

## A novel combined electrochemical-magnetic method for water treatment

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### ABSTRACT

Electrocoagulation (EC) is a wastewater treatment process in which aqueous pollutants can be removed by adsorption, entrapment, precipitation or coalescence during a coagulation step produced by electrochemically generated metallic species. When using Fe as the sacrificial electrode, Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are formed. As Fe<sup>3+</sup> species are paramagnetic, this property can in principle be used to facilitate their removal through the application of a magnetic field. In the present work we present a proof-of-concept for a combined electrochemical-magnetic method for pollutant removal. For this approach, the amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> produced in an EC cell at various voltages were measured by spectroscopic methods to confirm that Fe<sup>3+</sup> species predominate (up to 84%). The effectiveness of the presence of a magnetic field in the precipitation of coagulants from a suspension was confirmed by monitoring the turbidity change versus time with and without exposure to a magnetic field, up to a 30% improvement.

**Key words** | electrocoagulation, magnetic removal, water treatment

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### INTRODUCTION

Electrochemical methods are useful for treating many environmental remediation problems. Specifically, electrocoagulation (EC) has been proposed for the treatment of wastewater containing suspended solids, heavy metals, petroleum products, dyes, etc. (Rajeshwar *et al.* 1994; Rajeshwar & Ibanez 1997; Holt *et al.* 1999). EC has several advantages over chemical coagulation (Gu *et al.* 2009). For example, coagulants such as alum KAl(SO<sub>4</sub>)<sub>2</sub>·12(H<sub>2</sub>O) that are supplied in the conventional chemical method involve the concomitant addition of undesired counterions. Furthermore, such chemical coagulants contain only relatively small quantities of the coagulating agents on a weight basis. For instance, one ton of alum contains only ca. 57 kg of Al<sup>3+</sup>. EC is not, however, without flaws. It is marketed only by a small number of companies around the world, requires an expensive initial investment, and the cost of electricity will be an important decision factor in some countries.

EC consists of the *in situ* generation of metallic coagulants by the electrolytic oxidation of an appropriate anode, usually Fe or Al (Cañizares *et al.* 2007). For example, in an oversimplified scheme Fe is oxidized to Fe<sup>2+</sup> which is in

turn quickly oxidized to Fe<sup>3+</sup> in the presence of dissolved atmospheric oxygen.



These ions may react with OH<sup>-</sup> ions generated at the cathode by the reduction of water with the simultaneous production of H<sub>2</sub> (Ibanez *et al.* 1995; Den *et al.* 2006; Cañizares *et al.* 2007):



These insoluble metallic hydroxides are capable of removing pollutants out of the solution by adsorption. Depending on pH, they also contribute to the coagulation phenomenon by neutralizing negatively charged colloidal

particles. The sludge formed by the interaction between the metallic hydroxides and the pollutants may then be removed either by precipitation or by allowing it to float to the top (with the aid of the electrogenerated hydrogen gas) where it is separated by skimming (Ibanez *et al.* 1995).

EC is an environmentally friendly, competitive and effective process in the treatment of wastewater and in the past decade it has received renewed interest. It is also a complex process with a multitude of mechanisms that are yet to be completely understood. For example, pollutant type, concentration, pH, bubble size, electrode location, and agglomerate size influence the operation of the EC unit. The overall result is a combination of synergistic mechanisms where the predominant path may vary throughout the dynamic process as the reaction progresses (Holt *et al.* 1999). An extensive analysis of the chemical reactions that occur during EC is available. The precipitates thus produced involve Fe(II) and Fe(III) species (Moreno *et al.* 2009).

### Magnetically assisted sedimentation

According to the spectrochemical series,  $\text{OH}^-$  ions can produce orbital splitting on  $\text{Fe}^{n+}$  ions. As  $\text{Fe}^{2+}$  has a  $d^6$  electronic configuration, this approach may yield a low spin and diamagnetic species. By contrast,  $\text{Fe}^{3+}$  is a  $d^5$ , which yields a paramagnetic configuration. Thus, the application of EC under the necessary conditions to produce  $\text{Fe}^{3+}$  should *a priori* yield a paramagnetic oxide or hydroxide. If the sludge thus produced were exposed to a magnetic field, its precipitation could in principle be enhanced and a more powerful remediation technique achieved (Ibanez *et al.* 2009). In addition, the typical filtration step could be avoided. In the present paper, a proof-of-concept is presented.

Magnetic-based techniques have been studied for different applications in the environmental remediation arena. For example, ferrofluids comprising magnetite nanoparticles that dissolve preferentially in certain media have been proposed for the treatment of oil spills and other contaminants (Moesser *et al.* 2004; Raloff 2008) and even as auxiliaries for improving the efficiency of water electrolysis (Iida *et al.* 2007). Similarly, the removal of sludge generated from the use of Fenton's reaction as an advanced oxidation process (AOP), can be facilitated by a magnetic field (Ambashta *et al.* 2011), as well as the chemical separation of Cu(II) ions (Zhu *et al.* 2011). Another proposed application of these magnetically assisted processes is the separation of solid waste under microgravity and hypogravity conditions, such as

those encountered in long-duration manned missions in outer space (Sornchamni *et al.* 2005).

## METHODS

The reagents used were:  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (J. T. Baker),  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (J. T. Baker),  $\text{NaCH}_3\text{COO}$  (anhydrous, J. T. Baker),  $\text{H}_2\text{SO}_4$  (J. T. Baker, 97.9 %),  $\text{Na}_2\text{SO}_4$  (anhydrous, J. T. Baker), and *o*-phenanthroline (Merck, 99.5%) and were used as received. Solutions were prepared with Milli-Q deionized water. A single-compartment EC cell was used for all experiments and consisted of a 5 mL glass vial with a high purity Fe wire (Mallinkrodt, 5 cm long,  $\varphi = 0.5$  mm) as the anode and a graphite rod (Steadtler Mars HB, 5 cm long,  $\varphi = 2$  mm) as the cathode. A 0.5 cm length of each electrode was kept inside the solution at all times for electrolytic contact. The electrodes were carefully cleaned between experiments by dipping in dil. nitric acid, sanding with fine grit sand paper, and rinsing with water.

### Measurement of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ concentrations

#### Calibration curve

Calibration curves for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were obtained by forming complexes of both ions with *o*-phenanthroline, and measuring their absorbances with a UV-Vis Varian Cary 300 spectrophotometer at 510 nm for  $\text{Fe}^{2+}$  and 390 nm for  $\text{Fe}^{3+}$  (Paschoal & Tassarolo 2000). The Fe ions were obtained from 100 mg/L stock solutions of ammonium iron(III) sulfate and ammonium iron(II) sulfate, respectively. To form the complexes, 0.25% w/w of *o*-phenanthroline was used and 0.2 M solution of sodium acetate acted as a buffer.

#### Concentration of iron ions during EC

Iron ions were obtained by applying different potentials with an AC/DC converter (ELI-030, Steren) across the EC cell described above containing 0.1 M  $\text{Na}_2\text{SO}_4$  as electrolyte. The suspensions resulting after 5 min were treated with a 0.25% w/w solution of *o*-phenanthroline in 1/100 (vol/vol)  $\text{H}_2\text{SO}_4$  to a final volume of 10.0 mL with water. This procedure promoted the dissolution of the precipitates and the formation of complexes with the Fe ions. The resulting  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  concentrations were measured spectrophotometrically. The experiments were performed either under normal atmospheric conditions or under an inert nitrogen

atmosphere (Infra, 99.99% pure) to observe the effect of the presence/absence of atmospheric dioxygen on the relative distribution of the produced ions. Voltages and currents were monitored with TES 2310 multimeters to obtain the charge transferred during the 5-min experiments.

### Effect of a magnetic field upon the sedimentation process

As a significant presence of paramagnetic  $\text{Fe}^{3+}$  species was anticipated (Lakshmanan et al. 2009; Moreno et al. 2009), the resulting suspension was expected to respond positively to an external magnetic field. The test samples for these magnetically enhanced sedimentation experiments were prepared in the same EC cell described earlier and diluted to 10.0 mL without further treatment in a volumetric flask. To determine the sedimentation behaviour in the presence/absence of a magnetic field, the turbidity of the samples was monitored during the sedimentation process using a 2100P Portable Turbidimeter (Hach). This was allowed to proceed until important changes in turbidity were no longer observed. A neodymium permanent

magnet (Magnum Magnetic Corp., AFG-60001, 12,064 Gauss, 12.7 mm diameter, N35 grade) was positioned under the sample vial (touching its bottom) so as to have the magnetic field parallel to the sedimentation trajectory.

## RESULTS AND DISCUSSION

Figure 1 shows the spectrophotometric calibration curve obtained for  $\text{Fe}^{n+}$  ions.

The curves resulting from this calibration allowed the simultaneous quantitation of both ions during the EC process. By following the same spectrophotometric procedure, such data were obtained for a series of EC experiments under either ambient or nitrogen atmosphere. Table 1 summarizes these results.

The resulting charges were higher when operating under air than under nitrogen, possibly because the following parasitic cathodic reaction does not occur in the absence of dissolved oxygen:

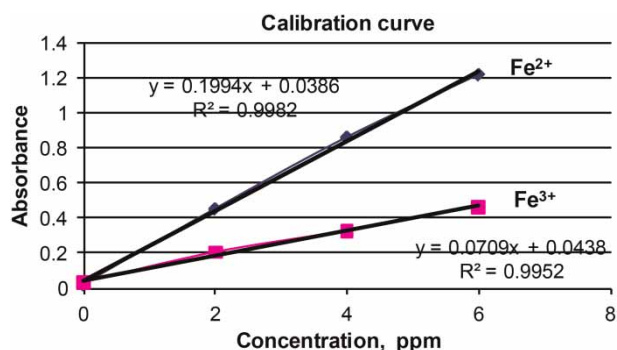


Figure 1 | Calibration curves for the UV spectrophotometric analysis of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

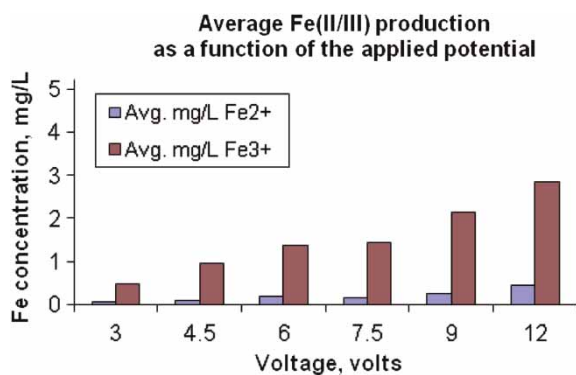
In addition, the resulting concentrations of  $\text{Fe}^{2+}$  under a nitrogen atmosphere were higher than those under normal air atmosphere, as would be expected due to the lack of an oxidizing environment (Lakshmanan et al. 2009). The concentration of  $\text{Fe}^{3+}$  increased steadily with potential in both cases. The results in air are plotted in Figure 2.

Because of the significant amount of  $\text{Fe}^{3+}$  found under both conditions, the sedimentation experiments were performed under ambient air atmosphere for the sake of simplicity. Turbidity changes of the samples are given in Figure 3 in Nephelometric Turbidity Units (NTU) versus time with and without the presence of a magnetic field.

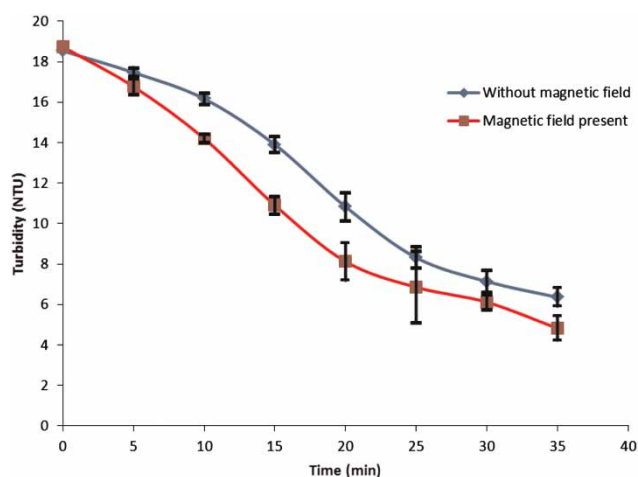
Table 1 | Concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  under ambient or nitrogen atmospheres and the electrical charge transferred during each experiment

Voltage, nominal (V) <sup>a</sup>	Under ambient atmosphere			Under a $\text{N}_2$ atmosphere		
	mg/L $\text{Fe}^{2+}$	mg/L $\text{Fe}^{3+}$	Charge transferred (C)	mg/L $\text{Fe}^{2+}$	mg/L $\text{Fe}^{3+}$	Charge transferred (C)
3	0.0532	0.4779	9.22	0.2928	0.4755	6.72
4.5	0.0858	0.961	15.69	0.1526	1.051	14.47
6	0.1829	1.3734	22.44	0.2097	1.1289	18.21
7.5	0.1629	1.432	29.87	0.2411	1.6698	25.21
9	0.2611	2.1407	37.67	0.3646	2.1609	33.73
12	0.4508	2.855	49.28	0.3985	2.4204	40.46

<sup>a</sup>Note: Experimental voltages (in parenthesis) are the result of the application of the following nominal voltages: 3 (5.9), 4.5 (7.7), 6 (9.6), 7.5 (11.2), 9 (13.3), 12 (16.7).



**Figure 2** | Fe(II/III) in the electrocoagulation product as a function of the nominal applied potential, in air. (Plotted are the averages of three replicate experiments for each point.)



**Figure 3** | Turbidity of EC samples versus time, with and without the application of a magnetic field. (Error bars correspond to one standard deviation for triplicate experiments.)

At equal times, the samples under the influence of a local magnetic field reached lower turbidity readings than those under only the influence of the Earth's gravity field. This finding confirms that the magnet has the desired salutary effect on the sedimentation of the EC solids, composed mainly of Fe<sup>3+</sup> oxy(hydroxide) species. Depending on their composition (Den *et al.* 2006; Lakshmanan *et al.* 2009; Moreno *et al.* 2009), the behaviour of turbidity with time might vary considerably.

## CONCLUSIONS

The spectroscopic analysis of the EC samples confirmed that Fe(III) is the predominant form of the oxidized iron even when generated under an inert atmosphere. A magnetic

field has a salutary influence on the sedimentation performance of EC agents derived from iron anodes. The sedimentation samples that were under the influence of a magnet reached lower turbidity levels faster than those without it. This proof-of-concept could potentially avoid a costly filtration step.

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