Research Article

Electrochemical Removal of Humic Acids from Water Using Aluminum Anode: Influence of Chloride Ion and Current Parameters

Sante Capasso,1 Stefano Salvestrini,1,2 Valentina Roviello,3 Marco Trifuoggi,4 and Pasquale Iovino1,2

1Environmental Technologies, University Spin-Off of University of Campania “Luigi Vanvitelli”, Via Vivaldi 43, Caserta, Italy
2Department of Environmental Biological and Pharmaceutical Sciences and Technologies, University of Campania “Luigi Vanvitelli”, Via Vivaldi 43, Caserta, Italy
3CeSMA-Advanced Metrologic Service Center, University of Naples Federico II, Corso Nicolangelo Protopisani, 80146 Naples, Italy
4Department of Chemical Sciences, University of Naples Federico II, Via Cintia, Naples, Italy

Correspondence should be addressed to Pasquale Iovino; pasquale.iovino@unicampania.it

Received 15 November 2018; Accepted 14 January 2019; Published 6 February 2019

Academic Editor: Wenshan Guo

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The removal by electrochemical treatment in batch of humic acids (HA) extracted from leonardite has been analyzed using aluminum electrodes at 25 °C and neutral pH, under galvanostatic conditions. HA removal, inferred from UV-Vis spectra and total organic carbon determination, occurred within few minutes of treatment under the experimental conditions tested, and no electrode passivation was observed. The removal rate increased with NaCl concentration and electric current density. Our data indicate that energy consumption per unit weight of HA removed can be significantly reduced by operating at low current density under galvanostatic conditions and/or high salt concentration, thus confirming electrochemical treatment as a powerful technology for wastewater treatment.

1. Introduction

Humic substances (HS) are formed in nature by biological decomposition of organic matter, particularly plants [1] and are an important fraction of the biologically recalcitrant material from landfill leachates [2]. HS are organic macromolecules of high structural complexity, composed of a skeleton of aromatic blocks and alkyl chains with a diversity of functional groups, notably carboxyl, phenol, hydroxyl, and quinone groups [3]. Humic acids (HA) are the fraction of HS soluble in water at neutral and basic pH [4].

Owing to their solubility, HA are common water contaminants, hence procedures for their removal from water have been extensively investigated [5, 6]. The most common and economically feasible process is considered to be coagulation/flocculation with iron, aluminum, or calcium ions, followed by precipitation [7]. In recent years, there has been increasing interest on the application of electrochemical processes (EC) to wastewater treatment [8, 9]. Depending on the operating conditions and the type of pollutants, a diversity of reactions can occur at the electrodes and in solution. With appropriate electrodes, oxidation of organic pollutants can occur directly on the anode, or in solution by the action of oxidant compounds produced at the anode, resulting in complete mineralization of the pollutant [10].

Many different anode materials have been investigated, and particularly promising results have been obtained with boron-doped diamond (BDD) and BDD-coated metals such as niobium, tantalum, or tungsten, yet their large-scale utilization is generally hampered by high cost [11]. A convenient electrochemical technology for wastewater
treatment is electrofloculation using relatively cheap aluminum or iron anodes [12]. The $\text{Al}^{3+}$ cation is obtained at the aluminum anode:

$$\text{Al}_{(s)} \rightarrow \text{Al}^{3+}_{(aq)} + 3e^- \quad (1)$$

This cation rapidly hydrolyzes giving mono- and polynuclear complexes [13] that cause pollutant flocculation/coagulation [7, 14]. The anodic half-reaction is accompanied by the evolution of tiny bubbles of hydrogen at the cathode, due to water reduction:

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

which helps flocculated particles to rise to the surface [15]. For solutions containing chloride ion, already present in polluted water or added intentionally, the following anodic oxidation also occurs:

$$2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \quad (3)$$

followed by

$$\text{Cl}_2 (aq) \rightarrow \text{HClO}_{(aq)} + \text{Cl}^- (aq) + \text{H}^+ (aq) \quad (4)$$

Chlorine and its derivatives are largely used in municipal wastewater treatment. During the last decades, the electrochemical removal of HA has been extensively studied to understand the physicochemical process and the experimental parameters for a higher efficiency and analyze the emerging technical applications [16, 17].

In this study, we investigated electrochemical removal of humic acids with focus on the effect of electric current density and NaCl concentration on the energy requirement. Underground and surface water (lakes and rivers) usually contain chloride ion; moreover, this is commonly present in wastewater, due to contamination from seawater ([Cl$^-$]=0.5 mol·L$^{-1}$) or from human activities. A major drawback of electrochemical procedures for pollutant removal is the energy requirement.

2. Materials and Methods

2.1. Materials. A sample of leonardite was purchased from Biotron (Italy) and used as a source for humic acid (HA) extraction by basic/acid treatment according to the procedure reported in former work [18], total organic carbon of the HA sample $\approx 45\%$. All other chemicals used have been supplied from Sigma-Aldrich.

2.2. Electrochemical Treatments. Electrochemical experiments were performed at about 25°C in a 1.0 liter batch reactor containing 500 mL of 50 mg·L$^{-1}$ HA solution, pH = 7.0, obtained by adding, under magnetic stirring, few drops of dilute NaOH solution to an aqueous suspension of HA. NaCl salt was added to the HA solution to a final concentration of 0.04, 0.08 or 1.5 mol·L$^{-1}$. In some experiments, instead of NaCl, NaNO$_3$ 0.08 mol·L$^{-1}$ was added. The electrochemical cell consisted of two aluminum anodes and two aluminum cathodes of $100 \times 50 \times 2$ mm, with 1 cm gaps between them arranged as shown in Figure 1. The total immersed active surface was 75 cm$^2$. Before use, the electrodes were briefly treated with 10% sodium hydroxide and carefully rinsed with distilled water. The electrodes were connected to a direct-current power supply (Lavolta BPS305) with a 0–30 V variable voltage and 0–5 A variable intensity. The electrochemical tests were carried out under galvanostatic conditions at values of current intensity varying between 0.075 and 0.7 A.

At selected intervals, a small aliquot (~2 mL) of the liquid mixture was centrifuged at 3000 rpm for 10 min and HA amount in solution was determined by UV-Vis spectroscopy at 450 nm on a Lambda 40 spectrometer, PerkinElmer. Total organic carbon (TOC) was determined in selected experiments using a Shimadzu TOC-L total organic carbon analyzer. After each electrochemical treatment, the electrodes were washed with the Na$_2$P$_2$O$_7$ + NaOH solution (and the rinsing solution analyzed as reported above), in order to verify the occurrence of HA adsorbed on the electrode surface; in no case was HA present in measurable amount.

2.3. pH of Al(OH)$_3$ Saturated Solution. Ammonia concentrate solution was added drop by drop to a 100 g·L$^{-1}$ AlCl$_3$ solution until complete precipitation of Al(OH)$_3$. The precipitate was collected by centrifugation, washed with deionized water until a negative response with the Nessler test. Al(OH)$_3$ was then added to 0.08 mol·L$^{-1}$ NaCl solution, and the suspension was kept for two days under stirring. Finally, the pH was determined by a glass electrode.

2.4. Organic Carbon Determination. The total organic carbon has been determined at the end of some electroremoval runs using a TOC-L CSN carbon analyzer (Shimadzu). Samples were heated at 680°C in an oxygen-rich environment inside combustion tubes filled with a platinum catalyst. The carbon dioxide generated by oxidation was detected using an infrared gas analyzer.

3. Results and Discussion

3.1. HA Removal. In all the experiments, the HA starting concentration was 50 mg·L$^{-1}$ at pH 7.0. During the electrochemical processes, we visually observed the disappearance of the brown color imparted by HA to the solution and the formation of a flocculent precipitate of aluminum hydroxide as well as, in some cases, of organic material (see Section 3.3). In the course of electrochemical runs, the pH slowly increased from the initial value 7.0 to about 8.5. A 0.08 mol·L$^{-1}$ NaCl solution saturated with Al(OH)$_3$ has a pH value of 8.8. A similar pH change has been observed in other studies of electrocoagulation with an aluminum anode [19]. These suggest that the prevalent reactions in solution are as in equations (1), (2), and (5):

$$\text{Al}^{3+}_{(aq)} + 3\text{OH}^-(aq) \rightarrow \text{Al(OH)}_{3l} \quad (5)$$

In the pH range recorded during electrochemical runs, the chemical forms in solution undergo no important
alteration, aluminum ions remaining prevalently in the [Al(OH)₄]⁻ form [13], and HA molecules retaining much the same electric charge from deprotonation of carboxylic groups and protonation of phenolic groups. In contrast, the pH range from 7 to 8.5 covers the dissociation equilibrium of HClO (pK_a = 7.55) produced by disproportion of Cl₂.

Figure 2 reports the evolution of UV-Vis spectrum in a typical electrochemical removal run.

Apart from differences in absorbance values, the spectra were very similar, suggesting that the process does not produce new molecules active in the UV-Vis region analyzed. Dividing the absorbance of each curve by the value recorded at 350 nm, we obtained completely superimposable normalized spectra (data not shown). Similar results have been recorded under all the other experimental conditions tested. Our results are consistent with that of Trellu and coworkers [20] reporting no change in the UV spectrum of the reactant solution during HA removal by anodic electrooxidation. The absence of intermediates during HA electrocoagulation by aluminum electrodes has also been confirmed by FTIR spectra and HPLC analysis [19].

3.2. Electrolyte and Current Density Effect. Figure 3 reports some results of the electroremoval runs carried out using NaCl or NaNO₃ as electrolytes, at under different levels of current density.

Under lower levels of current density (1 or 5 A·m⁻²), the electroremoval rate was much higher using NaCl than NaNO₃; in contrast, with J = 10 A·m⁻², the two electrolytes produced a similar effect.

The effect of electrolyte concentration was tested using different NaCl concentrations; the results showed an increase in HA removal rate with higher electrolyte concentrations (Figure 4).

The last result is a clear indication that NaCl participates in HA removal not only as a simple carrier of electric charge but also exerting a more direct effect; this suggests that electrocoagulation is not the only process responsible for the observed abatement of HA concentration. Electrocoagulation directly depends on Al³⁺ formation, which in the absence of other reactions in solution is likely to be independent of NaCl concentration. A possible explanation for the effect of NaCl concentration is that this affects chlorine formation, which in turn contributes to reduce HA concentration in solution by oxidation reactions.

The effect of current density on the HA removal from water is displayed in Figure 5.

As can be seen, HA removal rate increases with J. This in accordance with the fact that the increase in J promotes an increase in the Al³⁺ and Cl₂ formation rate.
3.3. Total Carbon Amount. Total organic carbon (TOC) in solution was measured when residue HA level, determined by UV-Vis spectroscopic absorbance, was below 10% of initial concentration. Table 1 reports the results. With the only exception of the last experiment data, residual TOC in solution was less than 10% of the initial value, showing that the UV-Vis absorbance is a reliable indicator of HA removal.

3.4. Energy Consumption Evaluation. The electrical potential difference (ΔV) at the electrodes remained constant for the duration of the tests under all the experimental conditions (Figure 6). As reported in Materials and Methods, we imposed a constant current intensity. The observed stability of ΔV reflects a constant conductivity of the system and is a good indication for the absence of electrode passivation.

Table 2 reports variations in electrical potential during the time necessary for 90% HA removal at three values of current intensity. Energy consumption was computed from these data. The energy consumption varied considerably with experimental conditions. In particular, comparison of

![Figure 3: HA electroremoval run in the presence of NaCl 8.0 · 10⁻² mol·L⁻¹ or NaNO₃ 8.0 · 10⁻² mol·L⁻¹, under three different levels of current density (J).

![Figure 4: NaCl concentration effect on HA removal.

![Figure 5: Time dependence of the HA removal at different current density; [NaCl] = 0.08 mol·L⁻¹.

Table 1: Total organic carbon (TOC) recorded at the end of electroremoval runs (HA removal >90%). At t = 0, TOC = 22.6 mg/L.

<table>
<thead>
<tr>
<th>Salt concentration (mol/L)</th>
<th>Density current (A/m²)</th>
<th>TOC liquid phase (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001 NaCl</td>
<td>10</td>
<td>1.7</td>
</tr>
<tr>
<td>0.001 NaCl</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>0.08 NaCl</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>0.08 NaCl</td>
<td>50</td>
<td>0.8</td>
</tr>
<tr>
<td>0.08 NaCl</td>
<td>100</td>
<td>0.7</td>
</tr>
<tr>
<td>0.08 NaNO₃</td>
<td>10</td>
<td>1.3</td>
</tr>
<tr>
<td>0.08 NaNO₃</td>
<td>50</td>
<td>2.3</td>
</tr>
<tr>
<td>0.08 NaNO₃</td>
<td>100</td>
<td>4.6</td>
</tr>
</tbody>
</table>
experiments 2, 6, and 9 with 11, 12, and 13, respectively, shows that the process was much more energy-demanding when using NaNO₃ as electrolyte because of the higher voltage and a longer time was necessary for 90% HA removal. Of particular interest is that, leaving unchanged the other parameters, energy consumption decreased with lower values of current intensity and higher salt concentration, both conditions determining a reduction in the voltage measured. It is reasonable to suppose that higher $\Delta V$ values favour water oxidation in competition with the formation of Al³⁺ ions.

Intermediates and final products of electrochemical treatment in the presence of chloride anions and the cost of procedures aimed at reducing their formation, if necessary, are under study in our laboratories.

Table 2: Experimental parameters and corresponding energy consumption for 90% HA removal: starting concentration $= 50 \text{ mg L}^{-1}$, volume $= 0.5 \text{ L}$.

<table>
<thead>
<tr>
<th>Number of the experiment</th>
<th>Electrolyte</th>
<th>Current density (A·m$^{-2}$)</th>
<th>Current intensity (A)</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
<th>Energy (joule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl 0.001 M</td>
<td>10</td>
<td>0.075</td>
<td>6.1</td>
<td>30</td>
<td>824</td>
</tr>
<tr>
<td>2</td>
<td>NaCl 0.08 M</td>
<td>10</td>
<td>0.075</td>
<td>1.2</td>
<td>15</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>NaCl 1.5 M</td>
<td>10</td>
<td>0.075</td>
<td>0.8</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>NaCl 0.001 M</td>
<td>50</td>
<td>0.375</td>
<td>25.1</td>
<td>15</td>
<td>8470</td>
</tr>
<tr>
<td>5</td>
<td>NaCl 0.04 M</td>
<td>50</td>
<td>0.375</td>
<td>2.8</td>
<td>50</td>
<td>3150</td>
</tr>
<tr>
<td>6</td>
<td>NaCl 0.08 M</td>
<td>50</td>
<td>0.375</td>
<td>2.2</td>
<td>20</td>
<td>990</td>
</tr>
<tr>
<td>7</td>
<td>NaCl 1.5 M</td>
<td>50</td>
<td>0.375</td>
<td>1.0</td>
<td>10</td>
<td>225</td>
</tr>
<tr>
<td>8</td>
<td>NaCl 0.001 M</td>
<td>100</td>
<td>0.75</td>
<td>3.0</td>
<td>15</td>
<td>1890</td>
</tr>
<tr>
<td>9</td>
<td>NaCl 0.08 M</td>
<td>100</td>
<td>0.75</td>
<td>2.2</td>
<td>10</td>
<td>924</td>
</tr>
<tr>
<td>10</td>
<td>NaCl 1.5 M</td>
<td>100</td>
<td>0.75</td>
<td>1.1</td>
<td>10</td>
<td>462</td>
</tr>
<tr>
<td>11</td>
<td>NaNO₃ 0.08 M</td>
<td>10</td>
<td>0.075</td>
<td>3.5</td>
<td>90</td>
<td>1418</td>
</tr>
<tr>
<td>12</td>
<td>NaNO₃ 0.08 M</td>
<td>50</td>
<td>0.375</td>
<td>4.3</td>
<td>100</td>
<td>9675</td>
</tr>
<tr>
<td>13</td>
<td>NaNO₃ 0.08 M</td>
<td>100</td>
<td>0.75</td>
<td>5.3</td>
<td>10</td>
<td>2226</td>
</tr>
</tbody>
</table>

![Figure 6: Time dependence of $\Delta V$ during electrocoagulation runs ($[\text{NaCl}] = 0.08 \text{ mol L}^{-1}$).](image)

Table 2: Experimental parameters and corresponding energy consumption for 90% HA removal: starting concentration $= 50 \text{ mg L}^{-1}$, volume $= 0.5 \text{ L}$.

The data reported in figures are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful to the prof. Roberto Ligrone for comments and suggestions and to dr. Vincenzo Leone and dr. Antonio Ferone De Cristofaro for their support in chemical analyses.

References


