under non-isothermal heating conditions, with an electrolyte flow rate of 2 mL min^{-1} , as a function of the temperature can be assumed to follow $dE_{\text{equilibrium}}/dT = -1.7 \pm 0.05 \text{ mV K}^{-1}$ [15]. Fig. 1B shows the local electrode temperature data (which may be lower than the adjacent solution temperature) as a function of the applied microwave power (expressed as magnetron current). As expected, the

equilibrium potential shifts to more negative potentials in the presence of microwave radiation and similar temperatures are obtained at stainless steel compared to those reported in previous works for other electrodes [15].

3.2. Microwave effects on electrochemical processes at stainless steel II.: reduction of aqueous Fe^{2+}

Self-focused microwave radiation has been previously proven to be suitable to enhance electrochemical processes such as deposition and stripping detection of heavy metals [16,17] and, typically, platinum, gold, and glassy carbon electrodes have been employed [18,19]. There are no previous records of the direct application of self-focused microwave radiation at stainless steel electrodes or for the electrosynthesis of metal nanoparticles.

Aqueous Fe^{2+} can be easily reduced to Fe^0 at the surface of a stainless steel microelectrode under microwave conditions, from 1 mM Fe^{2+} solution at pH 3 [12], as shown in the scanning electron microscopy images (Fig. 2). Fig. 2a shows the featureless polished stainless steel surface; Fig. 2b shows the surface of the steel electrode after exposure to microwave radiation for 5 minutes (10 mA magnetron current) in a solution containing 0.1 M Na_2SO_4 (pH 3). It can be observed that the epoxy resin around the steel wire has been damaged by the action of the heat, causing some melting/leaching or swelling to partially cover the electrode surface. Fig. 2c and d show the surface after Fe^0 deposition, which turns into iron oxide in contact with air. It can be inferred that Fe^0 nanoparticles have been formed at the electrode surface and that, due to the high electrolyte flow, they have been dislodged or expelled from the surface towards the edge between the electrode and the resin that is porous probably due to the high temperatures reached at the vicinity of the electrode surface. Consequently, the electrode surface seems to be continuously generating Fe^0 nanoparticles.

Iron deposition onto the stainless steel surface was characterized voltammetrically by studying the evolution of the iron stripping peak under different conditions, i.e., Fe^{2+} concentration, temperature, and deposition time. The effect of the iron concentration on the Fe^0 formation at the steel microelectrode was evaluated studying the stripping peak under microwave radiation. Fig. 3A shows cyclic voltammograms obtained for solutions of FeSO_4 with different concentrations. The iron stripping peak is absent when a solution containing just 0.1 M Na_2SO_4 is used (Fig. 3A-a). On the other hand, in solutions containing Fe^{2+} from 0.5 mM to 4 mM, the stripping response for the iron re-dissolution is clearly observed. The stripping response starts at around -0.8 V and the stripping peak markedly increases with the Fe^{2+} concentration (0.5 mM Fe^{2+} being the lower limit concentration for the formation of Fe^0 under microwave constant power of 8 mA) (Fig. 3A-b–e). Peaks become narrower and more intense as the concentration increases until 4 mM Fe^{2+} and there is a clear shift in the peak position for the stripping process. However, peaks broaden at higher concentrations (data not shown). Cathodic currents increase with increasing the Fe^{2+} concentration as well, leading to sigmoidal cathodic currents typical of enhanced mass processes.

The influence of the temperature, measured as the magnetron anode current, in the iron deposition can be characterized by the iron stripping peak (Fig. 3B). The reductive deposition of iron at steel electrodes necessarily requires high temperatures, as shown by the absence of the stripping peak when no microwave radiation is applied (Fig. 3B, dotted line) or under microwave conditions but at low temperatures (Fig. 3B-a, 6 mA magnetron current, corresponding to ca. 343 K). At higher temperatures, the stripping peaks are better defined and become narrower since higher microwave radiation levels enhance the iron dissolution process, until the limit higher temperature is reached (at which the iron stripping peak no further changes), when 16 mA magnetron currents are applied and corresponding to ca. 440 K (Fig. 3B-f). Higher microwave power provokes an increase in the limiting current, attributed to the generation of a high-temperature region at the

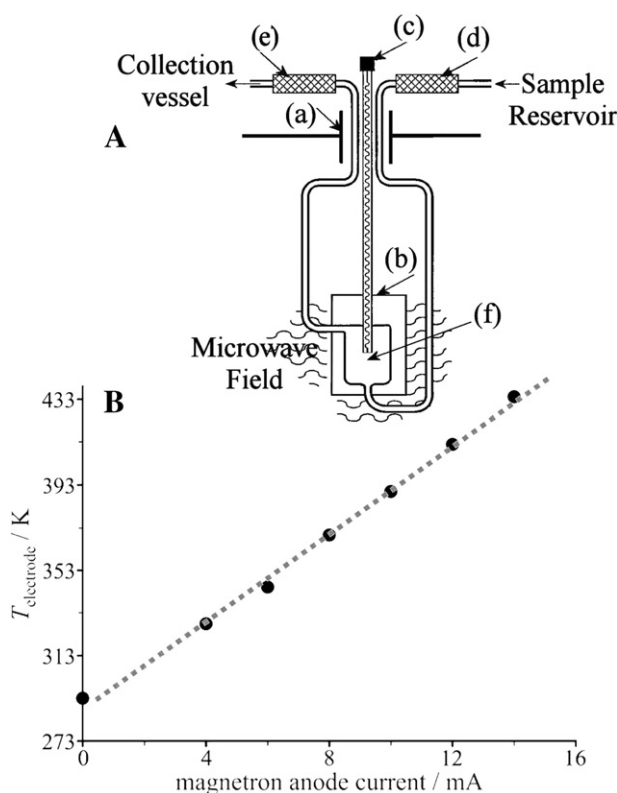


Fig. 1. (A) Schematic drawing of the flow-through microwave-electrochemical cell: (a) cavity port, (b) Teflon cell, (c) working electrode, (d) reference electrode, (e) counter electrode, and (f) location where microwave energy is focused. (B) Plot of the variation of the temperature of a $50 \mu\text{m}$ stainless steel electrode as a function of the applied microwave intensity (magnetron anode current), calculated from the equilibrium potential of 10 mM $\text{Fe}(\text{CN})_6^{3-}/10 \text{ mM } \text{Fe}(\text{CN})_6^{4-}$ in 1 M KCl.

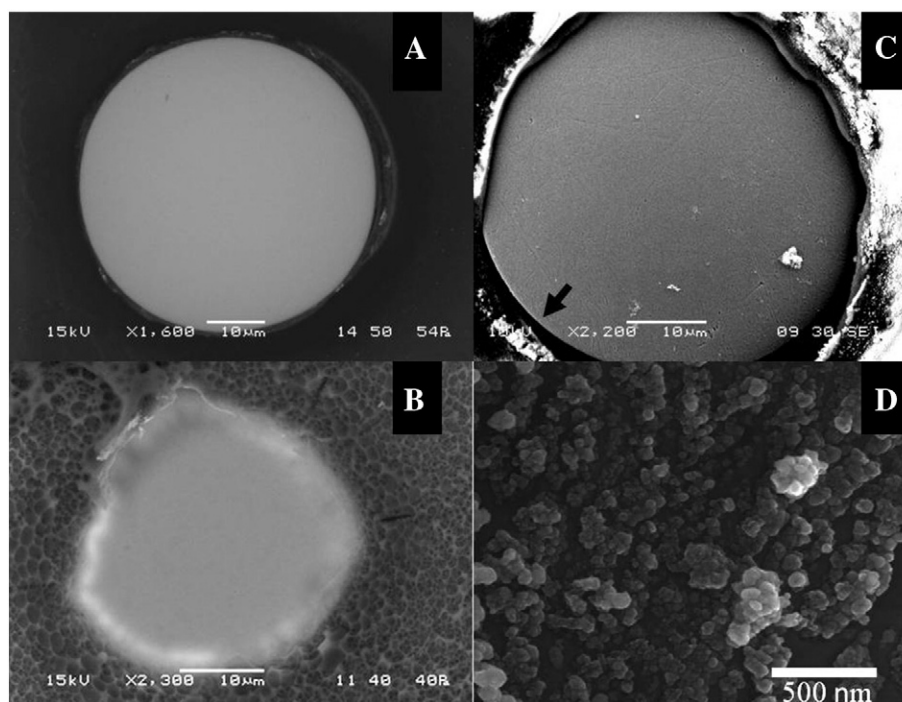


Fig. 2. SEM images showing the surface of a 50 μm stainless steel electrode. (a) Polished surface; (b) after microwave radiation exposure (10 mA magnetron current, 5 min) in a solution containing 0.1 M Na_2SO_4 (pH 3); (c) after microwave radiation exposure (10 mA magnetron current, 1 min) in a solution containing 1 mM FeSO_4 in 0.1 M Na_2SO_4 (pH 3); (d) inset of Fig. 2 c, where aggregated iron oxide nanoparticles of ca. 40 nm can be observed.

electrode/electrolyte interface [11]. Accordingly, the shape of the voltammograms changes from the conventional peak-shaped characteristic of room temperature (Fig. 3B, dotted line), into sigmoidal (Fig. 3B: a–f), indicating an increase in the mass transport as a consequence of convection processes [20]. The direct/additional heating effects induced by microwave adsorption into the metallic iron nanoparticles may also play a role, but experimental evidence for this is currently not available.

To study the effect of the deposition time on the stripping peak, cyclic voltammetry experiments were performed at different scan rates: 10, 20, 50, and 100 mV s^{-1} (Fig. 3C). The reduction of Fe^{2+} starts at -0.5 V and the reduction signal, attributed to Fe^0 nucleation, can be observed until -1.2 V where the hydrogen evolution starts taking place. In the positive-going sweep, the characteristic peak of the iron stripping can be observed, and a systematic decrease in the peak area occurs as the scan rate increases. Iron reduction has been performed only during the cathodic sweep. Consequently, improved stripping peaks are detected as the scan rate is slower, showing that the iron formation is scan rate dependent. Reduction currents increase with increasing the Fe^{2+} concentration as well, leading to the same sigmoidal cathodic currents typical of enhanced mass processes, in concordance with the data obtained in Fig. 3A.

3.3. Microwave effects on electrochemical processes at stainless steel III: reduction of chloroacetates

Dehalogenation processes of organic contaminants in water, using mainly iron in its zero oxidation state have extensively been studied for decades due to its reducing character [6] (Eq. (1)).



RX represents a halogenated hydrocarbon and X^- is the corresponding halide. It has been previously shown that this reaction follows the reductive sequence of tri-, di-, and mono-chloroacetic acid, until acetic acid is formed as the final product [21]. In order to characterize the

iron-modified steel electrode in cathodic electrode processes, the reduction of trichloroacetic acid (TCCA) has been studied.

Fig. 3D shows the cyclic voltammograms for the iron reduction and stripping in a solution containing 4 mM FeSO_4 (Fig. 3D-a); 4 mM FeSO_4 and 4 mM TCCA (Fig. 3D-b); and for the TCCA reduction of a solution containing 4 mM TCAA (Fig. 3D-c), all in 0.1 M Na_2SO_4 , pH 3. The reduction process of trichloroacetic acid starts at -0.8 V (Fig. 3D-c) coinciding with the potential of iron deposition. The highest reduction current observed when both Fe^{2+} and TCAA, are present in the solution, together with the ca. 3-fold decrease in the iron stripping peak area, compared to the solution in the absence of TCAA, suggest that the TCAA reduction is taking place (competitively with iron deposition) and the process is enhanced by microwaves and the higher concentration of Fe^0 at the electrode surface at more negative potentials. These are preliminary results and further study of the optimisation of the process and effects of microwaves on the chemical process are required.

4. Conclusion

Iron nanoparticles obtained by microwave-activated electro-reduction onto a stainless steel microelectrode have been studied for the degradation of trichloroacetic acid in aqueous solution. Preliminary results show that microwave radiation provides a beneficial reaction environment for the reduction of Fe(II) to iron at the steel electrode surface, with promising applications in the cathodic dehalogenation of chloroacetic acids. Furthermore, it highlights the difference in reactivity of pure iron and stainless steel. The method could be useful for a wider range of processes based on highly reactive iron nanoparticles.

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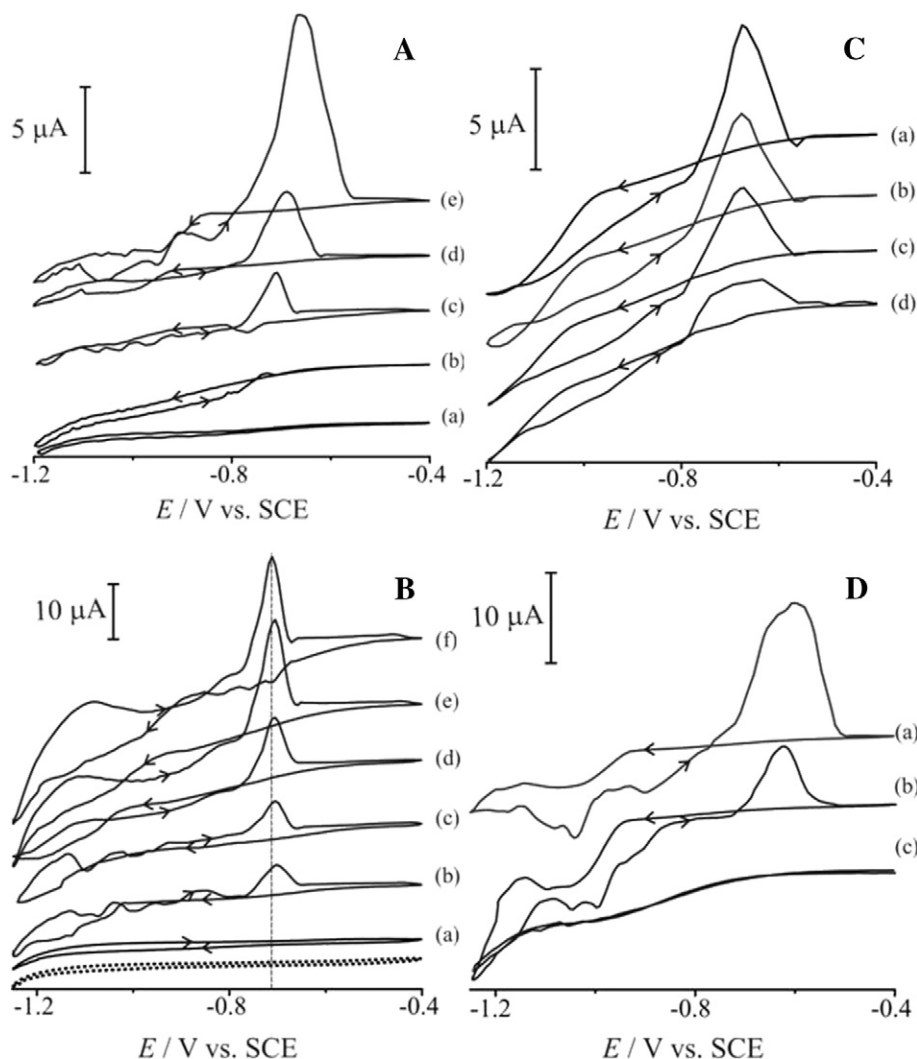


Fig. 3. Cyclic voltammograms for the reduction and stripping of Fe^{2+} , at a $50 \mu\text{m}$ diameter steel electrode (A) at 20 mV s^{-1} , in a solution containing (a) 0.0 mM, (b) 0.5 mM, (c) 1 mM, (d) 2 mM, and (e) 4 mM FeSO_4 in 0.1 M Na_2SO_4 (pH 3), 8 mA microwave magnetron current. In a solution containing 1 mM FeSO_4 in 0.1 M Na_2SO_4 (pH 3): (B) without (dotted line) and with (continuous line) microwave radiation, applying a magnetron current of (a) 6 mA, (b) 8 mA, (c) 10 mA, (d) 12 mA, (e) 14 mA, (f) 16 mA, at 20 mV s^{-1} and (C) at a scan rate of 10 (a), 20 (b), 50 (c), and 100 mV s^{-1} (d), 10 mA microwave magnetron current. (D) At a scan rate of 20 mV s^{-1} in a solution containing (a) 4 mM FeSO_4 , (b) 4 mM TCAA and 4 mM FeSO_4 , (c) 4 mM TCAA (all in 0.1 M Na_2SO_4 , pH 3), 7 mA microwave magnetron current.

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