

Separation of Metal Ions from Liquid Waste

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Abstract

The US and other areas of the world have aqueous sources contaminated with uranium and other actinides as a result of the activities of the nuclear weapons industry. Cleanup of these aqueous sources is a high national priority.

Electrosorption has been shown to be useful for removing uranium from groundwater or other aqueous streams. The technique involves using a flow-through electrolytic cell having a carbon nanofiber cathode. A potential applied to the cathode causes the uranium to adsorb onto the surface of the electrode. Reversing the potential causes the adsorbed uranium compound to precipitate in the aqueous phase thus allowing recovery by simple filtration. Very high uranium removal capacities have been demonstrated in a NETL program involving West Virginia University (WVU) working in conjunction with Applied Sciences, Inc. (ASI). This program evaluated a wide range of carbon nanofiber types to determine the most effective carbon nanofibers for use as the cathode for this process.

All of the carbon nanofiber types evaluated allowed uranium removal but to different extents and/or rates. In addition there were significant differences in the ultimate adsorption capacities. In spite of the fact that the carbon nanofibers evaluated differed widely in many of their inherent characteristics the data obtained did not present strong evidence supporting a specific mechanism.

Future plans are to determine the mechanism of this process, and to focus on the design, fabrication, testing and validation of a full scale unit capable of remediating known uranium wastes. Participation in studies at the Fernald site is in the planning stages to demonstrate the effectiveness of the process with a real world uranium waste stream.

Introduction

Collaborative research between West Virginia University and Applied Sciences Inc has experimentally proved the effectiveness of an electrosorption technique for removing uranium from waste water streams. In the best case, an inlet feed containing 100 ppm produced an outlet concentration of less than 20 parts per billion. Reverse polarizing the electrodes results in rejection of the uranium, which allows it to be easily concentrated for final disposal. The electrodes can then be reused. Thus, this method can be highly economical and efficient.

The key technology is the development of carbon nanofiber electrodes which are essential for promoting the electrosorption effect.

Carbon nanofibers, such as which are produced by ASI, consist of a catalytically grown inner layer of graphitic layers, surrounded by additional deposition of pyrolytic graphite. In total, perhaps 100 layers may be present, and the diameter is typically 100-200 nm. Carbon nanofibers are related to single-walled nanotubes (SWNT), which are composed of a single closed graphene sheet of carbon atoms arranged in hexagonal arrays. The diameter of the tube is about 1 nm. Other tubes are formed with integral numbers of catalytic layers, which are referred to as multi-walled nanotubes (MWNTs). For example, 8-walled tubes are commonly produced. MWNTs range in diameter from about 2 to 20 nm.

The terms SWNT, MWNT, and carbon nanofiber are not standard within the literature. In particular, MWNT and carbon nanofiber are often used interchangeably.

Research performed at West Virginia University showed that nanofiber electrodes can be highly effective at removing uranium ions from aqueous solutions. The removal of uranium is unexpected because the electrolysis potential for uranium removal is higher than the dissociation potential for water. Thus, electrodisassociation of water was expected to occur before useful electrolysis reactions involving uranium.

It is suspected that the unusual effectiveness for removing uranium may be related to the production of unique nanofiber surfaces with high surface density of graphitic edge plane sites, as depicted schematically below. It is known from x-ray diffraction studies that the planes for carbon nanofibers are not arranged in perfect cylindrical shapes, but in the form of cones, resulting in a “herringbone” pattern, as shown below.

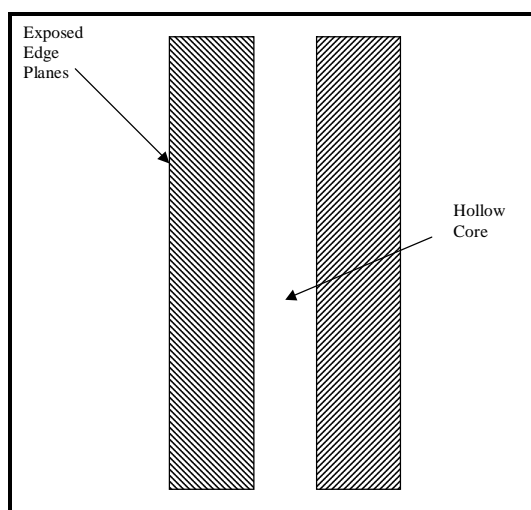


Figure 1. The inclination of the graphitic planes by 20° (exaggerated in this drawing) results in a “herringbone” pattern. The exposed edge planes with their high activity are the key to adsorption of uranyl ions from solution.

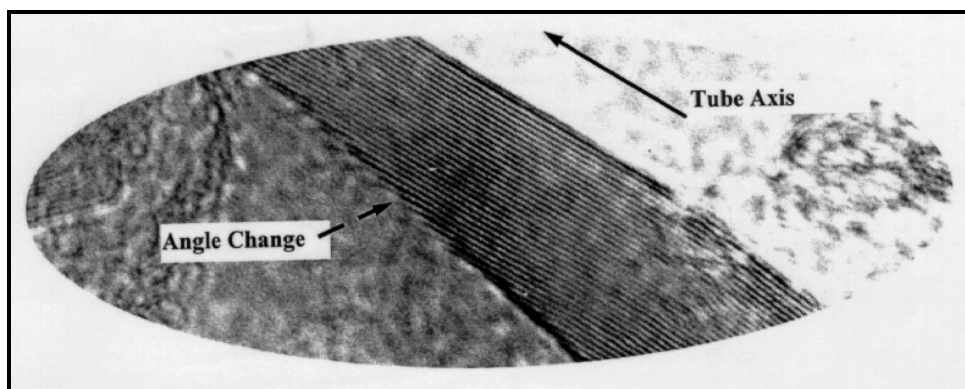


Figure 2. The high resolution transmission electron micrograph above shows that the individual graphene planes are angled with respect to the nanofiber axis (.).

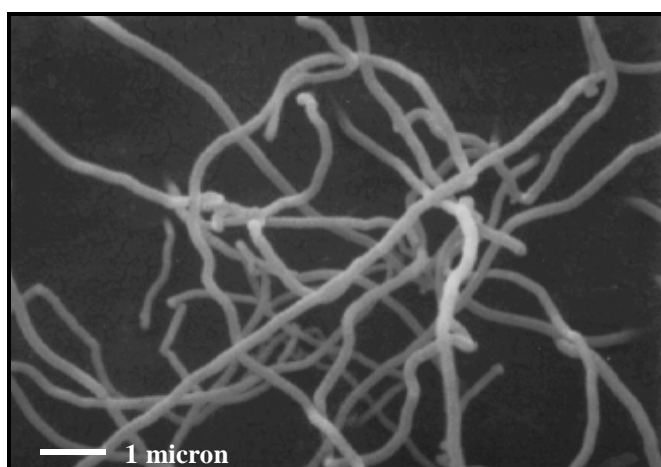


Figure 3. Typical appearance of carbon nanofibers, viewed with a scanning electron microscope.

Procedure

Several types of nanofibers with varying surface characteristics were evaluated. The specific properties of the fibers tested in this work are presented in Table 2. To date, seven fibers have been assessed for their performance in uranium removal; however, capacities for all have not yet been obtained. The designator PR19 refers to natural gas derived nanofibers. PR1 refers to a different protocol which results in smaller diameter nanofibers. PR21 contains natural gas with additional CO₂. The ending designators are coded as follows: ox400 nanofibers were oxidized in air at 400 C; ox500 nanofibers were oxidized at 500 C in air, PS nanofibers were pyrolytically stripped in CO₂ *in situ*, AG nanofibers are as-grown with no surface treatment (and thus may contain surface polyaromatic hydrocarbon layers); and HT nanofibers were heat treated at 3100 C to achieve full graphitization.

A small lab-scale three-electrode electrochemical cell was used for this study.¹ This cell is a typical flow-through design where current flows parallel to the solution flow. The diameter of the inner cylindrical chamber of the cell is 1 cm. The carbon nanofiber, used as the cathode, was placed between a platinum mesh screen and a paper-filter. The platinum mesh establishes

electrical contact with the carbon nanofiber electrode. The reference electrode was Ag/AgCl and a platinum wire was used as the auxiliary electrode.

Continuous electrosorption tests were conducted using the electrochemical cell described above. A negative DC charge in the range of -0.2 to -1.2 V vs. the Ag/AgCl reference electrode was applied onto the carbon cathode using a potentiostat. The prepared feed solution, with a concentration of 100 mg/L U, was pumped through the cell at flow rates of 0.7-1.0 mL/min. with a peristaltic pump. Samples were taken from the effluent at certain intervals ranging from 15 minutes to 1 hour.

Stripping was carried out in a similar way as electrosorption. A solution containing 0.1 N KNO_3 was pumped through the cell at a flow rate of 0.7 mL/min. and a positive charge, usually +1.0V, was exerted on the carbon electrode. The adsorbed uranium was stripped from the carbon nanofiber bed. A yellow-colored precipitate was observed in the solution. The precipitate was either dissolved with a tiny drop (0.03 mL; negligible change to the sample volume) of concentrated nitric acid for the measurement of uranium concentration or was filtered through a 0.45- μm filter paper, washed with water and air-dried for structural analysis.

A peristaltic pump (model 7518-60 (driver model 7521-50), Cole Parmer Instrument Company, Vermont Hills, IL) is used to transport the aqueous uranium solution through the cell at a flowrate of 0.7 mL/min. Samples were taken approximately every fifteen minutes during the first two to three hours and every hour thereafter. Experiments were allowed to continue overnight and samples were taken at the end and beginning of each day during this time. The voltage was monitored to ensure that it remained constant and that the reference electrode was operating properly. The electrical current being drawn throughout the experiment was also recorded at the time each sample was taken in an attempt to gain an understanding of the adsorption mechanism.

Differential pulse voltammetry (DPV) was used to analyze the concentration of uranium in the cell feed and effluent. The device consisted of a static mercury drop electrode (SMDE) (Model 303A, EG&G Instruments, Princeton Applied Research, Princeton, NJ), a potentiostat/galvanostat (Model 263 A, EG&G Instruments, Princeton Applied Research, Princeton, NJ), and electrochemical software (Model 250, EG&G Instruments, Princeton Applied Research, Princeton, NJ). Each 10-mL sample was placed into the measuring cell and purged for four minutes with nitrogen. The voltage scan started at -0.5 V and increased to 0.0 V (versus Ag/AgCl reference electrode). Uranium (VI) is reduced to uranium (V) during the scan causing a current peak to appear at approximately -0.15 V. The height of the peak is proportional to the concentration of uranium (VI) and was used to calculate the concentration of uranium based on a previously constructed calibration curve. Separate calibration curves were constructed for use in both high and low concentration ranges. The minimum detectable limit was approximately 0.01 ppm using DPV. It should be noted that the current peak can shift as the KCl-AgCl solution in the reference electrode is diluted through diffusion. The solution was therefore changed regularly (RDE0022, EG&G Instruments, Princeton Applied Research, Princeton, NJ).

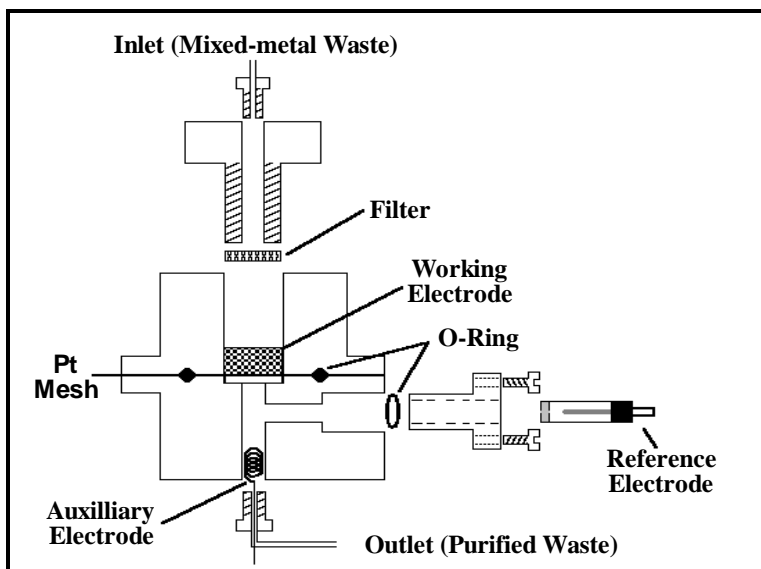


Figure 4. Schematic of the uranium electrosorption cell at West Virginia University, a high-precision device which allows quantitative time-dependent measurement of uranium concentration, even at levels below 20 parts per billion.

A second cell with a higher flow rate system was also used. The purpose of this cell was to address concerns about scalability, because of the small size of the system at WVU. The peristaltic pump is capable of circulating the entire liquid inventory (about 200 ml) in several seconds. It was typically operated in closed loop mode, so that the fluid inventory is continuously circulated.

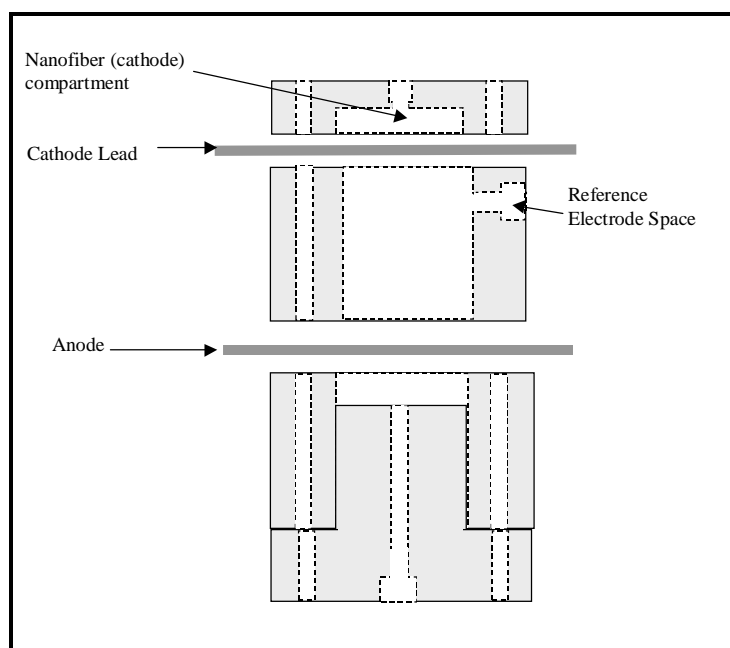


Figure 5. An expanded schematic of the uranium remediation cell. The overall length is 6". Not shown are the filters and nickel screens which hold the fibers in the electrode space, plus the tubing and pumps for handling the fluid outside the cell.

The fibers can also be stripped using the 0.1M potassium nitrate solution and applying a positive voltage potential of +1.00V. The uranium is recovered as a bright yellow solid, the form of which is yet to be determined. This phenomenon makes this technology unique when compared to current treatment methods.

Experimental

A single pass of a 100 ppm feed sample through the electrochemical cell produced an outflow containing less than 20 parts per billion, a factor of 5000 reduction. Electrosorption capacity as high as 10 g_U/g_{carbon fiber} has been obtained, which is many times higher than can be obtained from ion exchange resins. The adsorbed uranium can be recovered in the solid form by reverse polarizing the electrodes, which causes an immediate ejection of the uranium from the electrodes.

The specially treated carbon nanofiber electrodes are vastly more effective than any other material in terms of their ability to remove uranium from liquid waste streams using this technique. As shown below, carbon black electrodes were ineffective, showing only a slight reduction from a nominally 100 ppm uranium inlet stream. After about 45 minutes, the cathode evidently starts to reach its full capacity, and effectiveness diminishes. Within 90 minutes, the system appears to be completely ineffective. Normally, uranium electrodeposition occurs at a higher voltage than that for the electrolysis of water. Accordingly, water dissociates before uranium can be removed for normal electrode materials. The situation is different for carbon nanofiber electrodes. In this case, it was found that such electrodes have an extraordinary affinity for uranium.

The reference case is the PR-19-AG carbon nanofibers, which is produced using natural gas feedstock. The nanofiber electrode was much more effective than carbon black in removing uranium. The total capacity is also much higher, as the effect persists for a longer time.

The PR-1-AG nanofiber is manufactured according to a different protocol, using pure methane instead of natural gas, with oxidizing gas present and longer residence time, which results in a smaller average diameter. Probably the smaller diameter is due to oxidation of the outer pyrolytic layers.

Both PR-1-AG and PR-19-AG electrodes showed much more effectiveness than carbon black. The outlet attains a concentration of 70 ppb for the PR-19-AG electrode, although after about two hours the effectiveness is somewhat degraded.

The PR-21 PS protocol uses a mild oxidant to more gently pyrolytically strip surface polyaromatics, leaving a more intact surface than air-etched material. This resulted in the best electrode tested. Starting with 100 ppm uranium in solution, the outlet quickly reaches below 20 parts per billion within 60 minutes, and continues at that level for at least 20 hours.

It was predicted that the PR-19-ox400 nanofibers would be more effective than the as-grown version, due to the fact that the oxidation treatment was expected to be effective in cleaning the surface of the nanofibers, remove the layers of polyaromatic hydrocarbons which might remain on the surface. This appeared to not be the case, however. The reason why this material was less effective than the others is not understood at this time.

Table 1. Summary Data Log for Nanofiber Properties and Results

Parameter	Nanofiber Protocol Designator
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	PR19-ox400	PR-1-AG	PR19-HT	PR-19-AG	PR-1 ox400	PR-1 ox500	PR21-PS
Surface Oxygen (Atomic %)	--	1.1	--	0.6	4.6	--	1.9
Surface Area (m ² /g)	-- (5?)	25.0 (3)	21.0 (6)	15.0 (7)	29.0 (2)	-- (1?)	30 (4)
Surface Energy (mJ/m ² /g)	-- (3?)	48.0 (6)	275.0 (4)	27.0 (7)	350.0 (2)	-- (1?)	136.0 (5)
Diameter (nm)	180.0	125.0	190.0	200.0	120.0	115.0	190.0
Graphitization Index (%)	55.0 (3)	30.0 (7)	72.0 (1)	55.0 (4)	30.0 (6)	30.0 (5)	55.0 (2)
Surface PAH Content (mg/g)	0.0	<1.0	0.0	<1.0	0.0	0.0	0.0
Minimum U Conc. (ppb)	1630	530	490	70	50	<20	<20
Time of Minimum, min	135	60	485	90	87	105	75
Breakthrough time, min	135	135	not measured	90	135	<1200	>1250
Composite Ranking	11	16	11	18	10	7	11
Observed Rank Order	7	6	5	4	3	2	1

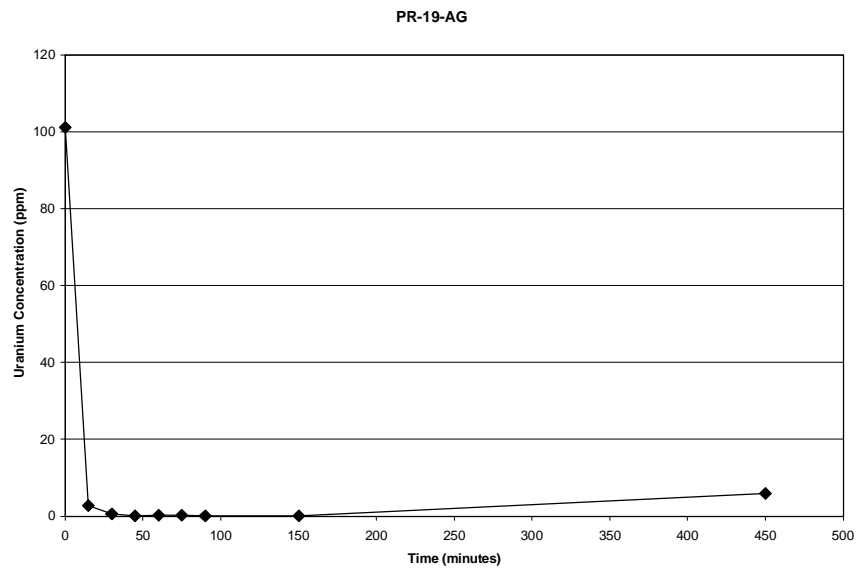


Figure 6. The PR-19-AG protocol results in a concentration of 70 ppb. The electrode begins to lose effectiveness after about two hours.

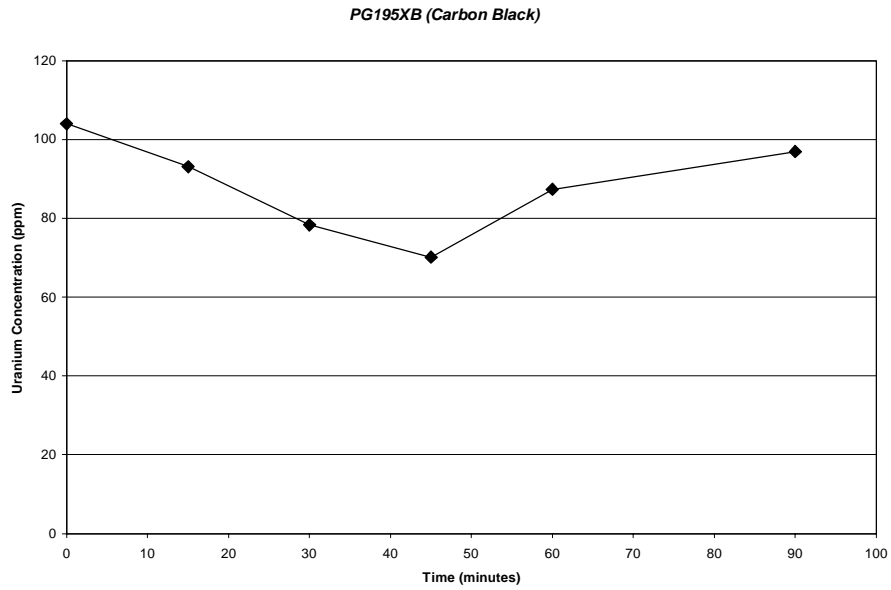


Figure 7. Carbon black and other control experiments showed almost no uranium removal effect.

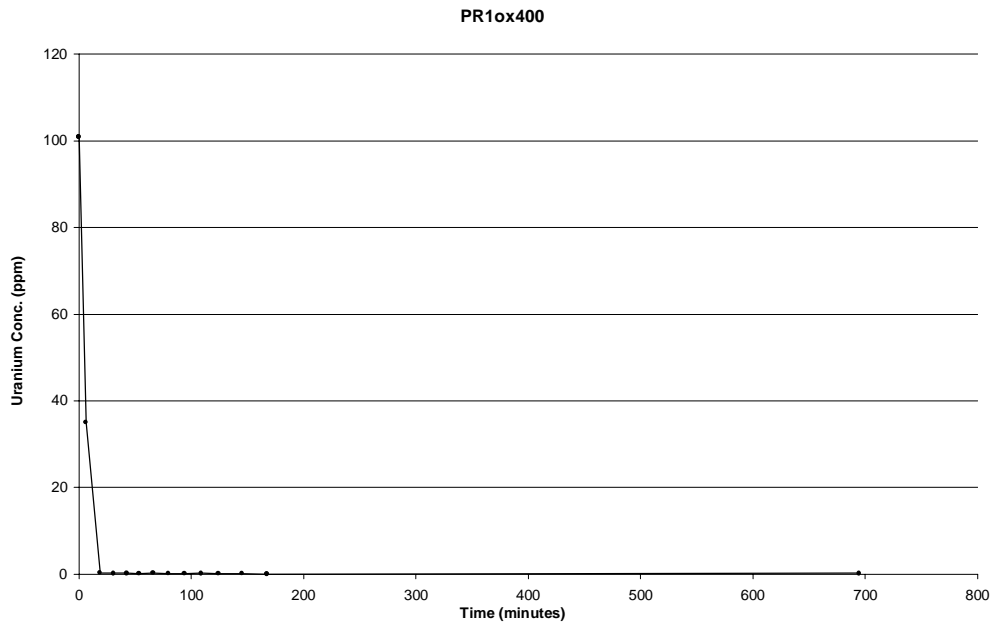


Figure 8. PR1-ox400 (oxidized) was shown to be more effective than the reference untreated nanofiber.

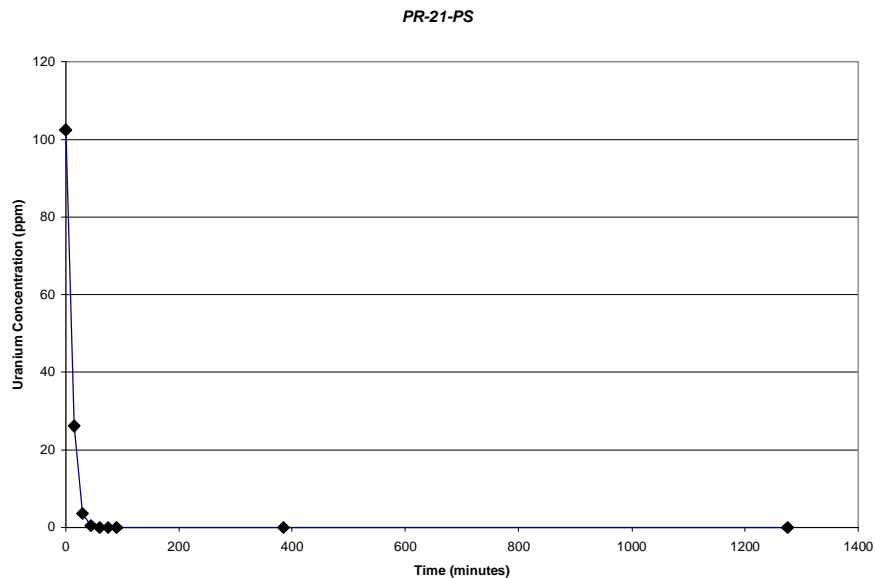


Figure 9. PR-21-PS produced the best results.

The observation that uranium concentration is reduced below 20 ppb (as observed for PR-21 PS electrodes, for example) is near the limit of resolution of the device. However, for these runs, the concentration goes below 20 ppb and gives no sign of random fluctuations. Thus, there is some confidence that these readings are indeed accurate. However, for runs in which the minimum concentration is based on one or two data points, random error must be suspected.

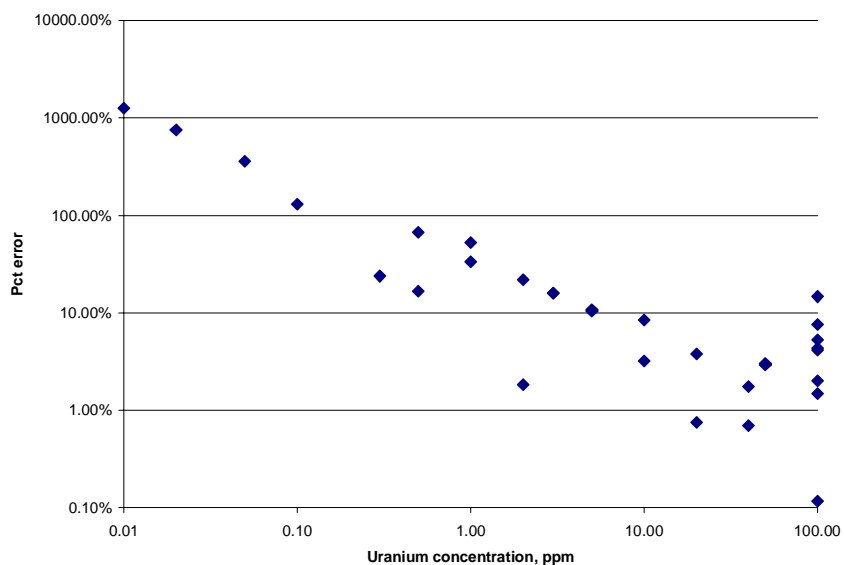


Figure 10. Linear regression error analysis as a function of magnitude of uranium concentration.

Thus the results are very positive for all types of nanofiber electrodes tested.

Although a satisfactory explanation for the mechanism has still not been identified, the amount of uranium removed from solution is too high to be a simple monolayer of adsorbate. The surface area of the nanofibers is too small by a factor of 10^2 . However, the reaction requires

carbon nanofibers and is not observed on carbon black or other electrodes. Thus simple electrodeposition does not explain the data.

Simple sorption is not a satisfactory explanation because the reaction requires a bias of -0.9 V. Also, the effect is not present if the flow direction is reversed; i.e., if the working fluid sees the anode before the anode. This could be due to trapping hydroxyl ions at the anode.

The results suggest that the electrosorption effect is very effective at removing uranium from aqueous solutions. Its effectiveness for other ions remains to be determined.

This data suggests that electrosorption could be considered for direct remediation of lightly-contaminated groundwater. In addition, an alternate near term application may be to use electrosorption to augment existing ion exchange systems, such as which are in use at DOE facilities such as the Fernald Environmental Management Project in Ohio, for example. Such systems use ion exchange resins for remediation of groundwater. Although highly effective, ion exchange systems are expensive and slow. In addition, a major “bottleneck” occurs when the systems are taken off-line for recharging the ion exchange resins. This results in a saturated salt water brine, typically with a few hundred parts per million uranium. This solution must be diluted and fed back into the inlet stream to be re-cleaned, resulting in diminishing the capacity of the system and increasing the time required to remediate a contaminated aquifer.

Recharging the resins results in large quantities of saturated brine containing ~ 300 ppm uranium. This composition is quite similar to the standard solution used in this project.

Acknowledgment

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References.

1. Yue Xu, “Electrochemical Treatment of Metal-Bearing Aqueous Wastes Based on Novel Forms of Carbon,” PhD Dissertation, West Virginia University, March 1999.