

# ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

Albert Brennstainer, John W. Zondlo, Alfred H. Stiller  
Department of Chemical Engineering, P.O. Box 6102  
West Virginia University  
Morgantown, WV 26506

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## Introduction

The purpose of this research was to assess the feasibility of using carbon devices for the electrochemical removal of heavy metal contaminants from aqueous streams. The ability of several carbonaceous materials to remove metal ions was evaluated using a porous flow-through electrochemical cell. The resulting effluent was monitored downstream using Anodic Stripping Voltammetry (ASV) to determine the decrease in analyte concentration and hence the electrode efficiency.

A schematic diagram of the apparatus used to carry out these experiments is shown in Figure 1. It is a two-cell system. The upstream working cell removes metal ions from the flowing stream, and the downstream analytical cell is used to measure the metal ion concentration in the resulting effluent.

The upper cell is used to test the various carbonaceous electrode materials for their ability to remove certain heavy metal ions from an aqueous stream. The cylindrical body is made of Lexan™. A solution flow channel is drilled through the Lexan™ body. The carbonaceous working electrode material to be tested is placed in the flow channel.

The analyte solution is pumped into the upper working cell and through the carbonaceous working electrode material. A peristaltic pump is used to control the flow rate for all experiments. For the cathodic removal of metal ions, a potential more negative than the standard reduction potential of the metal ion of interest is applied to the working electrode. This applied potential forces the plating of the metals onto the electrode surface thus removing the contaminants from solution. Various carbonaceous materials were obtained to assess their ability to operate as the cathode material. Reticulated Vitreous Carbon (RVC), a graphite fiber mat, a graphite felt and a proprietary carbon material were analyzed. The surface area of these materials was increased via a proprietary alteration technique. This increased surface area improves the ability of the carbon to remove metal ions from solution. Experimental parameters require optimization to maximize the removal of these metals. These parameters include pH, buffer concentration, solution flow rate, applied potential and carbon bed thickness. Conversion efficiency, long-term stability and loading capacity require appraisal. Finally, the pressure drop through the cell and flow characteristics of the solution flowing through the upper cell also need to be evaluated.

## EXPERIMENTAL

The surface areas of the carbonaceous samples have been determined and the data are shown in Table 1. These surface areas were obtained using a Gemini III 2375 Surface Area Analyzer (Micrometrics Instrument Corporation, Norcross, GA). Standard operating procedures were followed as outlined in the operator's manual.

The cylindrical body of the upstream metal removal cell was made of Lexan™ (5.0 cm diameter, 6.0 cm length). The flow channel (1.6 cm i.d.) was drilled through the Lexan™ body. The Ag/AgCl reference electrode (3M NaCl, Model RE-4, BioAnalytical Systems, Inc. (BAS), West Lafayette, IN) was introduced into the flow channel through a Lexan™ sleeve positioned 90 degrees to the flow channel. Leakage was prevented using an o-ring and compression fitting. A piece of coiled platinum wire at the outlet of the cell was used as the auxiliary electrode. Contact to the working electrode was established via a platinum mesh positioned through the cell wall and sealed with an o-ring. The potential of the flow-through cell was controlled using a BAS Model PWR-3 Power Module.

The downstream, thin-layer flow cell (Model LC-44-01000, BAS) was used to measure the metal ion concentration before and after the solution is passed through the metal removal cell. The working electrode was a glassy carbon disk (0.3 cm diameter) over which the solution flowed. Two 50 µm spacers were used to produce the flow channel and direct the solution flow across the carbon disk. Prior to use, the glassy carbon disk was polished using successive slurries of 1.0, 0.3, and 0.05 µm alumina until a mirror-like surface was obtained. The glassy carbon electrode was then thoroughly washed with deionized water. A thin mercury film was plated onto the glassy carbon surface. The metal ions to be analyzed were accumulated into the mercury film. Following accumulation, the metal ions were electrochemically stripped from the mercury film and the measured current used to calculate the metal ion concentration. All potentials were measured relative to the Ag/AgCl reference electrode (BAS). Stripping voltammograms at the thin-layer flow cell were obtained using the

BAS Model CV-27 Voltammograph in conjunction with a Hewlett Packard Model 7044B X-Y recorder.

Stock solutions of metal ions were prepared using AA standard solutions (Fisher Scientific, Fair Lawn, NJ) and deionized water. The deionized water was further purified using a NANOpure™ ultrapure water purification system (Barnstead/Thermolyne, Dubuque, IA). These solutions were stored in Nalgene™ containers to avoid contamination. The  $1 \times 10^{-4}$  M Hg(II) solution for mercury plating was prepared from  $\text{Hg}(\text{NO}_3)_2$  as needed. The mercury ion solution and sample solutions were prepared in 0.1M  $\text{KNO}_3$  supporting electrolyte. The pH was adjusted to 3.5 using nitric acid. All chemicals were certified ACS grade purchased from Fisher Scientific unless otherwise noted.

#### PROCEDURE

The carbon material to be studied was pretreated to oxidize it and assist in the wetting of the carbonaceous surface. This was accomplished by placing the carbon material in a dilute solution (10%) of nitric acid over night in a covered beaker. The material was then thoroughly washed using deionized water. The carbonaceous material was then positioned into the metal removal cell. A threaded plug was used to press the material between a platinum mesh and a piece of filter paper. The pressure on the carbonaceous material can be easily adjusted by turning the threaded plug. This was important because it established contact between the carbon cathode material and the platinum mesh. A 0.1M  $\text{KNO}_3$  electrolyte solution was pumped through the cell. In order to remove air bubbles and wet the electrode surface, a mild electrochemical pretreatment was used. The cell potential was held at +1.00 V for 10 minutes followed by -1.00 V for 10 minutes. The performance of the carbonaceous material under study was tested by placing a solution containing a known concentration of metal ion into the sample reservoir. The solution was then allowed to pass through the metal removal cell at a known flow rate and applied potential. The performance was assessed by measuring the metal ion concentration in the effluent and comparing it to the initial ion concentration. The percentage efficiency of the cell is equal to the percentage of metal ions removed from the solution by the electrolytic cell.

A pre-plated mercury film was used for downstream anodic stripping voltammetric (ASV) detection of the metal ion in the effluent stream. A  $1 \times 10^{-4}$  M Hg(II) solution in 0.1M  $\text{KNO}_3$  was purged with nitrogen for 20 minutes to remove any oxygen. The mercury film was produced by applying a potential of -1.00 V at the glassy carbon electrode while passing the Hg(II) solution through the cell at 0.87 mL/min for 5 minutes. After this period, the potential was held at +0.05 V for 90 seconds. Following this conditioning, the stopcock was turned to stop the flow of mercuric ions and allow the flow of the deaerated sample solution through the cell. This flow was continued for 3 minutes to flush any mercuric ions from the system and replace all of the solution in the system with the sample to be measured. While the solution was flowing at a known flow rate (0.87 mL/min), the ASV deposition potential was applied to the thin-layer flow cell (usually for 1 minute) and the metal ions accumulated. At this point, the solution flow was stopped and after a 30 second equilibrium period, a potential ramp was initiated (-1.00 V to +0.20 V) and the stripping voltammogram recorded. The scan was terminated at +0.20 V. Solution flow was renewed and the electrode cleaned at +0.50 V for 90 seconds to prepare the system for the next determination. The mercury film was removed at the end of a series of experiments using a moist Kimwipe. The electrode was subsequently polished for the next series of studies.

#### RESULTS and DISCUSSION

The effectiveness of commercially available Reticulated Vitreous Carbon (RVC) was examined for its performance as the cathode material of the upstream metal removal cell. Minimal removal of ions was observed for the RVC via adsorption (no applied potential). Upon the application of a potential negative enough to reduce the metal ions, removal efficiencies of 10.2% and 50.0% were observed for Pb and Cd, respectively. In order to improve these efficiencies, several parameters must be addressed. By increasing the ratio of cathode surface area to electrolyte solution volume, increasing the time that the solution remains in the electrode material and/or by optimizing the potential applied to the cell, greater efficiencies can be obtained. This work examined the ability to improve removal efficiencies via greatly increasing the surface area either by altering the surface of the cathode material or by utilizing a proprietary high surface area carbonaceous material.

Two samples of the proprietary carbon material were received from an independent laboratory. Of the two, the more conductive and graphitic sample (Sample A) was used for analysis. The surface area of this material was measured to be 115  $\text{m}^2/\text{g}$ . This surface area is 1000 times greater than that of the RVC. This large surface area should enhance the removal efficiencies of the working cell over those seen using planar cathodes or the RVC. The material was pretreated as described above. The pretreatment improved the wetting ability of the carbon surface and it also increased the measured surface area to 228  $\text{m}^2/\text{g}$ . Good electrical contact was easily established between the carbonaceous cathode material and the platinum mesh lead. The ability of this material to remove cadmium and lead was addressed.

No effect was observed for the removal of the metal ions due to adsorption alone (i.e. no applied potential). Application of a negative potential greatly improved this material's ability to remove the metal ions. Figure 2 shows the effectiveness of this carbon material to remove cadmium and lead. The stripping voltammograms are shown for the metal ion solution (1) prior to being passed through the metal removal cell (FEED), (2) after the solution is passed through the cell with no applied potential (0.00 V) to assess adsorption and (3) after the solution was passed through the cell with an applied potential sufficient to reduce the metal ions at the cathode surface (-1.00 V). Minimal removal was observed due to adsorption. Efficiencies of 91% for cadmium and 95% for lead were obtained for the reductive removal of the metal ions. These large removal efficiencies show great promise for the use of high surface area carbonaceous materials for the cathodic removal of metal ions from aqueous streams.

A graphite fiber mat was assessed for its ability to remove metal ions. Following the employment of the graphite mat to remove metal ions, the mat's surface was altered in a proprietary manner to increase the surface area. Prior to altering the surface, the mat had a surface area of 0.59 m<sup>2</sup>/g. The surface area of the graphite fiber mat following alteration was 99.9 m<sup>2</sup>/g. This was 167 times greater than that of the graphite fiber mats alone. The performance of the graphite fiber mats before and after alteration was assessed. The removal via adsorption alone resulted in the minimal removal of metal ions from solution. Upon the application of a sufficiently negative potential, improved removal was obtained. For the unaltered mat, virtually no removal was noted. However, when the altered mat was tested, removal efficiencies of 99%, 91% and 88% were accomplished respectively for Cu, Pb and Cd using an applied potential of -1.00 V. At a potential of -1.20 V, an effluent concentration of zero was measured for each of the metals.

A conductive graphite felt was analyzed in the next study. Both unaltered and altered graphite felt were utilized. Surface area measurements demonstrate the ability to increase the surface area by alteration. Prior to alteration, the surface area of the graphite felt was 0.17 m<sup>2</sup>/g. Upon altering the surface, this was increased to 55.41 m<sup>2</sup>/g, over a 300-fold increase. The performance of the bare graphite felt was first assessed. Minimal removal was seen due to adsorption. Upon applying a potential of -1.00 V, most of the lead (97%), but only 22% of the cadmium was removed. Solutions treated under the same conditions using the altered graphite felt removed the lead below detectable limits, as well as improved the removal of cadmium (46%). Application of a more negative potential and optimization of experimental parameters can be employed to improve these efficiencies.

To confirm minimal contribution from the platinum mesh, the system was tested in the absence of any carbonaceous cathode material. It was found that the platinum mesh does not contribute significantly (<2%) to the removal of the metal ions from solution.

Continuous removal of lead from an aqueous stream using electroplating on the proprietary carbon material was used to demonstrate the long-term effectiveness of the carbonaceous cathode. The lead solution was passed through the remediation cell and the ions were removed by applying the desired potential. A potential of -1.00 V was applied to remove lead via electroplating. Over a continuous period of 72 hours, a removal efficiency of 89% or greater was achieved for an inlet lead concentration of 100 ppm. Calculation of the lead removed over this period demonstrates a capacity of 0.90 g<sub>Pb</sub>/g<sub>carbon</sub>, but it should be stressed that even at 72 hours, the carbon showed no signs of saturation (see Figure 3).

The final desire is the recovery of the metals once they have been removed from the aqueous stream. It is possible to recover the metal ions plated onto the cathode surface simply by reversing the potential. This was demonstrated using a feed solution concentrated 100 ppm in lead ions. The lead ions were removed at a potential of -1.00 V for 3 hours. Subsequent recovery of the lead at a potential of +1.00 V produced an effluent stream more concentrated in lead. This concentration was 331 ppm lead, which demonstrated a 3:1 concentration of the waste stream. For mixed metal streams, individual metal ions can be selectively removed and recovered by these means.

A summary of the removal efficiencies for all of the carbonaceous cathodic materials is given in Table 2. As can be seen, some of these devices are extremely effective for the removal of heavy metal contaminants from aqueous streams.

## CONCLUSION

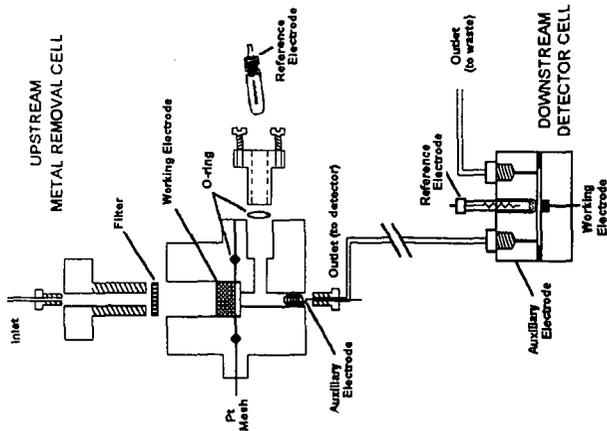
The use of carbonaceous cathodes is an effective means to remove heavy metal contaminants from aqueous streams. By increasing the surface area of existing cathode materials or by using new high surface area materials, improvements in the removal efficiencies are obtained without the vast increase in the electrode volume. By careful selection of the appropriate experimental parameters, the selective removal and recovery of these metal ions is feasible.

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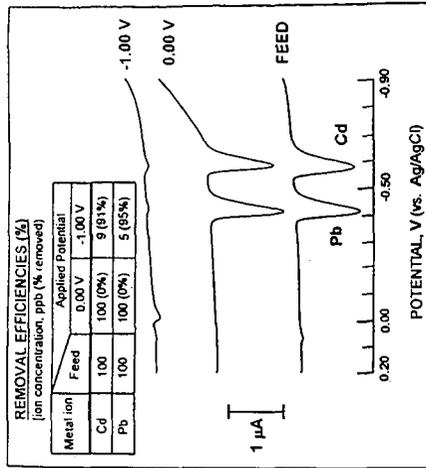
**PROPERTIES of CARBON MATERIALS**

**Surface Areas**

| Material                   | Surface Area (m <sup>2</sup> /gram) | Langmuir |
|----------------------------|-------------------------------------|----------|
| Proprietary Carbon Cathode |                                     |          |
| Sample A                   | 115.13<br>(227.8)*                  | 186.78   |
| Sample B                   | 182.77<br>(192.3)*                  | 286.03   |
| Graphite Fiber Mats        |                                     |          |
| Untreated                  | 0.59                                | -        |
| Treated                    | 99.92 (112.8)*                      | -        |
| Graphite Felt              |                                     |          |
| Untreated                  | 0.17                                | -        |
| Treated                    | 55.41                               | -        |
| RVC                        |                                     |          |
| 100 ppi                    | 0.092                               | -        |
| 80 ppi                     | 44.80                               | -        |



**Figure 1: Schematic of Metal Removal Cell and Detector.**



**Figure 2: Metal Ion Removal Using the Proprietary Carbon Cathode.**

## TABLE OF REMOVAL EFFICIENCIES

| Cathode Material        | Cathode Potential, V | Metal Ion Removed |     |
|-------------------------|----------------------|-------------------|-----|
|                         |                      | Cd                | Pb  |
| RVC                     | 0.00                 | 16%               | 0%  |
|                         | -1.00                | 50%               | 8%  |
| Sample A                | 0.00                 | 0%                | 0%  |
|                         | -1.00                | 81%               | 95% |
| Untreated Graphite Mat  | 0.00                 | 0%                | 0%  |
|                         | -1.00                | 5%                | 17% |
| Treated Graphite Mat    | 0.00                 | 0%                | 0%  |
|                         | -1.00                | 90%               | 92% |
| Untreated Graphite Felt | 0.00                 | 13%               | 7%  |
|                         | -1.00                | 22%               | 97% |
| Treated Graphite Felt   | 0.00                 | 0%                | 0%  |
|                         | -1.00                | 46%               | 99% |
| Platinum Mesh           | 0.00                 | 0%                | 0%  |
|                         | -1.00                | 0%                | 9%  |

Table 2: Removal Efficiencies of Various Carbon Cathodes.

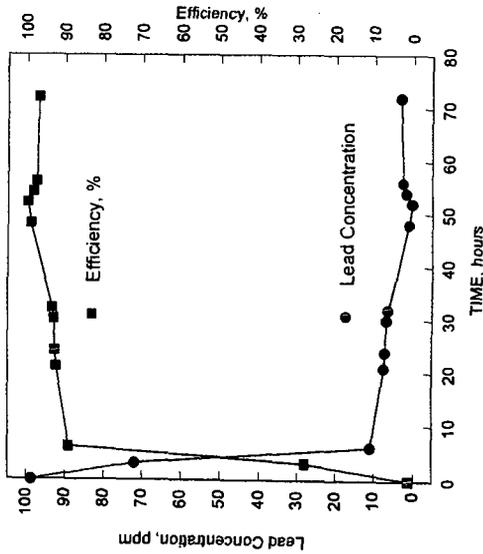


Figure 3: Long-term (72 hour) Removal of Lead via Electroplating.