

REMOVAL OF URANIUM AND NITRATE IONS IN SLUDGE WASTE BY ELECTROSORPTION

C. H. Jung, W. Z. Oh, J. K. Moon, Y. D. Choi, J. H. Park
Korea Atomic Energy Research Institute
P.O.Box 105, Yuseong-gu, Daejeon, 305-600, Korea

Y. R. Lee
Department of Chemical Engineering
Chungnam National University
220 Gung-dong, Yuseong-gu, Daejeon, 305-764, Korea

ABSTRACT

The electrosorption of U(VI) and NO_3^- from waste water was carried out by using an activated carbon fiber(ACF) felt electrode. Electrosorption experiments showed that the applied negative potential increased the adsorption kinetics and capacity in comparison to the open circuit potential(OCP) adsorption for uranium ions. The absolute value of the applied negative potential controlled the adsorption rate of the uranium. For the feed concentration of 100 mg/L, the concentration of U(VI) in the cell effluent is reduced to less than 1 mg/L. In order to enhance the electrosorption capacity at a lower potential, the ACF electrode was chemically modified. The electrosorption capacity of U(VI) on the base treated electrode at -0.3 V corresponds to that of the as-received ACF electrode at -0.9 V.

Effective nitrate removal is obtained by the application of a positive potential in the range of $+0.6$ to $+0.8$ V to the ACF electrode. A copper metal modified ACF enhanced the sorption of the nitrate ions. Copper atoms incorporated on the ACF surface worked as adsorption sites when the potential was applied, thus enhancing its electrosorption.

INTRODUCTION

For the removal and recovery of uranium(VI) from contaminated water and waste streams, a variety of physical and chemical methods such as precipitation, coagulation, ion exchange and adsorption have been used. But, these techniques have been restricted in application due to their limited capacity when the concentration of U(VI) in the waste water is relatively high[1-3]. As an efficient electrochemical method for the removal of a high concentration of uranium, an electrodeposition on carbon materials has been extensively investigated. Electrodeposition is being used to cover the faradaic transformation of ionic material in the solution phase into another phase such as metals and a liquid amalgam or compounds. For the

uranium having a high reduction potential, electrodeposition is not a practical method[4]. An alternative to electrodeposition is electrosorption, that is an adsorption of the metal cations onto a negatively charged carbon surface[5]. This electrosorption is a non-faradaic process and the maximum voltage that can be used will be limited by the onset of faradaic processes.

The nitrate component is one of the major water quality problems due to its adverse effects on the environment[6]. The electrochemical reduction or ion exchange technique has been used as a conventional method to remove the nitrate, but the removal capacity by an ion exchange is not so high as to satisfy an unlimited release to the environment and an electrochemical reduction has drawbacks in its operation at a high reduction potential. One of the efficient methods to treat nitrate-containing waste is electrosorption[7].

Electrosorption technique, which may use the electrical potential as the 3rd driving force to the traditional adsorption and ion exchange mechanism, has the reversible characteristics of purifying a waste solution by adsorption and a concentration of the contaminants by desorption. The amount of material adsorbed in electrosorption depends on the electrochemical potential applied to the adsorbent. When the electric potential is loaded, the electric double layer generated at the surface of the electrode is charged or discharged. Using this phenomenon, electrosorption can be accomplished. The adsorption of ionic species or non-ionic species in a solution is influenced by the electric properties of the electrode materials. Therefore, the adsorption capacity can be controlled.

The selection of a proper electrode for an efficient removal of the trace components from a solution is of high importance in the design of an electrochemical system. The basic requirements for an efficient electrode material are the chemical and electrochemical inertness for a wide variety of chemicals and a wide range of potentials; high specific area (to achieve this requirement the electrode should be porous and the pores should be accessible by the electrochemically active species); high fluid permeability of the pore system; easily shaped for cell design considerations; high electronic conductivity and a continuity of the electronic contact throughout the electrode bed; and cost effective[8]. Carbon-based materials (activated carbon and activated carbon fiber etc.) satisfy the requirements described above and have a good radiation and chemical resistance[9]. Activated carbons are widely used to irreversibly remove trace amounts of heavy metallic ions, transition ions and for a number of technological and analytical applications, such as a precious metal enrichment and the purification of water. Especially, activated carbon fiber, which can be easily made into a variety of types (textures or sheet), has a high specific surface area and good fluid permeability[10]. Many studies have shown that it is possible to remove trace amounts of metallic ions such as copper, lead, zinc, cadmium, mercury and chromium.

In this study, we conducted experiments on the selective adsorption of uranium(VI) from a high concentration chemical salt and an adsorption of the nitrate component respectively, to investigate the application feasibility of the electrosorption technique using ACF and modified ACF as a good conductive electrosorption adsorbent. In a continuous flow-through cell, the adsorption behavior was investigated with a varying applied potential. The result was compared with the adsorption behavior when the potential is not applied.

Experimental

Electrosorption Electrode and Reagents

The electrosorption electrode used in this study was pitch-based ACF felts (Osaka Gas Co., FN-200PS-15) with a thickness of 4~6mm. Table I shows the physico-chemical properties of the ACF felt. ACF has a large BET specific surface area, and most of the pores can be classified as a micropore which has an average pore radius of about 7.1Å. It is known that the electrical conductivity of carbons used in the electrochemical process is in the range from 0.1~1.0($\Omega\cdot\text{cm}$)⁻¹, and a good carbon electrode has electrical conductivity values of more than 1.0($\Omega\cdot\text{cm}$)⁻¹. The electric conductivity values of the ACF felt used in this experiment was 72($\Omega\cdot\text{cm}$)⁻¹. Therefore the ACF felt can be used as a good conductive electrosorption adsorbent.

Table I. Physical and Chemical Characteristics of ACF Felts

Physical property		Electro/chemical property	
Specific S/A(m ² /g)	1733	Conductivity($\Omega\cdot\text{cm}$) ⁻¹	72
Total pore vol.(cc/g)	0.83	pH	6.4
Micro pore vol.(cc/g)	0.59	Surface acidity(meq/g)	2.46

Uranium solutions were prepared by diluting a concentrated UO₂(NO₃)₂·6H₂O solution with sodium nitrate and deionized water(over 16M $\Omega\cdot\text{cm}$). 1 M NaNO₃ was used as the supporting electrolyte solution and the concentration of the uranium nitrate was 0.05mM. A nitrate solution was prepared by diluting a concentrated KNO₃ solution, the concentration of which was 10 mM. The pH of the solution was adjusted by adding 0.1 M NaOH and/or 0.1 M HCl as required. The solutions of U(VI) and NO₃ were purged by nitrogen gas for 40min prior to

the experiment because of the easy reduction of the dissolved oxygen in the solution.

Electrochemical Cell

Flow-through adsorption experiments were carried out using a three-electrode electrochemical cell. Electric current flows parallel to the solution flow. ACF felts used as the working electrode were placed on a platinum mesh which was used as a current collector and ACF supporter. The counter electrode was platinum wire and an Ag/AgCl electrode was used as the reference electrode. All the potentials reported in this paper are relative to this reference electrode. The electrochemical cell was connected with a potentiostat (Radiometer, PGP201). The fixed flow rates through the cell were controlled by a peristaltic pump. The effluent from the electrochemical cell was collected in a fractional collector and analyzed by UV spectroscope (Cecil Instruments, CE2021). The adsorption behavior was investigated at various applied potentials and it was compared with the adsorption behavior of the OCP (open circuit potential).

Results and Discussion

Electrosorption of U(VI) on ACF

A test for the electrosorption with a 100 mg/L U(VI) feed on to the ACF felt at various negative potentials in the range of -0.1 to -0.9 V(vs. Ag/AgCl) was carried out. The uranium concentration in the effluent from this test is shown in Figure 1. Effective U(VI) removal is accomplished at all the negative potentials. At a potential of -0.3 V, the U(VI) concentration in the effluent is reduced to 1 mg/L in 2h and then increased continuously. At a potential of -0.9 V, a complete removal (99.8%) of U(VI) is rapidly reached in 1h and maintained throughout the test. However, in the case of OCP the effluent concentration of U(VI) increased within 3h and finally reached the level of the feed, indicating a saturation of the sorption capacity by the ACF. From these results, it can be confirmed that the external negative potential exerted on the ACF electrode has a great impact on the adsorption capacity of the ACF.

The above results are replotted in Figure 2, the kinetics of the uranium sorption can be examined. The specific sorption rate can be obtained from the cumulative uranium sorption divided by the time interval and by the weight of the activated carbon fiber. At OCP, the rate of uranium sorption starts at 0.12 mg/g·min and decreases with time, approaching zero within 3h. It represents a typical adsorption break-through curve in which a saturation occurs. When the potential is -0.3 V or more negative, the cumulative uranium adsorption plots are essentially straight lines, indicating a constant specific sorption rate within the time of the test. Extension of the constant sorption rates can be expected over a longer time. It is clear that

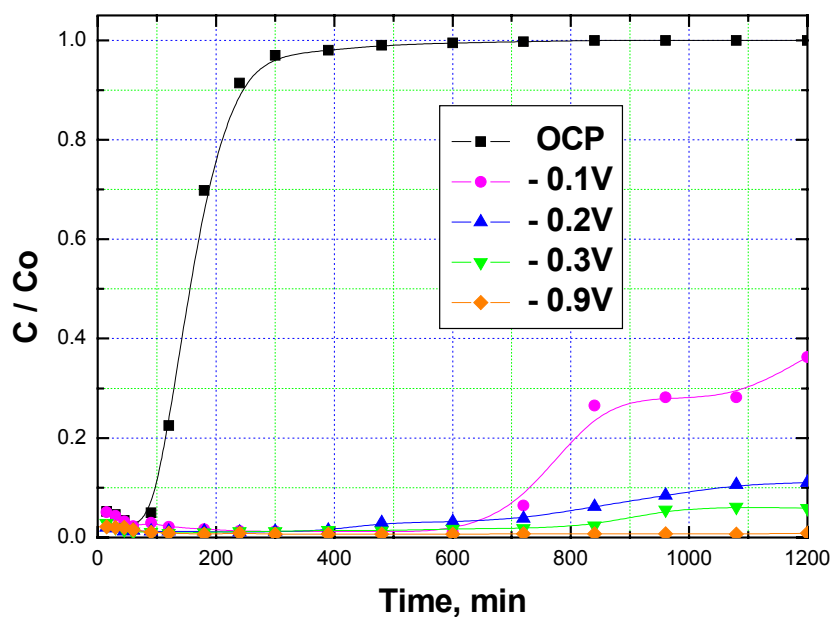


Fig. 1. Electrosorption of U(VI) with a variation of the potentials at pH 4

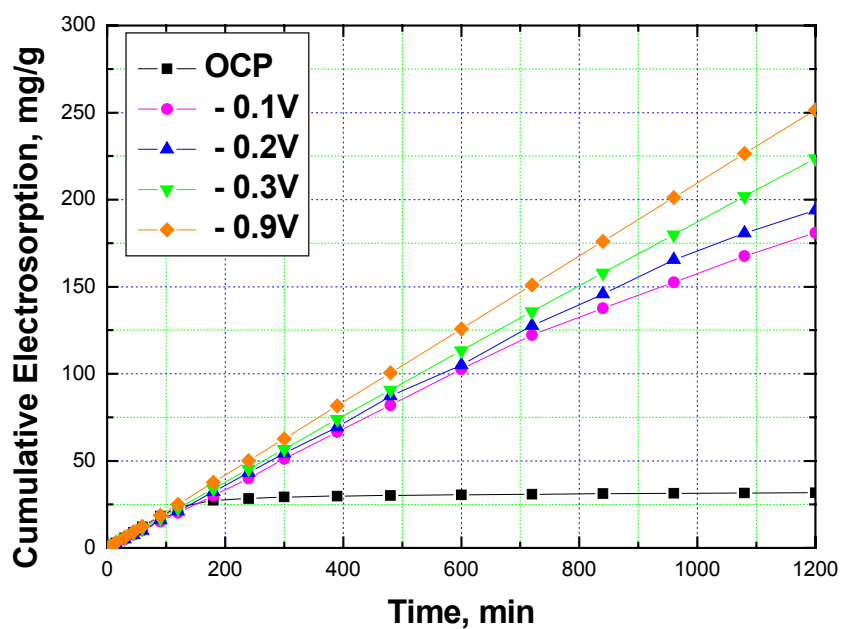


Fig. 2. Cumulative electrosorption of U(VI) with a variation of the potentials at pH 4

the magnitude of the negative potential applied to the carbon electrode controls the uranium, sorption rate. Especially, in a long-term test conducted with a 100 mg/L U(VI) feed at -0.9 V,

the effluent concentration is maintained at less than 1 mg/L, corresponding to a specific sorption rate of 1.68 mg/g·min. The cumulative uranium amount within 20 h is about 250 mg uranium/g carbon.

The capacity for U(VI) calculated at various potentials is represented in Table II. The difference of the amount adsorbed in the OCP and the applied potential is 159 mg uranium/g carbon. Apparently, the external negative potential exerted on the activated carbon fiber has an impact on the adsorption capacity of the carbon fiber. The increase of the adsorption capacity for a cation is due to the electrostatic attraction by Coulomb's interaction. Many researchers reported that the adsorption capacity of a carbon-based material was increased by an applied potential.[9, 11,12]

Table II. Data for the adsorption of U(VI) on the ACF electrode at various potentials

Applied potential (vs. Ag/AgCl)	OCP	-0.1 V	-0.2 V	-0.3 V	-0.9 V
Amount of adsorbed (mg uranium/g carbon)	21	180	193	223	252

Electrosorption of U(VI) on a Modified ACF

In order to enhance the electrosorption capacity at a lower potential, the ACF felt was chemically modified in an acidic, basic and neutral solution. Table III shows the physico-chemical property of the ACF felt by each modification. Specific surface area of all the ACFs decreased in the modified conditions. The amount of the acidic functional groups decrease with the basic and neutral modifications, while the amount increases a lot with the acidic modification when compared to the as-received ACF.

Figure 3 shows the electrosorption of the U(VI) on various ACF at -0.3 V. The electrosorption capacity of U(VI) decreased by using the acid modified electrode while it was greatly increased by using the neutral and base modified electrode. The electrosorption amount of U(VI) on the neutral and base modified electrode at -0.3 V corresponds to that of the as-received ACF electrode at -0.9 V.

From these results, the electrosorption capacity is affected by surface acidity more than specific surface area. It can be confirmed that the electrosorption of U(VI) depends on chemical property of the electrode.

Table III. Specific surface area and acidity of the ACFs

Property ACF	Specific S/A (m ² /g)	Funtional group(meq/g)			Total acidity (meq/g)
		carboxyl	lactone	phenol	
As-received ACF	1733	0.32	1.30	0.84	2.46
Acid modified ACF	482	3.68	1.67	1.77	7.12
Base modified ACF	1234	0.61	0.13	0.09	0.83
Neutral modified ACF	1617	0.33	0.12	0.89	1.34

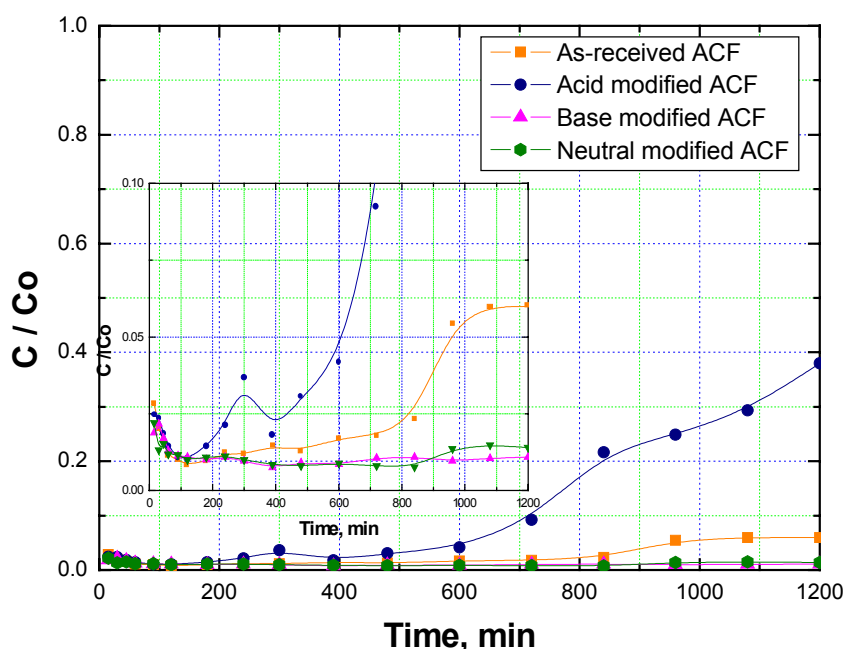


Fig. 3. Electroadsorption of U(VI) on various ACF at -0.3 V

Electroadsorption of NO₃ on ACF

The electroadsorption tests on the NO₃⁻ ion were performed in the electric potential ranges from +0.6 to +0.8 V (vs Ag/AgCl). Figure 4 shows the results for the removal of the nitrate ions with a variation of the applied potentials. The amount of nitrate adsorbed per gram of ACF increased with an increase of the applied positive potential to the ACF, and a better result for the electroadsorption of the nitrate ions was obtained at the potential of +0.8 V than at +0.6 V. Much of the amount of the nitrate adsorbed in the test-run was removed within an initial 1h

(84% for +0.6 V, 67% for +0.8 V, in as-received ACF).

The effect of the modification of the ACF on the adsorption of the nitrate was studied. In Figure 4, the electrosorption of the nitrate for the as-received ACF and the modified ACF is shown. A metal modification of the ACF brought about a significant increase in the electrosorption. Nitrate ions were adsorbed on the Cu modified electrode surface in all ranges of the investigated positive electric potential, when compared to the as-received ACF. Capacity by Cu-ACF is 1.5-2 times as large as the as-received ACF. Copper atoms incorporated on the ACF surface worked as an adsorption sites when the potential was applied, thus enhancing its electrosorption[13]

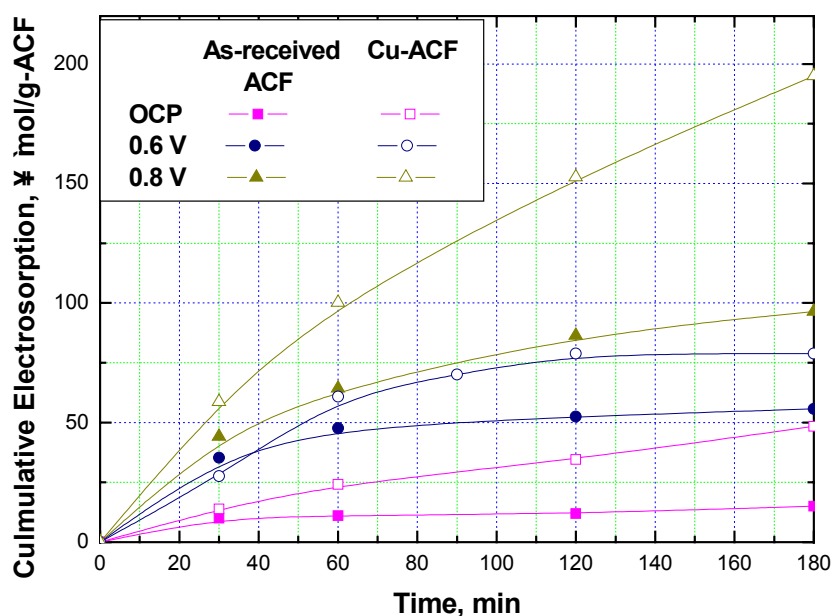


Fig. 4. Electrosorption of nitrate on ACF.

CONCLUSIONS

A study on the electrosorption of U(VI) and NO_3^- onto a porous activated carbon fiber (ACF) felt was carried out to treat waste water. The result of the continuous flow-through cell electrosorption experiments showed that the applied negative potential increased the adsorption kinetics and capacity in comparison to the OCP (open circuit potential) adsorption for uranium ions. Effective U(VI) removal is accomplished when a negative potential is applied to the ACF electrode. For the feed concentration of 100 mg/L, the concentration of U(VI) in the cell effluent is reduced to less than 1 mg/L. In order to enhance the

electrosorption capacity at a lower potential, the ACF electrode was chemically modified. The electrosorption capacity of U(VI) on the base treated electrode at -0.3 V corresponds to that of the as-received ACF electrode at -0.9 V.

Effective nitrate removal is obtained by the application of a positive potential in the range of $+0.6$ to $+0.8$ V to the ACF electrode. A copper metal modified ACF enhanced the sorption of the nitrate ions. Copper atoms incorporated on the ACF surface worked as adsorption sites when the potential was applied, thus enhancing its electrosorption.

ACKNOWLEDGMENT

This work has been carried out under the Nuclear R&D program by MOST.

REFERENCES

1. Sauer, N. N., Smith, B. F., "Metal-ion recycle technology for metal electro-plating waste waters". LA-12532-MS, 1993.
2. Oren, Y. and Soffer, A., "Water desalting by means of electrochemical parametric pumping", *J. Applied Electrochemistry*, 1983, 13, 473-484.
3. Jayson, G.G., Sangster, J. A., Thompson, G. and Wilkinson, M. C., "Adsorption and Electrosorption of Mercury(II) Acetate onto Activated Charcoal Cloth from Aqueous Solution", *Carbon*, 1987, 25, 523-531
4. Carley-Macauly, K. W. and Gutman, R. G., *Radioactive Waste: Advanced management methods for Medium Active Liquid Waste*, Harwood Academic Pub., 1981.
5. Woodard, F. E., McMackins, D. E. and Jansson, R. E. W., "Electrosorption of Organic on Three Dimensional Carbon Fiber Electrode", *J. Electroanal. Chem*, 1986, 214, 303-330
6. Basova, Y., Kanoh, H., Ooi, K., Carbon flow-through electrodes for electrochemical removal of nitrate ions from aqueous solutions, Japan.
7. Abbas Afkhami, Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples, *carbon*, 2003, 41, 1320-1322.
8. Defay, R., Prigogine, I., Bellemans, A., Everett, D. H., "Surface tension and Adsorption", Longmans, London, 1980, 218.
9. Tomizuka, I., Meguro, T., Kuwagaki, H., Chiba, A., Miyazaki, A., Okamoto, M., "Elimination behavior of metallic ion from its dilute solution by activated carbon fiber under applied electrical potential", *Proceeding of Carbon '94, Granada, Spain*, 1994, 222.
10. Hatfield, T. L., Kleven, T. L., Pierce, D. T., *J. Appl. Electrochem.* 1996, 26, 567.
11. Xu, Y., Zondlo, J. W., Finklea, H. O. and Brennstainer, A., "Electrosorption of uranium on carbon fibers as a means of environmental remediation", *Fuel Pro. Tech.*, 2001, 63(3),

189-208

12. Niu, J., Conway, B. E., "Adsorption and electroosmotic removal of aniline and bipyridyls from waste-water-waste", *Journal of Electroanalytical Chemistry*, 2002, 536(1), 83-92
13. Ryoo, M. W., Seo, G., "Improvement in capacitive deionization function of activated carbon cloth by titania modification", *Water Research*, 2003, 37, 1527-1534.