Electrochemical Removal of Cu\textsuperscript{II} in the Presence of Humic Acid

Claudimiro P. Barbosa,\textsuperscript{a} Geoffroy R. P. Malpass,\textsuperscript{a,b} Douglas W. Miwa,\textsuperscript{a} Luciano Gomes,\textsuperscript{a} Rodnei Bertazzoli\textsuperscript{c} and Artur J. Motheo*\textsuperscript{a}

\textsuperscript{a}Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970 São Carlos-SP, Brazil

\textsuperscript{b}Universidade Federal do ABC, 09210-170 Santo André-SP, Brazil

\textsuperscript{c}Universidade Estadual de Campinas, CP 6122, 13083-970 Campinas-SP, Brazil

A remoção de Cu\textsuperscript{II} (10 mg L\textsuperscript{-1}) complexado por ácido húmico comercial (100 mg L\textsuperscript{-1}) foi estudada a diferentes densidades de corrente (30-80 mA cm\textsuperscript{-2}) usando uma célula filtro-prensa, ánodo de Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} e cátodo de aço inoxidável. As eletrólises foram feitas com e sem membrana separando os compartimentos da célula [aniónica homogênea (Nafion R117), catiónica heterogênea (Ionac MC-3470) e aniónica heterogênea (Ionac MA-3475)]. A influência da membrana na velocidade de remoção de Cu\textsuperscript{II} foi maior com as catiónicas. Foi obtida eficiência de corrente de ca. 55% (Ionac MC-3470) para remoção de Cu\textsuperscript{II} a 30 mA cm\textsuperscript{-2}. Combinando oxidação e redução, foi obtida remoção de 100% de Cu\textsuperscript{II} com eficiência de corrente de 75%. A etapa principal para a remoção é interação eletrostática com o ánodo, seguida pela difusão através da membrana e deposição sobre o cátodo. Adicionalmente, a degradação oxidativa de ácido húmico contribui com a velocidade de remoção de Cu\textsuperscript{II}.

The removal of Cu\textsuperscript{II} (10 mg L\textsuperscript{-1}) complexed by commercial humic acid (100 mg L\textsuperscript{-1}) was studied at different current densities (30-80 mA cm\textsuperscript{-2}) using a filter-press cell, Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} anode and stainless steel cathode. The electrolyses were performed with and without membrane separating the cell compartments [(homogeneous anionic (Nafion R117), heterogeneous cationic (Ionac MC-3470) and heterogeneous anionic (Ionac MA-3475)]. The influence of the membrane on the rate of Cu\textsuperscript{II} removal was bigger for cationic membranes. Current efficiencies up to ca. 55% (Ionac MC-3470) for Cu\textsuperscript{II} removal at 30 mA cm\textsuperscript{-2} were obtained. By combining oxidation and reduction, 100% Cu\textsuperscript{II} removal was achieved at current efficiencies of 75%. The main path for the removal is the electrostatic interaction with the anode followed by diffusion through the membrane and deposition at the cathode. Additionally, the oxidative degradation of humic acid contributes to the rate of Cu\textsuperscript{II} removal.

Keywords: humic acid, copper removal, water treatment

Introduction

Humic acid (HA) is one of the principal components of humic matter, which is the major constituent of soil organic content. Humic matter can be described as a refractory, dark-colored organic substance, which is produced as a by-product of microbial metabolism in the environment.\textsuperscript{1} The structure of humic substances (HS) is still a matter for debate; previously it was thought they consisted of randomly coiled macromolecules of between 20,000-50,000 Da. More recently a supramolecular model has been favored, in which many small organic species form clusters that are held together by H-bonding and hydrophobic interactions.\textsuperscript{2}

Humic acids generally account for approximately 50\% of dissolved organic material (DOM) found in natural waters.\textsuperscript{3} Due to its complex and refractory structure the presence of HA in water destined for treatment is of considerable concern, complicating treatment procedures.\textsuperscript{4}

Humic substances present an important source of dissolved organic functional groups (e.g., phenolic and carboxylic groups, –OH and –COOH), which complex metal ions found in the soil, sediment or water systems. For instance, Merce \textit{et al.}\textsuperscript{5,6} studied the complexing behavior...
of some HA models in the presence of molybdenum (VI) ions in order to determine the affinity of these substances towards the metal ion, in aqueous systems.

Due to this strong complexing ability, metal ions complexed by HA may remain in solution after treatment with most of the technologies currently available. One of the possible alternative methods for the treatment of water and wastewater containing HA and metal ions is a paired electrochemical reduction/oxidation, where electro-oxidation of humic substances may set metal ions free for reduction at the cathode surface. Literature has reported a number of case studies in which metal ions in solution have successfully been removed by electro-reduction at different electrode materials.\(^7\text{-}^\text{10}\)

Some studies\(^1\text{11-13}\) have also shown the feasibility of electro-degradation of humic substances. As already stated, electrochemical methods are interesting when considering the treatment of metal-complexed HA where not only the HA can be degraded, but also the metal ions can be removed by deposition on a cathode with reasonable current efficiencies. In a recent paper, Chaudary et al.\(^1\text{4}\) studied the simultaneous degradation/removal of the EDTA/Cu system and noted that the electrochemical-based system was only capable of reducing the Cu content, but did not appreciably degrade the EDTA found. Also, the simultaneous application of UV radiation was observed to enhance the removal of EDTA.\(^1\text{4}\)

Similar results are reported by Grimes et al.\(^1\text{5}\) for solutions containing phthalic acid and cobalt. Overall, for a reasonable degradation of organics insolution, in the electrochemical system, it is necessary the generation of strong oxidizing agents (e.g., OH radicals, $\text{H}_2\text{O}_2$, or $\text{O}_3$). An inexpensive and easily generated series of oxidizing agents are produced by the electrolysis of brine solutions and this has been demonstrated in many studies.\(^1\text{6-18}\)

Ion-exchange membranes are usually presented in many industrial processes, including water treatment.\(^1\text{9}\) They are also intensely used in Donnan membrane process for drinking water and wastewater treatment.\(^2\text{0}\) The ionic transport into these membranes is dependent of their structures, preparation methods and selectivity concerning to the ion polarity. Basically, two different types of ion-exchange membranes are considered: $i$) homogeneous, which consist mainly of ion-exchange material, having the fixed ionogenic groups almost uniformly distributed, and $ii$) heterogeneous, which present conducting and non-conducting areas corresponding to the resurgence of the ion exchanger and binder, respectively.\(^2\text{1,22}\)

The aim of the present paper is to study the electrochemical removal of Cu$^{II}$ ions complexed with humic acid in solution, using a flow-cell. It is well known that membranes can be used to separate the anodic and cathodic compartments, enhancing the flow of ions toward the electrodes but restricting the reverse flow, minimizing the possibility of intermediate chemical reactions taking place that would otherwise produce unwanted substances. Also, the inclusion of the membrane therefore, gives a more concentrated separation of the ions produced and more efficient operation. So, in present work the influence of the ion-exchange membrane used to divide anodic and cathodic compartments of the electrochemical cell is investigated, as well as the effect of varying the current density. The strategy adopted was to first investigate the extent of Cu$^{II}$ removal in an undivided cell and then repeat the measurements with a membrane (homogeneous and heterogeneous) separating the anodic and cathodic compartments. The results provided information about whether HA break-up or electrostatic (Cu$^{II}$-cathode) interactions have the greatest influence on the break-up of the Cu$^{II}$-HA complex. Finally, to better understand the mechanism of Cu$^{II}$ removal, the effect of first performing either oxidation or reduction for 90 min followed by reduction or oxidation (for 90 more min) on the rate of Cu$^{II}$ removal was investigated.

**Experimental**

**Electrochemical apparatus**

A two-compartment filter-press cell was mounted using Viton and Teflon spacers of different thickness (Figure 1). The anode was a DSA\(^2\) plate of a nominal composition of Ti/Ru\(_{0.8}\)Ti\(_{0.2}\)O\(_2\) (exposed area = 2 cm\(^2\)) and a stainless steel cathode of the same area.\(^2\text{3,24}\) The anodic and cathodic compartments were separated (or not) by a membrane, depending on the experiment. Additionally, the type of membrane used also varied. When using a membrane, the electrolyte flow through the cell from two independent electrolyte reservoirs (each containing 50 mL), provided by peristaltic pumps working at 80 rpm (28 cm\(^2\) min\(^{-1}\)).\(^2\text{4}\) The anolyte (working solution) was prepared with HA complexed (100 mg L\(^{-1}\)) with Cu$^{II}$ (10 mg L\(^{-1}\)) dissolved in NaCl (0.05 mol L\(^{-1}\)) and the catholyte consisted of NaCl (0.05 mol L\(^{-1}\)). Samples were removed from the anolyte and catholyte at predetermined times during the electrolysis and were then submitted to analysis.

The cyclic voltammetry experiments were performed at a sweep-rate of 50 mV s\(^{-1}\) using a potentiostat (EG&G/PAR model 273). For the cyclic voltammetry experiments the same set up as given above was used, but the electrode was a Pt plate (exposed area = 2 cm\(^2\)). Where quoted, all potentials are reported against the saturated calomel electrode (SCE).

Three types of membranes were used and classified as: homogeneous -Nafion R117 from DuPont and
heterogeneous-Ionac anionic (MA-3475) and Ionac cathionic (MC-3470) from Sybron Chemicals, NJ. The Nafion R117 membrane consists of a non-reinforced resin of the copolymer of perfluorosulfonic acid/PTFE in the H\(^+\) form. The Ionac membranes consist of a fiber web covered with a suitable chemically stable paste and characterized by strongly ionized functionality, which results in high permselectivity for industrial processes. Some characteristics of the membranes used are provided in the Table 1.

### Table 1. Characteristics of the membranes

<table>
<thead>
<tr>
<th></th>
<th>Homogeneous Nafion R117</th>
<th>Homogeneous MC-3470</th>
<th>Heterogeneous Ionac MA-3475</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>0.127</td>
<td>0.381</td>
<td>0.406</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>1.5</td>
<td>25 (in 0.1 mol L(^{-1}) NaCl)</td>
<td>50 (in 0.1 mol L(^{-1}) NaCl)</td>
</tr>
<tr>
<td>Conductivity (S cm(^{-1}))</td>
<td>0.083</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Molar mass (g mol(^{-1}))</td>
<td>1100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ionic exchange capability</td>
<td>0.9</td>
<td>1.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**Reagents and solutions**

The NaCl and CuSO\(_4\) salts (both Merck p.a.) were used without further purification. The HA (Aldrich) was dissolved in water, passed through an Amberlite IR-120 ionic resin column (acid form) to remove metallic cations and then through an Amberlite IRA-400 column (basic form) to remove chloride ions. After purification the water was removed and the resulting solid was stored in a desiccator until use.

The solution of Cu\(^{II}\) complexed by HA was prepared in the following manner: a solution of the purified HA (100 mg L\(^{-1}\)) was added to a solution of NaCl (0.05 mol L\(^{-1}\)) and subsequently CuSO\(_4\) (10 mg L\(^{-1}\)) was added. The pH was adjusted to 5 with NaOH (0.1 mol L\(^{-1}\)) and the solution was left under magnetic stirring for 24 h.

**Cu analysis**

Samples of 350 µL were removed from the reaction mixture and prepared by adding 2 mL of concentrated nitric acid, heating until reflux, mixed with 2 mL H\(_2\)O and then submitted for analysis. The determination of Cu\(^{II}\) removal by atomic absorption spectroscopy (AAS) analysis was performed by using a Hitachi model z-8100 equipped with a flame-atomizer and a Zeeman polarizer. The values of Cu\(^{II}\) obtained represent the concentration from both compartments (anodic and cathodic). All experiments were performed in triplicate.

**Humic acid analysis**

The degradation of HA was followed by UV-Vis spectroscopy and quantified by the decrease in absorbance at 400 nm, given as UV\(_{400}\) which is commonly used in the literature. Total organic carbon (TOC-Shimadzu) was also employed to determine the extent of overall degradation. All experiments were performed in triplicate.

**Results and Discussion**

**Cyclic voltammetry**

As a first stage analysis, the voltammetric behavior of a Pt electrode immersed in a solution of Cu\(^{II}\) (0.68 mol L\(^{-1}\)) in the presence and absence of HA was analyzed at 50 mV s\(^{-1}\). From Figure 2 it can be observed that in the absence of HA there is a distinct Cu stripping peak (peak 1) at approximately 0.1 V vs. SCE on the reverse sweep. However, when Cu\(^{II}\) complexed by HA is studied, there is a discernable decrease in the current associated with the Cu stripping process in peak 1, as observed by the inset of Figure 2 where the values of...
Electrochemical Removal of Cu\textsuperscript{II} in the Presence of Humic Acid


the current variation of peak 1 is represented as a function of the concentration of HA. The current has an exponential dependence with the HA concentration. However, it is possible to consider that up to ca. 1 g L\textsuperscript{-1} HA, the decrease in the current density presents linear behavior with a decrease of approximately 0.280 mA for every 1 g L\textsuperscript{-1} of HA added to the solution. Following this interpretation, as the HA concentration increases above 1 g L\textsuperscript{-1} the peak current reaches an almost steady state at a value of 0.9 mA cm\textsuperscript{2}. This value can be consider as a residual peak current value due to the electrostatic interaction between the Cu\textsuperscript{II} complexed with HA and the negatively charged electrode.

Previous studies indicate that the Cu\textsuperscript{II} level of complexation by HA is in the region of 28 mg (Cu\textsuperscript{II}) g\textsuperscript{-1} (HA).\textsuperscript{21} In the Figure 2 inset one can consider that 40 mg L\textsuperscript{-1} of Cu\textsuperscript{II} is in solution with 1.5 g L\textsuperscript{-1} of HA; over this concentration a steady state occurs. Therefore, the ratio Cu\textsuperscript{II}:HA is 1.5 g L\textsuperscript{-1}, and we have a value of ca. 26.7 mg (Cu\textsuperscript{II}) g\textsuperscript{-1} (HA), which is in broad agreement with the literature.\textsuperscript{25} These observations indicate that the Cu\textsuperscript{II} complexes almost completely with HA in solution; the literature provides a reference value of > 99%.\textsuperscript{26}

Cu\textsuperscript{II} removal using an undivided cell

Galvanostatic treatment of Cu\textsuperscript{II} solution (10 mg L\textsuperscript{-1}) complexed with HA (100 mg L\textsuperscript{-1}), with 0.01 mol L\textsuperscript{-1} NaCl added as supporting electrolyte, was performed varying current densities (30-85 mA cm\textsuperscript{2}) with no membrane between the anodic and cathodic compartments. Electrolyses were performed in time intervals of 3 h and the removal of Cu\textsuperscript{II} is exemplified for three values of current density in Figure 3. It can be seen that the lower the current density, the faster the copper concentration decreases. In fact, the initial rate of Cu\textsuperscript{II} removal decrease (up to 40 min of electrolysis) falls with increasing current density. Comparing the two limiting current densities used (30 and 85 mA cm\textsuperscript{2}) it is possible to estimate that after 3 h of treatment there is a difference of approximately 22% between the remaining copper in solution, which is shown in the inset of Figure 3. To support these observations, the current efficiency values associated with the Cu\textsuperscript{II} removal are presented in Table 2. This would appear to be unusual behavior, but it must be remembered that this phenomenon is probably due to the presence of HA in solution, which is free to interact at the anode or cathode and such an interaction would probably increase with increasing

![Figure 2](image-url)

**Figure 2.** Voltammetric profile of the Pt electrode in the presence of 40 mg L\textsuperscript{-1} Cu\textsuperscript{II} at different HA concentrations: (solid line) no HA, (dotted line) 0.30 g L\textsuperscript{-1} HA and (dashed line) 1.50 g L\textsuperscript{-1} HA. v = 50 mV s\textsuperscript{-1}. Arrows represent the sweep direction. *Inset:* Variation of current density for peak 1 with HA concentration. Sweep rate = 50 mV s\textsuperscript{-1}.

![Figure 3](image-url)

**Figure 3.** Removal of Cu\textsuperscript{II} in the presence of 100 mg L\textsuperscript{-1} HA during electrolysis at (○) 30; (□) 50; (▲) 85 mA cm\textsuperscript{2} using an undivided cell. *Inset:* quantity (%) of Cu\textsuperscript{II} removed as a function of current density.

<table>
<thead>
<tr>
<th>Cationic membrane</th>
<th>Heterogeneous (Ionac)</th>
<th>Homogeneous (Nafion)</th>
<th>No membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>j (mA cm\textsuperscript{-2})</td>
<td>ΔCu\textsuperscript{II} (%)</td>
<td>I\textsubscript{Cu} (%)</td>
<td>ΔCu\textsuperscript{II} (%)</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>55.86</td>
<td>91.4</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>41.90</td>
<td>98.6</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>33.52</td>
<td>90</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>27.93</td>
<td>100</td>
</tr>
<tr>
<td>85</td>
<td>100</td>
<td>19.72</td>
<td>90</td>
</tr>
</tbody>
</table>

![Table 2](image-url)

**Table 2.** Current efficiency (I\textsubscript{Cu}) for the removal of Cu\textsuperscript{II} (ΔCu\textsuperscript{II}) from solutions containing 40 mg L\textsuperscript{-1} Cu\textsuperscript{II} and 100 mg L\textsuperscript{-1} HA using a flow cell with and without membranes dividing the anodic and cathodic compartments.
current density. The recent literature demonstrates that the presence of chelating agents decreases the rate of Cu\(^{II}\) removal and this is attributed to the formation of the chelate-metal complex, transport to the electrode surface and increase in activation energy required to deposit the complexed metal. In addition, at higher current densities hydrogen evolution will be more significant, competing with Cu deposition.

It is well know that the chlorine species distribution in solution is a function of pH, and also that HOCl is the predominant species at the pH range 3 to 6. In the production of HOCl by electrolysis of salt solution, chlorine is produced at the anode where it reacts with water to form HClO:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \tag{1}
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ \tag{2}
\]

Meanwhile, in the cathode occurs the formation of hydroxyl species (OH\(^-\)):

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \tag{3}
\]

When copper is present in solution, its deposition occurs simultaneously:

\[
\text{Cu}^{II}(\text{aq}) + 2e^- \rightarrow \text{Cu}^{(s)} \tag{4}
\]

Depending on the cell design, flow rate and the presence or not of a membrane dividing the anodic and cathodic compartments, it is possible to have some parallel reactions, as the reaction of Cl\(_2\) with OH\(^-\) with the formation of hypochlorous ion (OCl\(^-\)):

\[
2\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OCl}^- + \text{Cl}^- \tag{5}
\]

The UV-Vis spectra of the HA solution in the absence and presence of Cu\(^{II}\) shows the peak of electro-generated hypochlorite (290 nm) after 3 h of electrolysis at 50 mA cm\(^{-2}\) (Figure 4). It can be observed that in the presence of Cu\(^{II}\) the height of the hypochlorite peak is reduced by about 35% when compared to the same peak in its absence. This can be explained by the deposition of the metal on the cathode (reaction 4) competing with reaction 3.

It should be noted that the color due to the presence of HA is removed (UV\(_{\text{app}}\)) extremely fast, achieved under 15 min. Under the conditions employed this oxidation process can be illustrated as:

\[
\text{HOCl} + \text{HA} \rightarrow \text{Intermediates} \rightarrow \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \tag{6}
\]

Previous studies\(^{11,13}\) have indicated that HA can be partially degraded to CO\(_2\) under the conditions used in this study, though it must be remembered that the break-up of such a complex, as that presented by HA, is much more complicated than for smaller molecules.

Before each electrolysis, the pH was set to 5 and in the literature is described that HA-Cu\(^{II}\) complexes are stable in the pH range 4 to 5,\(^{25}\) indicating that a simple decomplexation of the Cu\(^{II}\)-HA system due to pH change would not occur. The local pH (at the electrode surface) may vary, but as the system was used under flow conditions, it is improbable that local pH change greatly affected the extent of Cu\(^{II}\) removal.

Comparing cationic membranes: homogenous and heterogeneous

As observed in the previous section, in which the formation of ClO\(^-\) seems to inhibit the Cu\(^{II}\) removal, it was decided to study the effect of dividing the electrochemical cell using cationic membranes. In fact, a comparison between two types of membranes (homogeneous and heterogeneous) was performed.

The removal of Cu\(^{II}\) for both the membranes used was between 90 and 100%, after 3 h of electrolysis. The current efficiencies are given in Table 2 and for both membranes there is almost no observable effect of current density. The removal of Cu\(^{II}\) is generally faster in the case of the Ionac membrane. The UV spectra demonstrate that there is a distinct difference in the use of both membranes. For the Nafion membrane the peak at ca. 290 nm (ClO\(^-\)) does not appear, whereas in case of the Ionac membrane it is present at a value that is almost unchanged when compared to the undivided cell, thus indicating that there is significant HO\(^-\) cross-over to the anodic compartment to form hypochlorite.

For the Ionac membrane set up, it is probable that the break-up of the Cu-HA complex (and subsequent liberation
of Cu$^{II}$) is quicker than for the Nafion membrane due to the presence/formation of HClO in the anodic compartment. In the presence of the Nafion membrane the degradation will most likely be entirely due to the $\text{Cl}_2$ formed on the anode and drives electrochemical degradation. It is evident that the degree of HA degradation is an important factor for the removal of Cu$^{II}$; however it is also important to consider electrostatic (interaction cathode-Cu$^{II}$ ion) effects.

Using a anionic heterogeneous membrane

The separation of the electrochemical cell compartments using a heterogeneous anionic membrane resulted in the extent of Cu$^{II}$ removal with the current efficiencies, as presented in Table 2. It can be seen that the current efficiency is much reduced when compared to the cathionic membrane, indicating that cross-over of the Cu$^{II}$ cation is avoided. It should be noted that the rate of Cu$^{II}$ removal is initially slow, becoming quicker after 90 min. This phenomenon might suggest that HA is first destroyed before liberating Cu$^{II}$ to be deposited on the cathode.

Combined oxidation/reduction studies

Aiming to understand the possibility of either electrostatic interaction or the break-up HA, which is vital for the removal of Cu$^{II}$ complexed with the organic material, it was decided to study the effect of combining the oxidation/reduction processes. This was achieved by performing the following experiments using the anionic heterogeneous membrane.

Experiment A

In this experiment the degradation was performed with the HA-Cu$^{II}$ solution first undergoing oxidation (present in the anodic compartment while a positive current is applied) for 90 min and then inverting the electrical connections and performing reduction. The solution remained in the same compartment and only the external electrical connection was changed.

Experiment B

The same as experiment A, but reduction was performed first and then oxidation.

Both experiments A and B were performed for current densities between 30 and 80 mA cm$^{-2}$. From Figure 5a it is possible to observe that the Cu$^{II}$ removal during experiment A is slow in the oxidation step (1), but fast in the reduction step (2). As previously observed for the anionic membrane there was almost no dependence of Cu$^{II}$ removal on the current density. Considering a linear relationship for the data presented in Figure 5a, an average slope of $-0.011 \text{ mg L}^{-1}\text{min}^{-1}$ is obtained during the reduction step, whereas values from $-0.097$ to $0.130 \text{ mg L}^{-1}\text{min}^{-1}$ are obtained during the oxidation step range 30-80 mA cm$^{-2}$, respectively.

For the removal of Cu$^{II}$ during experiment B (Figure 5b) a similar behavior to that observed for experiment A is observed. During the reduction step the rapid Cu$^{II}$ removal is observed with a coefficient of $-0.07 \text{ mg L}^{-1}\text{min}^{-1}$, approximately 7 times faster than for experiment A. For the oxidation step, two linear grouped points can be considered with slopes of $-0.011$ [Figure 5b, (2)] and $-0.07 \text{ mg L}^{-1}\text{min}^{-1}$[Figure 5b, (3)], much lower than that obtained for experiment A.

Comparing current efficiencies for the reduction step given in Figure 6, it is apparent that experiment A at that stage of the treatment is more efficient than B. Figure 6 inset demonstrates that differences of up to 28% are possible, depending on the current density. The results stimulate the question: for the removal of Cu$^{II}$ from HA complexes what is more important, destruction of HA and liberation of Cu$^{II}$ or electrostatic interaction (overcoming of metal-functional group interactions)? The results of this study...
indicate that both considerations are important. When the removal of Cu\textsuperscript{II} is aided with the initial anodic break-up of the HA, structure efficiencies and removal rates tend to be much greater.

Considering the results obtained here, it is apparent that electrostatic interaction is the main mechanism for Cu\textsuperscript{II} removal from the solution. However, in experiment A it is also clear that the degradation of HA has a significant effect on the final amount of Cu\textsuperscript{II} deposited. It should be noted that the degradation of HA is primarily achieved in this study due to the use of NaCl as the supporting electrolyte and the subsequent reactions 1 to 3.

When experiment A is repeated with Na\textsubscript{2}SO\textsubscript{4} (without chloride in solution) almost no degradation of HA over 3 h of electrolysis was observed; however, the removal of Cu\textsuperscript{II} was quite expressive in the second phase of the experiment (reduction, Figure 7). It is possible that when using Na\textsubscript{2}SO\textsubscript{4} as the supporting electrolyte, another oxidizing species (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–}) can be generated, with a lower oxidizing power than of the Cl\textsuperscript{2}/ClO\textsuperscript{–} system. The slope for Cu\textsuperscript{II} removal in Figure 6 is $\sim$0.95 mg L\textsuperscript{–1} min\textsuperscript{–1} in the oxidation step, which is only slightly lower than the value obtained in the presence of NaCl. This, again, is a strong indication that electrostatic interactions play a vital role in the process.

**Total organic carbon removal (TOC) removal**

In order to obtain an idea of the extent of total organic carbon (TOC) removal, electrolyses (40 mA cm\textsuperscript{–2}) of 100 mg L\textsuperscript{–1} HA solutions (+ 10 mg L\textsuperscript{–1} Cu\textsuperscript{II}) for the membranes employed and also in the undivided cell were performed. In the case of the undivided cell, TOC removal in both the absence and presence of Cu\textsuperscript{II} was evaluated.

Figure 8 presents the extent of TOC removal as a function of electrolysis time and it can be seen that the greatest extent of removal is obtained when no membrane is used to separate the cell, and in this case a TOC removal of ca. 46% is obtained in both the absence and presence of Cu\textsuperscript{II}. This is an interesting result considering that the presence of Cu\textsuperscript{II} with other chelating agents like 2,4,5-trichlorophenoxyacetic acid\textsuperscript{27} or ethylenediaminetetraacetic acid (EDTA),\textsuperscript{28} decreases the rate of removal for both chelating agent and organic content. When a membrane is used to separate the cell there is a decrease in the amount of TOC, which varies with the type of membrane used. For the heterogeneous Ionac membranes removals of ca. 32% (cathionic) and ca. 19% (anionic) are obtained, whereas for the homogeneous Nafion membrane ca. 9% is removed. From Figure 8 it can also be observed that the removal is practically linear with time. If this linear relationship is quantified, a slope of approximately $2.5 \times 10^{-3}$ min\textsuperscript{–1} is obtained when no membrane is used. When the membranes are used, slopes of 1.7, 1.0 and $0.5 \times 10^{-3}$ min\textsuperscript{–1} are obtained for the Ionac (anionic), Ionac (cathionic) and Nafion membrane, respectively. The results for TOC removal are well compared to those of color removal obtained under the same conditions.

**Conclusions**

The membrane transport plays an important role in water treatment and, in the particular case described here, generated a comparison between some of the most used commercial membranes. However, this study started with the question: for the removal of Cu\textsuperscript{II} from HA complexes what is more important, the destruction of HA and liberation of Cu\textsuperscript{II} or the electrostatic interactions? The answer to this, considering the experimental evidences, is that both aspects are important so, the choice of an adequate membrane seems to be crucial in order to maximize the efficiency of the process. Taking into account the Cu\textsuperscript{II} removal, the cationic heterogeneous membrane (Ionac MC-3470) is more efficient probably because the break-up of
the Cu-HA complex (and subsequent liberation of Cu$^{II}$) is quicker than for the Naion membrane due to the presence/formation of hypochlorite in the anodic compartment. On the other hand, the TOC removals observed for the experimental setup with different membranes show also that the cationic heterogeneous membrane is the more efficient.

In addition, by performing combined oxidation/reduction experiments it was possible to obtain 100% Cu$^{II}$ removal at maximum current efficiencies of about 75%, which gives an indication of the treatment to be applied to real systems.

Acknowledgments

The financial support and individual grants are acknowledged to the Brazilian science support agencies: CNPq and CAPES.

References


Received: May 26, 2009
Web Release Date: December 16, 2009

FAPESP helped in meeting the publication costs of this article.