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USE OF A FLOW-THROUGH POROUS ELECTRODE FOR REMOVAL OF MERCURY FROM CONTAMINATED BRINE SOLUTIONS

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ABSTRACT

Experiments conducted in this laboratory show that mercury-contaminated brine solutions can be purified by reduction of the mercury in a flow-through porous carbon electrode (fixed-bed electrochemical reactor). Diffusion-limited currents can easily be attained under potentiostatic operation, and mercury concentrations in 4 M NaCl solutions can be decreased, without serious side reactions, from 34 ppm to less than 5 ppb with flowrates as high as 12 bed-volumes per hour. These results indicate that a flow-through porous electrode may be an attractive processing alternative for contaminated brine solutions. In addition, the mercury system appears to be an ideal candidate for the general study of reactors of this sort.

Introduction

The use of flow-through porous electrodes for removal of heavy metal ions from contaminated aqueous solutions has been discussed frequently in the electrochemistry literature. Many possible systems have been suggested (such as silver, gold, mercury, copper, lead, cadmium and antimony). This work concerns removal of mercury from contaminated brine (concentrated salt water) and follows closely previous investigations of copper removal using a similar technique (1). In all of these systems the basic principle of separation is the same: the heavy metal is removed by electrodeposition while the solution is passing through a high surface area porous bed cathode. Results of this study on mercury show that the method is efficient and effective for decontamination of brine solutions, and, in addition, the results indicate that the mercury deposition system, due to its simplicity, is ideal for the general study of flow-through reactors of this type.

There exist both practical and theoretical reasons for pursuing an investigation of the mercury system. Firstly, the removal of mercury from brine solutions has been a problem of interest in the chlor-alkali industry, and the removal of mercury from contaminated aqueous streams is a matter of general environmental concern as well. Present technology for removing mercury from these solutions uses a chemical method (precipitation of the mercury as mercuric sulfide by addition of hydrogen sulfide to the solution). A flow-through porous electrode is a possible alternative to this technique. Secondly, single metal deposition experiments, such as these for mercury, without side reactions, are extremely useful in general studies of flow-through porous electrodes due to the simplicity of the chemical reaction phenomena.

Electrochemical System

The overall electrochemical system used in this study is shown below:
Cathode: Mercury Reduction

\[ \text{HgCl}_4^{-2} + 2e^- \rightarrow \text{Hg} + 4\text{Cl}^- \]

Anode: Oxygen Evolution

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \]

In all of the experiments presented here, the catholyte is composed of 4 M NaCl solution containing mercury concentrations of about 50 ppm. Mercury is highly soluble in chloride solutions due to the complexing of the mercuric ion. In the range of concentrations and potentials of this study, \( \text{HgCl}_4^{-2} \) ion is the predominant mercuric species. The solution is slightly acidic (pH = 4); however, hydrogen is not evolved due to the location of the operating potentials for the mercury deposition reaction. At the anode, oxygen is evolved from an anolyte of the same salt concentration as the catholyte (without the mercury). Although chlorine evolution is possible thermodynamically, none is observed under the conditions of this study.

Figure 1 shows a plot of the Nernst equation for this system. An electrochemical method for the removal of mercury would be expected to be effective due to the low equilibrium mercury concentrations which exist even at moderate polarizations. (The abscissa (\( V - \Phi_{\text{ref}} \)) represents the potential of the working electrode with respect to a saturated calomel reference electrode (SCE).) It can be seen that the concentration drops by orders of magnitude (logarithmic ordinate) over potential ranges of only a few millivolts. In this study, inlet concentrations of Hg of 50 ppm correspond to \(-5\) mV with respect to an SCE.

Electrode Configuration

Once a decision to attempt an electrochemical method of this type has been made, it is necessary to determine the arrangement of the electrodes which constitute the reactor. Figure 2 shows two possible electrode configurations. Both of these configurations are considered flow-through. The term flow-through here indicates a configuration wherein the fluid flow and current flow are parallel. Consequently, one can use a one-dimensional model as a theoretical representation of the system.

Figure 2 (a) shows upstream (before fluid inlet) placement of the counterelectrode, and Figure 2 (b) shows downstream placement. If the electrical conductivity of the solid packed bed is much higher than the electrolyte solution (which is the case here and is very typical of porous electrode applications), much better performance can be expected from upstream placement of the counterelectrode (2). In the upstream counterelectrode configuration, lower effluent concentrations are attainable, and the resistance losses (ohmic potential drop) are smaller than in the case of downstream placement. Therefore, only the upstream counterelectrode placement is used in this study.

Experimental Apparatus

Figure 3 shows a sketch of the experimental reactor. The cell is glass, and the packing material consists of carbon flakes and chips (Union Carbide GP-22 granules plus powder). The cell diameter is 7.62 cm (cross sectional area of 45.6 cm\(^2\)). Five rows of 6 mm diameter glass beads (not shown in the figure) are placed above the carbon bed in order to distribute the fluid flow. The anode and cathode current collectors are made of tantalum. (This is necessary in order to eliminate corrosion due to the high chloride ion concentration in solution.)

During the experiments, the feed catholyte solutions are sparged with nitrogen in order to eliminate the interference of oxygen reduction at the cathode. A metering pump (Fluid Metering, Inc.) followed by a flow damper regulates the fluid flow, and the reactor compartment is kept at 25 °C by cooling water flowing through a jacket on the reactor.
Two reference electrodes (Beckmann Quartz Fiber Junction Saturated Calomel Reference Electrodes) are placed in the system in order to monitor the solution potential. An upstream reference potential is measured from a capillary placed in the cell above the carbon bed. A downstream reference potential is measured at the catholyte outlet. Experimental polarization curves are obtained potentiostatically; the potential of the working electrode (cathode) with respect to the saturated calomel reference electrode in the exit stream is regulated by a Princeton Applied Research Model 173 Potentiostat/Galvanostat.

**Experimental Results and Discussion**

Figure 4 shows two experimentally determined steady-state polarization curves. (The total current (mA) is plotted versus the potential of the working electrode with respect to an SCE in the exit stream.) Diffusion-limited current plateaus, which are flat and reproducible, are easily obtained at low overpotentials. No side reactions are indicated.

Figure 5 shows the ratios of exit to inlet concentrations versus potential which correspond to the polarization curves of Figure 4. Based on the given flowrates and bed heights, the open circled data correspond to 3.7 superficial bed volumes per minute (bv/min) and the closed circled data to 1 bv/min. These flowrates are very rapid for a single pass separation process of this nature. (For example, typical units for flowrates through packed bed adsorption systems are bv/hr.) This highly efficient behavior is due to the large driving force and rapid kinetics for mercury deposition.

Experiments at low bed heights and high flowrates were necessary, at first, due to the lack of a suitable analytical method for the measurement of the mercury concentrations of the effluent solutions. The low mercury concentrations and high salt concentrations in solution create difficulties for most common analytical techniques. (Only mercury concentrations in the ppm range can be measured accurately.)

Recently, however, a Jerome Instruments Gold Film Mercury Analyzer (Model 301) was purchased, which allows measurement of mercury concentrations down into the moderate ppt range. Hence, additional experiments can be performed with higher bed heights, and some preliminary data are now available. For example, for a bed height of 6 cm and a flowrate of 57 ml/min (12 bv/hr), a feed concentration of 34 ppm can be reduced to less than 5 ppb ($c_{exit}/c_{inlet} = 1.5 \times 10^{-6}$). This demonstrates clearly the efficacy of the method.

The equation below illustrates the effects of various parameters on the removal efficacy of a mass-transfer-controlled system.

$$\frac{c_{exit}}{c_{inlet}} = \exp \left[ - \frac{a k_m L}{v} \right].$$

This relationship is valid under purely diffusion-limited conditions (i.e., under conditions in which kinetic rates are so rapid that the concentration at the surface of all of the solid particles in the packed bed approaches zero and the reaction rate is determined solely by mass transfer). Low effluent concentrations result from high $k_m$ (overall mass-transfer coefficient), high $a$ (surface area per unit volume), high $L$ (bed height), and low $v$ (solution velocity). The effect of bed height ($L$) is much greater than velocity ($v$) because $k_m$ (mass-transfer coefficient) depends strongly on $v$. This dependence of $k_m$ on $v$ is typically expressed as follows:

$$k_m \propto v^{\frac{1}{2}}.$$

Typical values of the relevant parameters are shown in Table 1.
Table 1. Parameter Values

\[
\begin{align*}
c_{\text{inlet}} &= 34 \text{ ppm} \\
c_{\text{exit}} &= 5 \text{ ppb} \\
\text{flowrate} &= 57 \text{ ml/min} \\
a &= 25 \text{ cm}^2/\text{cm}^3 \\
\nu &= 0.0208 \text{ cm/s} \\
L &= 6 \text{ cm} \\
k_m &= 1.23 \times 10^{-3} \text{ cm/s} \\
\frac{\nu}{ak_m} &= 0.1 \text{ cm}
\end{align*}
\]

A comparison of the mass-transfer coefficients observed in this mercury system with those observed for copper (1) shows \(k_m\) to be about two to three times greater for mercury. The reasons for this difference are not certain at this time.

The limiting-current relationship shows an exponential decrease in concentration as the fluid moves through the bed. Thus, most of the mercury is removed in a very small section near the entrance to the bed. The exponent shows that this distance is on the order of \(v/k_m a\). For the conditions given in Table 1, this distance is about 0.1 cm. Therefore, a bed height on the order of centimeters should be sufficient for fairly complete removal of mercury under these conditions.

This high rate of current transfer from the solution phase to the solid carbon phase at the entry to the bed has an interesting effect on the ohmic potential drop. With upstream counterelectrode placement (Figure 2 (a)), the current travels from the counterelectrode to the working electrode in the solution phase and then, over a length on the order of \(v/k_m a\), the current is transferred to the solid carbon phase. In this system, the solid phase conductivity is very large in comparison with the solution conductivity. Hence, although additional bed height effects changes of orders of magnitude in the effluent concentration, additional bed height has little effect on the ohmic potential drop. In fact, this can be verified experimentally. Table 2 shows two cases with similar flowrates but radically different bed heights. As expected, there are large (order of magnitude) differences in the removal efficacy but little change in the ohmic potential drop through the bed.

Table 2. Effect of Bed Height on Ohmic Potential Drop
(Downstream — Upstream Solution Potential)

<table>
<thead>
<tr>
<th>Flowrate (ml/min)</th>
<th>Bed Height (cm)</th>
<th>(c_{\text{exit}}/c_{\text{inlet}}) (at limiting current)</th>
<th>Ohmic Drop (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>0.5</td>
<td>(4.3 \times 10^{-1})</td>
<td>98</td>
</tr>
<tr>
<td>57</td>
<td>6</td>
<td>(1.5 \times 10^{-4})</td>
<td>62</td>
</tr>
</tbody>
</table>

Finally, Figures 6 and 7 show the effect of flowrate on the removal at limiting current. The increase in the mass-transfer coefficient is not sufficient to offset the increased convection. Hence, increasing flowrates cause a decrease in the mercury removal \(c_{\text{exit}}/c_{\text{inlet}}\) increases. In addition, the strong effect of bed height can easily be seen. (The scale of the ordinate is reduced by a factor of ten from Figure 6 \((L = 0.5 \text{ cm})\) to Figure 7 \((L = 1 \text{ cm})\).)
Conclusions

This study demonstrates that mercury can be removed very effectively (down to ppb) at high flowrates (bv/min) without serious interference from side reactions in a single-pass flow-through porous electrode. The method shows promise for decontamination of aqueous streams and the chemical system seems promising as a tool for the general study of flow-through porous electrodes.

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REFERENCES


FIGURE CAPTIONS

Figure 1. Nernst Relation: Equilibrium Mercury Concentration versus Potential

Figure 2. Electrode Configurations: (a) Upstream Counterelectrode Placement; (b) Downstream Counterelectrode Placement

Figure 3. Sketch of Experimental Flow-Through Porous Electrode Reactor

Figure 4. Steady-State Polarization Curves: Current versus Potential

Figure 5. Concentration versus Potential

Figure 6. Effluent Concentration versus Flowrate (at limiting current), $L = 0.5$ cm

Figure 7. Effluent Concentration versus Flowrate (at limiting current), $L = 1$ cm
Figure 1.
FLOW-THROUGH CONFIGURATIONS

(a)

WORKING ELECTRODE

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COUNTER ELECTRODE

GAP OR SEPARATOR

(b)

WORKING ELECTRODE

COUNTER ELECTRODE

Figure 2.
FLOW-THROUGH POROUS ELECTRODE REACTOR

Figure 3.
Figure 4.
Figure 5.
Figure 6.

L = 0.5 cm
Figure 7.
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