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Electrosorption of Uranium Ions in Liquid Waste

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Abstract

A study on the electrosorption of uranium ions onto a porous activated carbon fiber (ACF) was performed to treat uranium-containing lagoon sludge. 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 open-circuit potential (OCP) adsorption for uranium ions. Effective U(VI) removal is accomplished when a negative potential is applied to the activated carbon fiber (ACF) electrode. For a feed concentration of 100 mg/L, the concentration of U(VI) in the cell effluent is reduced to less than 1 mg/L. The selective removal of uranium ions from electrolyte was possible by the electrosorption process.

Keywords : *Electrosorption, Activated carbon fiber, Uranium ion, Lagoon, Sludge*

1. 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, electrodeposition on carbon materials has been extensively investigated and used very effectively. For uranium having a high reduction potential, electrodeposition is not a practical method [4].

An alternative to electrodeposition is electrosorption that is defined as the reversible adsorption or the reversible retention of ions, molecules, or particles from a liquid phase on or near an electronic conducting surface as a function of electric potential difference between the surface and the liquid [5]. 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, the electrosorption can be accomplished [6-8]. The adsorption of ionic species or non-ionic species in the solution should be influenced by the electric potential at the surface of the electrode and electric properties of electrode materials [9]. Therefore, the adsorption capacity can be controlled. This technique has reversible characteristics for purifying a waste solution by adsorption and concentrating contaminants by desorption.

The selection of a proper electrode for an efficient removal of trace components from a solution is of high importance in the design of an electrochemical system [10]. The basic requirements for an efficient electrode material are chemical and electrochemical inertness for a wide variety of chemicals and a wide range of potentials; high specific surface 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 continuity of the electronic contact throughout the electrode bed; and cost effective [11]. Carbon-based materials (activated carbon and activated carbon fiber etc.) satisfy the requirements described above and have good radiation and chemical resistance [12]. 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 precious metal enrichment and the purification of water. Especially ACF, which can be easily made into a variety of types (textures or sheet), has a high specific surface area and good fluid permeability [13]. 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 a selective adsorption of uranium (VI) from a high concentration of chemical salt to investigate the technical feasibility of the electrosorption process using ACF as an electrosorption adsorbent. In the continuous flow-through cell, the adsorption behaviors were investigated, with a changing pH, applied potential, and the concentration of the electrolytes. The result was compared with the adsorption behavior when the potential is not applied.

2. Experimental

2.1. 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 4~6 mm. Table 1 shows the physico-chemical properties of 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 7.1 Å. It is known that the electrical conductivity of carbons used in the electrochemical process is in the range from 0.1 to $1.0(\Omega\cdot\mathrm{cm})^{-1}$, and a good carbon electrode has electrical conductivity values of more than $1.0(\Omega\cdot\mathrm{cm})^{-1}$. The electrical conductivity value of ACF felt used in this experiment was $7.2(\Omega\cdot\mathrm{cm})^{-1}$. Therefore the ACF felt can be used as a good conductive electrosorption adsorbent.

Table 1. Physical and chemical characteristics of ACF felts

Physical property		Electro/chemical property	
Specific S/A (m^2/g)	1680	Conductivity $(\mathrm{ohm\cdot cm})^{-1}$	72
Total pore vol. (cm^3/g)	0.86	pH	6.4
Micro pore vol. (cm^3/g)	0.84	Surface acidity (meq/g)	0.38

Various solutions were prepared by diluting a concentrated $UO_2(NO_3)_2\cdot 6H_2O$ solution with sodium chloride and deionized water (over 16 MΩ-cm). 0.1~3 M NaCl was used as the supporting electrolyte solution and the concentration of uranium nitrate was 0.05~0.175 mM. The pH of the solution was adjusted by adding 1 M NaOH and/or 1 M HCl as required. The solutions of U(VI) were purged by nitrogen gas for 40 min prior to the experiment because of the easy reduction of the dissolved oxygen in the solution.

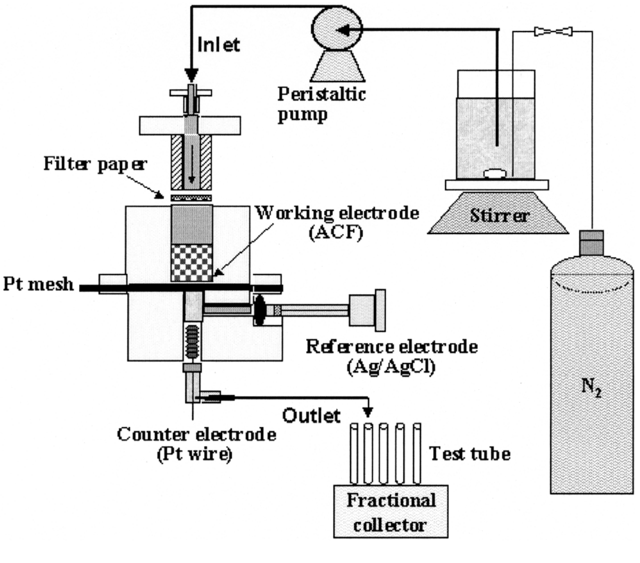

Fig. 1. Schematic diagram of continuous flow-through cell adsorber.

2.2. Electrochemical cell

Flow-through adsorption experiments were carried out using a three-electrode electrochemical cell as shown in Fig. 1. Electric current flows parallel to the solution flow. ACF felt used as the working electrode was placed on a platinum mesh which was used as a current collector and ACF-supporter. The counter electrode was platinum wire and the Ag/AgCl electrode was used as the reference electrode. All the potentials reported in this paper are relative to this reference electrode. The electro-chemical cell was connected with a potentiostat (EG&G Model 273). 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 (CE2021, Eecil Instrument, England). The adsorption behavior was investigated at various potentials, of pH and concentrations and it was compared with the adsorption behavior of the OCP (open circuit potential). Various concentration of NaCl salt were tested for the supporting electrolyte.

3. Results and Discussion

Uranium can be present in solutions as U(III), U(IV), U(V) and U(VI). Among them the most stable form in a solution is U(VI), in the form of uranyl ion UO_2^{2+}. U(VI) is present in solutions as the uranyl ion at pH≤2.5. At higher values of pH, hydrolyzed ions dominate. The hydrolysis of U(VI) depends mainly on the uranium concentration and the pH.

Hydrolysis products are obtained according to the following equilibria [14].

$$UO_2^{2+} + OH^- = UO_2OH^+ \qquad \log\beta_{11} = 8.8 \tag{1}$$

$$UO_2^{2+} + 2OH^- = UO_2(OH)_2 \qquad \log\beta_{12} = 16.0 \tag{2}$$

$$UO_2^{2+} + 3OH^- = UO_2(OH)_3^- \qquad \log\beta_{13} = 22.8 \tag{3}$$

$$UO_2^{2+} + 4OH^- = UO_2(OH)_4^{2-} \qquad \log\beta_{14} = 23.0 \tag{4}$$

$$2UO_2 + OH^- = (UO_2)_2OH^{3+} \qquad \log\beta_{21} = 11.3 \tag{5}$$

$$2UO_2 + 2OH^- = (UO_2)_2(OH)_2^{2+} \qquad \log\beta_{22} = 22.4 \tag{6}$$

$$3UO_2 + 4OH^- = (UO_2)_3(OH)_4^{2+} \qquad \log\beta_{34} = 44.1 \tag{7}$$

$$3UO_2 + 5OH^- = (UO_2)_3(OH)_5^{+} \qquad \log\beta_{35} = 54.5 \tag{8}$$

$$4UO_2 + 7OH^- = (UO_2)_4(OH)_7^{+} \qquad \log\beta_{47} = 76.1 \tag{9}$$

The percentage of each species versus pH can be calculated, a species diagram for U(VI) is shown in Fig. 2. The diagrams are based on equilibrium data for an initial concentration of 4.2×10^{-4} M (100 ppm) in an electrolyte 1.0 M NaCl. Considering the existence of polynuclear species such as $(UO_2)_3(OH)_4^{2+}$ and $(UO_2)_4(OH)_7^{+}$. It can be seen that the major U(VI) species is UO_2^{2+} at a pH of less than 4. At pH 4~5, uranium exists as uranium hydrates. Above pH 5, $(UO_2)_3(OH)_5^{+}$ and $(UO_2)_4(OH)_7^{+}$ species are dominant. Formation of the $UO_3\cdot H_2O$ precipitation begins when the pH is above 6 or higher.

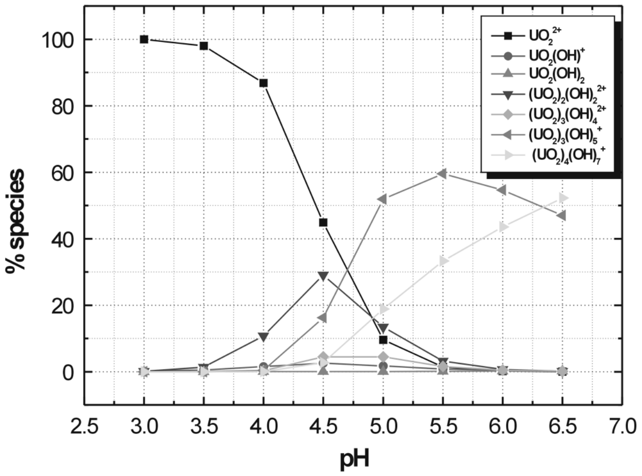

Fig. 2. Uranium speciation at U concentration of 100 ppm.

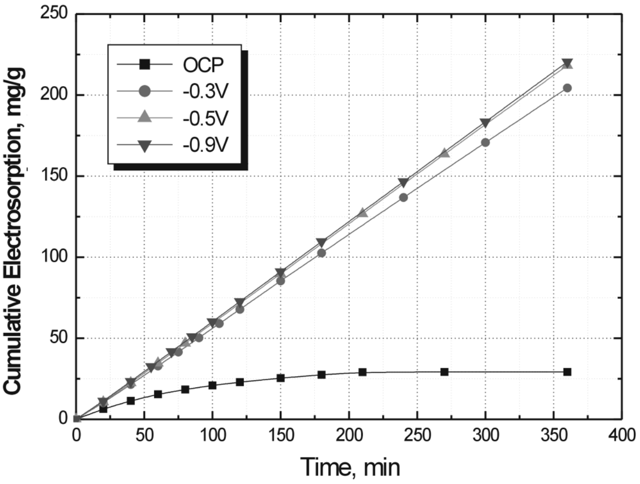

Fig. 4. Cumulative electro-adsorption of 100 ppm U(VI) with variation of potentials at pH 4.

Test on the electrosorption with a 100 mg/L U(VI) feed onto the ACF felt at various negative potentials in the range of -0.3 to -0.9 V (vs. Ag/AgCl) was carried out. The uranium concentration in the effluent from this test is shown in Fig. 3. 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 2 h and then increased continuously. At a potential of -0.5 and -0.9 V, a complete removal of U(VI) is rapidly reached in 1h and maintained throughout the test. However, in the case of OCP (open-circuit potential) the effluent concentration of U(VI) increased within 3 h and finally reached the level of the feed, indicating 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 Fig. 4. In terms of the cumulative uranium adsorption on the variation of treatment time, 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 the magnitude of the negative potential applied to the carbon electrode controls the uranium sorption rate.

To determine the electrosorption capacity of this ACF, a test was conducted with a 350 mg/L U(VI) feed at -0.9 V. As shown in Fig. 5, the effluent concentration is rapidly reached at less than 1 mg/L and it corresponds to a specific sorption rate of 662 μg/(g·min). The cumulative amount of uranium within 15 h is about 552 $mg_{uranium}/g_{ACF}$. When the electrosorption process is applied in the treatment of a waste solution containing an ion species, they can be adsorbed in the electric double layer of the electrode electrostatically without any phase change or they can be removed by an ion exchange type adsorption.

During electrosorption, an H^+ ion was adsorbed onto a

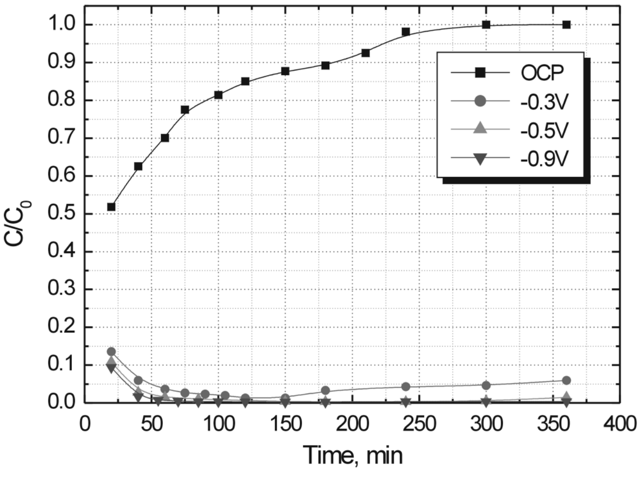

Fig. 3. Electro-adsorption % of 100 ppm U(VI) with variation of potentials at pH 4.

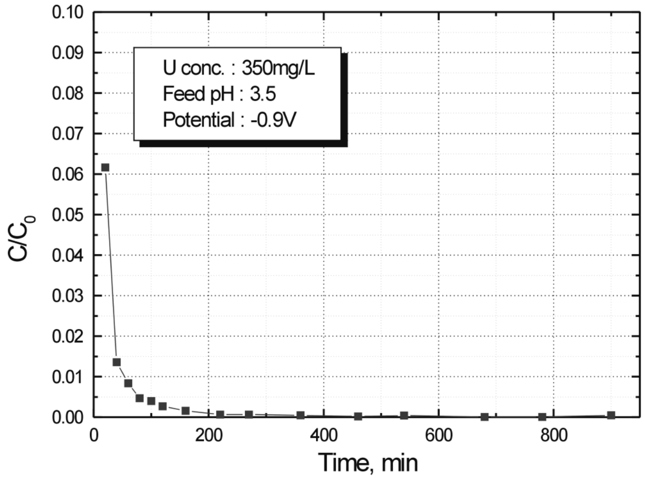

Fig. 5. Electro-adsorption % of 350 ppm U(VI) at -0.9 V and pH 4.

carbon surface charged with anion, selectively [15, 16].

$$2H_2O + 2e^- \Leftrightarrow 2H_{ads} + 2OH^- \quad (10)$$

where H_{ads} is considered to be a hydrogen atom bound to the surface. The sorption of cations onto the porous carbon electrode as a type of ion exchange between the cations and surface acid groups as illustrated by the following reactions:

$$2C^*\text{– COOH} + 2OH^- \Leftrightarrow 2C^* \text{– COO}^- + 2H_2O \quad (11)$$

$$2C^*\text{– COO}^- + UO_2^{2+}\ (C^*\text{-COO})_2UO_2 \quad (12)$$

where C^* stands for the carbon matrix.

Generally, the electro-adsorption capacity of the porous carbon electrode for the absorbed ion depends on the double layer capacity, surface area and applied potential. The ACF electrode of 1 g with a surface area of 1680 m^2/g and double layer capacity of 30 F/g can adsorb and desorb around 74 $mg_{uranium}/g_{ACF}$ with a changed potential of 1 V. This value is rather small compared to the observed capacity of 552 $mg_{uranium}/g_{ACF}$ by the experiment. This is the reason that adsorption with an electro double layer charging of the adsorbent, ion exchange and the other reaction happened during the electro-adsoprtion of the uranium.

The electrosorption behavior of U(VI) with a variation of solution pH at -0.9 V is shown in Fig. 6. As the solution pH was lowered, the adsorbed uranium decreased. At pH 2.1, the effluent uranium concentration is 50 mg/L in the beginning but rapidly increases to 200 mg/L in about 6 h, showing an extremely low uranium sorption capacity. The electrosorption at pH 3 and 4 shows very similar results except for the slightly higher uranium removal during the first hour of electrosorption at pH 4.

The effect of electrolyte concentration was studied and the results are shown in Fig. 7. It can be seen that the adsorption kinetics increased by increasing the electrolyte concentration. It is due to the increase of ion mobility and decrease of ohmic voltage drop occurring because of the increase of the electrolyte concentration. When the potential is applied to the electrode immersed in the solution, electric conduction occurred with ion transfer playing the role of charge carrier. As the electrolyte concentration becomes higher, the ion concentration becomes more dense and the charge transfer becomes active, which is favorable for an electrosorption reaction.

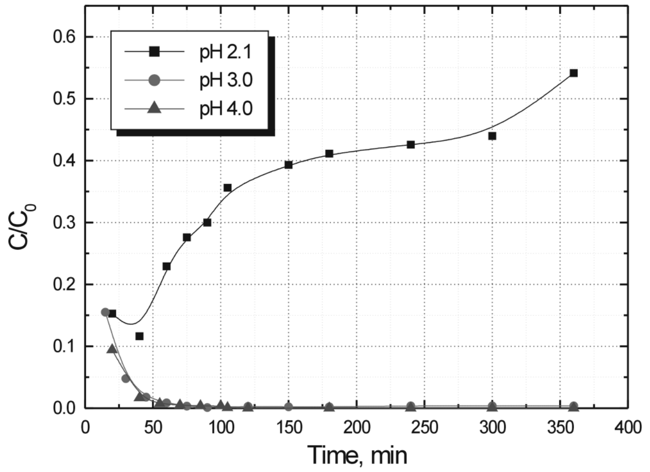

Fig. 6. Electro-adsorption % of 100 ppm U(VI) with variation of pH at -0.9 V.

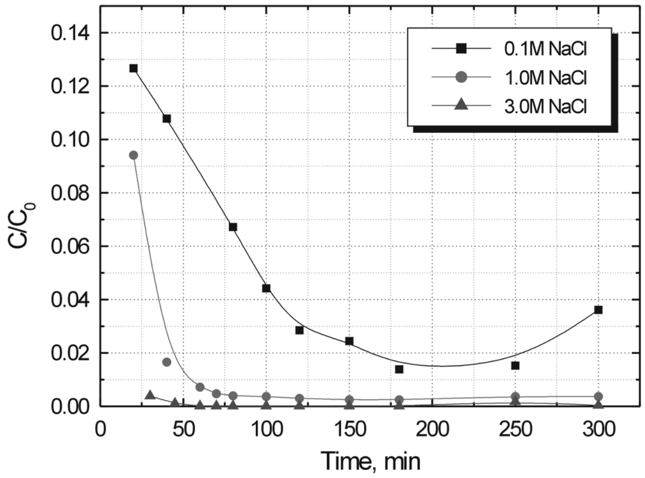

Fig. 7. Electro-adsorption % of 100 ppm U(VI) with variation of electrolyte concentration at -0.9 V and pH 4.

4. Conclusions

From this study, the following conclusions can be drawn.

(1) In our experimental condition (uranium concentration =100 ppm, pH=4), major hydrolysis species are present in the solutions as UO_2^{2+}.

(2) U(VI) ion in lagoon sludge can be effectively removed by the electrosorption process and the adsorption rate increases at more negative potentials.

(3) When applying potential ranges from -0.5 to -0.9 V, up to 99.9% of the uranium is removed from the 100~350 mg/L feed solution by electrosorption, and the cumulative amount of uranium within 15 h is about 552 $mg_{uranium}/g_{ACF}$ at a 350 mg/L feed solution.

(4) Electrosorption behaviors for U(VI) ion at negative potentials is considered to be the result of double layer charging, ion-exchange sorption of uranyl ions onto surface functional groups and other reactions such as uranium precipitation.

Acknowledgements

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References

[1] Sauer, N. N.; Smith, B. F. “Metal-Ion Recycle Technology for Metal Electro- plating Waste Waters”, LA-12532-MS, 1993.

[2] Hazourli, S.; Bonnecaze, G.; Astruc, M. *Environmental Technology*, “Adsorption and Electrosorption of Organic Compounds on Granular Activated Carbon”, **1996**, *17,* 1275.

[3] Jayson, G. G.; Sangster, J. A.; Thompson, G.; Wilkinson, M. C. “Adsorption and Electrosorption of Mercury(II) Acetate onto Activated Charcoal Cloth from Aqueous Solution”, *Carbon* **1987**, *25,* 523.

[4] Carley-Macauy, K. W.; Gutman, R. G. “Radioactive Waste: Advanced management methods for Medium Active Liquid Waste”, Harwood Academic Pub., **1981**, 41-130.

[5] Woodard, F. E.; McMackins, D. E.; Jansson, R. E. W. “Electrosorption of Organic on Three Dimensional Carbon Fiber Electrode”, *J. Electroanal. Chem.* **1986**, *214,* 303.

[6] Frumkin, A. “The Influence of an Electric Field on the Adsorption of Neutral Molecules”, *Z. Physik* **1926**, *35,* 792.

[7] Trainham, J. A.; Newman, J. “A Flow-Through Porous Electrode Model: Application to Metal-Ion Removal from Dilute Streams”, *J. Electrochem. Soc.* **1997**, *124,* 1528.

[8] Oren, Y.; Soffer, A. “Graphite Felts as an Efficient Porous Electrode for Impurity Removal and Recovery of Metals”, *Electrochemica Acta* **1983**, *28*, 1649.

[9] Bockris, J. O'M.; Devanathan, M. A. V.; Muller, K. “On the Structure of Charged Interfaces”, *Proc. Royal Society* (London) **1963**, *A 274*, 55.

[10] Shmidt, J. L.; Pimenov, A. V.; Lieberman, A. I.; Chen, H. Y. “Kinetics of Adsorption with Granular, Powdered and Fibrous Activated Carbon”, *Sep. Sci. & Tech.* **1997**, *32,* 2105.

[11] Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. “Surface Tension and Adsorption”, Longmlans, London, 1970, 218.

[12] 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.

[13] Hatfield, T. L.; Kleven, T. L.; Pierce, D. T. *J. Appl. Electrochem.* **1996**, *26*, 567.

[14] Grenthe, I.; Fuger, J. et al., Chemical Thernodynamics of Uranium, Wanner, H. & Forest, I. (ed.) OECD, 1992.

[15] Evans, S. “Electrochemiclly Controlled Ion-Exchange”, *J. Electrochem. Soc.* **1966**, *113*, 2975.

[16] Seron, A.; Benaddi, H.; Beguin, F.; Frakowiak, E.; Bretelle, J. L.; Thiry, M. C.; Bandosz, T. J.; Jagiello, J.; Schwarz, J. A. “Sorption and Desorption of Lithium Ions from Activated Carbons”, *Carbon* **1996**, *34,* 481.