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\(^{2+}\) and Fe\(^{3+}\) ions are formed. As Fe\(^{3+}\) 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\(^{2+}\) and Fe\(^{3+}\) produced in an EC cell at various voltages were measured by spectroscopic methods to confirm that Fe\(^{3+}\) 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.

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\(_4\))\(_{2}\)-12(H\(_2\)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\(^{3+}\). 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 \textit{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\(^{2+}\) which is in turn quickly oxidized to Fe\(^{3+}\) in the presence of dissolved atmospheric oxygen.

\begin{equation}
\text{Fe}^0(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^- \quad (1)
\end{equation}

\begin{equation}
\text{Fe}^{2+}(aq) \rightarrow \text{Fe}^{3+}(aq) + e^- \quad (2)
\end{equation}

These ions may react with OH\(^-\) ions generated at the cathode by the reduction of water with the simultaneous production of H\(_2\) (Ibanez et al. 1995; Den et al. 2006; Cañizares et al. 2007):

\begin{equation}
2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (aq) \quad (3)
\end{equation}

\begin{equation}
\text{Fe}^{3+}(aq) + 3\text{OH}^- (aq) \rightarrow \text{Fe}(	ext{OH})_3(s) + \text{FeOOH}(s) \quad (4)
\end{equation}

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. 2007). 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, OH⁻ ions can produce orbital splitting on Fe³⁺ ions. As Fe²⁺ has a d⁶ electronic configuration, this approach may yield a low spin and diamagnetic species. By contrast, Fe³⁺ is a d⁵, which yields a paramagnetic configuration. Thus, the application of EC under the necessary conditions to produce Fe³⁺ 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 (Moese 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: Fe(NH₄)₂(SO₄)₂·6H₂O (J. T. Baker), FeNH₄(SO₄)₂·12H₂O (J. T. Baker), NaCH₃COO (anhydrous, J. T. Baker), H₂SO₄ (J. T. Baker, 97.9 %), Na₂SO₄ (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, φ = 0.5 mm) as the anode and a graphite rod (Steadler Mars HB, 5 cm long, φ = 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 Fe²⁺ and Fe³⁺ concentrations**

**Calibration curve**

Calibration curves for Fe²⁺ and Fe³⁺ 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 Fe²⁺ and 390 nm for Fe³⁺ (Paschoal & Tessarolo 2006). 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 Na₂SO₄ 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) H₂SO₄ 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 Fe²⁺ and Fe³⁺ 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 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 Fe$^{3+}$ 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:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

In addition, the resulting concentrations of 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 Fe$^{3+}$ increased steadily with potential in both cases. The results in air are plotted in Figure 2.

Because of the significant amount of 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>
<thead>
<tr>
<th>Voltage, nominal (V)$^a$</th>
<th>Concentrations of Fe$^{2+}$ and Fe$^{3+}$ under ambient or nitrogen atmospheres and the electrical charge transferred during each experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under ambient atmosphere</td>
<td>Under a N$_2$ atmosphere</td>
</tr>
<tr>
<td>Voltage, nominal (V)$^a$</td>
<td>mg/L Fe$^{2+}$</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>3</td>
<td>0.0532</td>
</tr>
<tr>
<td>4.5</td>
<td>0.0858</td>
</tr>
<tr>
<td>6</td>
<td>0.1829</td>
</tr>
<tr>
<td>7.5</td>
<td>0.1629</td>
</tr>
<tr>
<td>9</td>
<td>0.2611</td>
</tr>
<tr>
<td>12</td>
<td>0.4508</td>
</tr>
</tbody>
</table>

$^a$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).
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\(^{3+}\) 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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