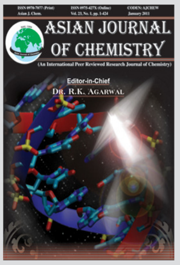
Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 2247-2249

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Electrochemically Modified Activated Carbon Fiber for the Removal of Uranium Ions†

CHONG-HUN JUNG*, YU-RI LEE, JEI-KWON MOON, HUI-JUN WON and KUNE-WOO LEE

Decontamination & Decommissioning Technology, R&D Division, Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon, 305-600, South Korea

*Corresponding author: E-mail: nchjung@kaeri.re.kr

AJC-9541

The electrosorption of U(IV) from wastewater was carried out by using an activated carbon fiber felt electrode in a continuous electrosorption cell. Pore structure and functional groups of the activated carbon fibers electrochemically modified in an acidic or a basic solution were examined. It is believed electrosorption capacity is not affected by a surface acidity and the specific surface area of activated carbon fiber. The applied negative potential increased the adsorption capacity in comparison to an open circuit potential adsorption for uranium ions. The electrosorption amount of U(IV) on the base modified activated carbon fiber electrode at -0.3 V corresponds to that of the as-received activated carbon fiber electrode at -0.9 V. Such a high adsorption capacity on the base modified activated carbon fiber electrode probably was caused by the uranium precipitation on activated carbon fiber surface due to an increase of the hydroxyl by the base modification of activated carbon fiber.

Key Words: Electrosorption, Modified activated carbon fiber, Uranium ions.

INTRODUCTION

For the removal of uranium(IV) 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 for removal of high concentration of U(IV) in the wastewater[1-4]. As an efficient electrochemical method for the removal of a high concentration of uranium having a high reduction potential, an electrosorption is practical[5,6]. It was reported that the amount of material adsorbed in an electrosorption depends on the electrochemical potential applied to the adsorbent[7,8].

The selection of a proper electrode for an efficient removal of the trace components from a solution is very important in the design of an electrochemical system. Carbon-based materials satisfy the requirements for a good radiation and chemical resistance. Especially activated carbon fiber (ACF) which can be easily made into a variety of types (textures or sheet), has a high specific surface area and good fluid permeability[9].

In this study, we conducted experiments on the electrosorption of uranium ions [U(IV)] using the ACF electrode that was electrochemically modified in an acidic and a basic solution. The U(IV) electrosorption properties of the modified ACFs are investigated in terms of the BET specific surface area, surface acidity of the modified ACFs.

EXPERIMENTAL

Electrosorption electrode and reagents: The electrosorption electrode used in this study was pitch-based ACF felts (Osaka Gas Co., FN-200PS-15). The electrochemical modification of as-received ACF (namely, R-ACF) was performed in a continuous system, where the ACFs were fixed over a graphite anode roller. A graphite plate cathode was also submerged in 10 wt % H_3PO_4 electrolyte solution (namely, A-ACF) or 10 wt % NaOH electrolyte solution (namely, B-ACF). The current intensities and treatment time for the surface modifications is 1.0 A, 1.0 min, respectively. The modified ACFs emerging from the electrolytic cell are placed in a hot dryer oven at 110 ºC for 24 h.

Uranium solutions were prepared by diluting a concentrated $UO_2(NO_3)_2\cdot6H_2O$ solution with sodium nitrate and de-ionized water(over 16 MΩ-cm). 1 M $NaNO_3$ was used as the supporting electrolyte solution and the concentration of the uranium nitrate was 0.05 mM. The pH of the solution was adjusted by adding 0.1 M NaOH and/or 0.1 M HCl as required.

Electrochemical cell: Flow-through adsorption experiments were carried out using a three-electrode electroche-mical cell. The 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

---

†Presented to the 4th Korea-China International Conference on Multi-Functional Materials and Application.

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 a UV spectroscope (Cecil Instruments, CE2021). The adsorption behaviour was investigated at various applied potentials and it was compared with the adsorption behaviour of the OCP (open circuit potential).

RESULTS AND DISCUSSION

Surface property of the activated carbon fiber (ACF) electrode: The porosity and specific surface area of ACF electrodes were measured by the construction of an adsorption isotherm of nitrogen at 77 K using a gas sorption system (Quantachrome, Autosorb-1 MP) in the range of 10^{-3}-1.0 Torr. The total pore volume was derived from the amount of N_2 vapour adsorbed at a relative pressure of about 1.0, by assuming that the pores are then filled with liquid adsorbate. The micrpore volume was calculated using the t-plot method. The textural properties of the as-received and the electrochemically modified ACFs are listed in Table-1. It is evident that most of the pore volume of the samples is filled below a relative pressure of about 0.1, indicating these samples are highly microporous. However, the specific surface area of the ACFs are decreased by the electrochemical modification. Kou *et al.*[9] reported that the BET surface area of acidic carbon is considerably decreased due to a blocking of the narrow pores by the surface complexes introduced from an acid treatment. Pittman *et al.*[10] found that the BET surface areas of acidic carbons were substantially smaller than those obtained by a methylene blue and NaOH uptake and this difference was caused by the pores, voids and cracks which can partially open or swell in the presence of aqueous base. Results on the isotherm and the porosities of the electrochemically modified ACFs revealed that some of the pores were blocked by the oxide functional groups introduced by the electrochemical modification. The decrease of the surface area was mainly ascribed to the decrease of the micropore volume.

TABLE-1
PHYSICO-CHEMICAL PROPERTY OF ACTIVATED CARBON FIBERS (ACFs)

	Porosity and specific S/A			Surface acidity (meq/g)		
	S_{BET} (m^2/g)	V_{tot} (cc/g)	V_{mic} (cc/g)	Carboxyl	Lactone	Phenol
R-ACF	1733	0.83	0.59	0.32	1.30	0.84
A-ACF	998	0.48	0.31	2.35	1.64	1.50
B-ACF	1211	0.58	0.39	0.01	0.27	0.32

For a reasonable study of the surface functional groups of ACFs, the titration method by Boehm neutralization technique was used. As shown in Table-1, the A-ACF produces a lot of acidic surface groups and this leads to an increase in the amount of the base required to neutralize the oxidized carbon, while the B-ACF resulted in a decrease of the surface acidity. It is clear that the chemical nature of ACFs can be significantly altered by the acidic or basic modification.

Electrosorption of U(IV) on a as-received activated carbon fibre: A test for the electrosorption with a 100 mg/L U(IV) feed on to the R-ACF at various negative potentials in the range of -0.1 to -0.9 V (*vs.* Ag/AgCl) was carried out and it was compared with the adsorption behaviour of the open circuit potential (OCP). The uranium concentration in the effluent from this test is shown in Fig. 1. Effective U(IV) removal is accomplished at all the negative potentials. At a potential of -0.3 V, the U(IV) concentration in the effluent is reduced to 1 mg/L in 2 h and then increased continuously thereafter. At a potential of -0.9 V, a complete removal (99.8 %) of U(IV) is rapidly reached in 1 h and maintained throughout the test. However, in the case of OCP the effluent concentration of U(IV) increased within 3 h and finally reached the level of the feed, indicating a saturation of the sorption capacity by the ACF. The capacity for U(IV) calculated at various potentials is represented in Table-2. 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.

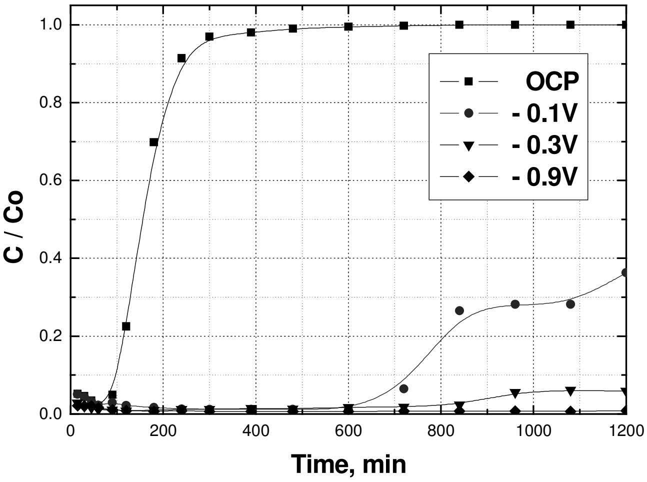


Fig. 1. Electrosorption of U(IV) with a variation of the potential at pH 4 on as received activated carbon fibre

TABLE-2
ELECTROSORPTION CAPACITY OF U(IV) WITH R-ACF

Applied potential (*vs.* Ag/AgCl)	OCP	-0.1 V	-0.3 V	-0.9 V
Amount of adsorbed ($mg_{uranium}/g_{carbon}$)	21	180	223	252

The electrosorption of U(IV) on the acid and the base modified ACF electrode at -0.3 V was investigated and was compared with that of the as-received ACF electrode as shown in Fig. 2. The electrosorption capacity of U(IV) decreased by using the A-ACF electrode while it was greatly increased by using the B-ACF electrode. Adsorption amount of A-ACF decreases by about 10 % when compared with that of the R-ACF at -0.3 V. The electrosorption amount of U(IV) on the B-ACF electrode at -0.3 V corresponds to that of the R-ACF electrode at -0.9 V.

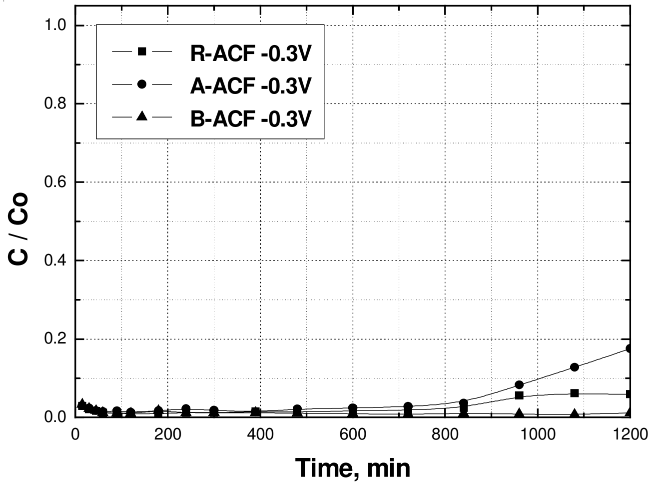


Fig. 2. Electrosorption of U(IV) on various activated carbon fibres at pH 4 and a potential of -0.3 V

The order of specific surface area magnitude of activated carbon fibres tested is:

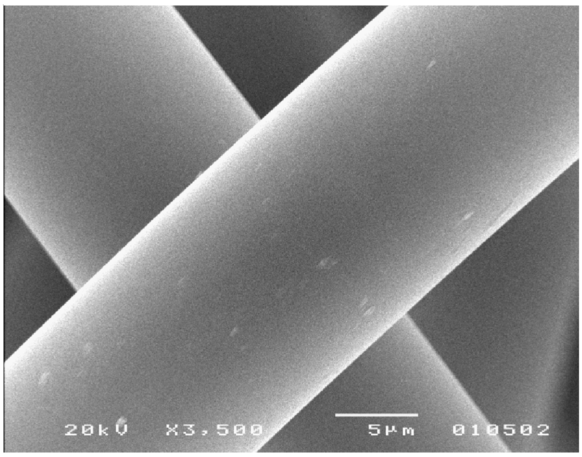
A-ACF < B-ACF < R-ACF

But surface acidity sequences look as follows:

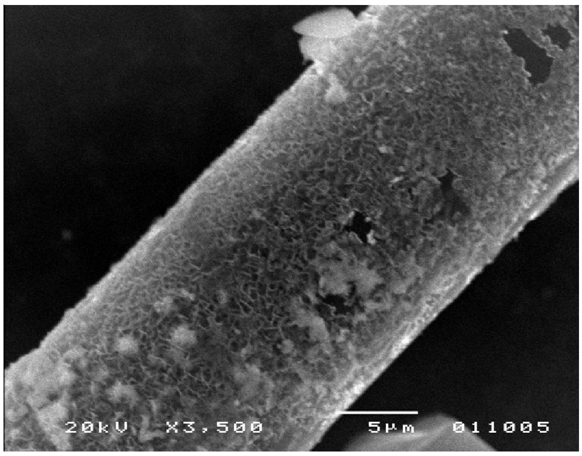
B-ACF < R-ACF < A-ACF

It was repoted that the surface functional groups formed by an acid modification of active carbon worked as an adsorption sites, enhancing its adsorption capacity[11]. The adsorption of cations onto the porous carbon electrode can be illustrated as a type of ion exchange between the cations and surface acid groups. U electrosorption on A-ACF decreased, despite it had functional groups most. Therefore it is believed electrosorption capacity is not affected by a surface acidity as well as the specific surface area of ACF.

Such a high adsorption capacity on B-ACF might be probably due to an increase of the hydroxyl ions on the ACF surface by the base modification of ACF. To confirm this results, the SEM analysis on the ACF surface before and after electrosorption was performed. As shown in Fig. 3, ACF surface had great difference before and after the electrosorption and some precipitate was observed on the ACF surface after electrosorption. The significant increase of electrosorption capacity on B-ACF is caused by the uranium precipitation on ACF surface.



(a) Before electrosorption



(b) After electrosorption

Fig. 3. SEM of activated carbon fibre before and after five cycling

Conclusion

The electrosorption of U(IV) from wastewater was carried out by using an activated carbon fiber (ACF) felt electrode in a continuous electrosorption cell. The applied negative potential increased the adsorption capacity in comparison to an open circuit potential (OCP) adsorption for uranium ions. The electrosorption amount of U(IV) on the ACF electrode electro-chemically modified in a basic solution at -0.3 V corresponds to that of the as-received ACF electrode at -0.9 V. Such a high adsorption capacity on the base modified ACF electrode probably was caused by the uranium precipitation on ACF surface due to an increase of the hydroxyl ions formed on the surface by the base modification of ACF.

ACKNOWLEDGEMENTS

This work has been carried out under the Nuclear R&D Program funded by the Ministry of Education, Science and Technology of Korea.

REFERENCES

1. D. Kaplan, T. Gervais and K. Krupka, *Radiochim. Acta*, **80**, 201 (1998).
2. T. Sato, T. Murakamit, N. Yanase, H. Isobe, T. Payne and P. Airey, *Environ. Sci. Technol.*, **31**, 2854 (1997).
3. H. Guler, G. Sahiner, A. Aycik and O. Guven, *J. Appl. Polym. Sci.*, **66**, 2475 (1997).
4. Y. Wei, M. Kumagai, Y. Takashima, M. Asou, T. Namba, K. Suzuki, A. Maekawa and S. Ohe, *J. Nucl. Sci. Technol.*, **35**, 357 (1998).
5. C. Riordan, M. Bustard, R. Putt and A. Mchale, *Biotechnol. Lett.*, **19**, 385 (1997).
6. M. Hu and M. Reeves, *Biotechnol. Progress*, **13**, 60 (1997).
7. N. Sauer and B. Smith, Metal-Ion Recycle Technology for Metal Electroplating Wastewaters, LA-12532-MS (1993).
8. S. Hazourli, G. Bonnecaze and M. Astruc, *Environ. Technol.*, **17**, 1275 (1996).
9. C. Hou, T. Patricia, Y. Sotira and T. Costas, *J. Chem. Phys.*, **129**, 224703 (2008).
10. Jr C. Pittman, G. He, B. Wu and S. Gardner, *Carbon*, **35**, 317 (1997).
11. S. Park, Y. Kim and J. Shim, *Korean Ind. Eng. Chem.*, **14**, 41 (2004).