

Isotherm And Kinetic Studies On The Electrosorption Of Uranyl Tricarbonate Complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ From Aqueous Solutions By Activated Carbon Electrodes

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1. Introduction

One of the important issues that need to be addressed regarding the future of nuclear power is the availability of uranium. Current projection of the well-known, easily obtainable sources of uranium indicates that global nuclear industry can be supported through the end of the century under the once-through cycle. If the speculative uranium resources are taken into account, the coverage could be extended up to 250 years. Other uranium resources are also available from unconventional uranium sources such as phosphate rock but their extent and recovery cost are uncertain. To ensure the long-term availability of uranium supply, a new uranium resource and recovery technology are needed [1]. Uranium is also available from seawater. The theoretical amount of uranium available in seawater is about 4.5×10^9 tonnes ($U \sim 3.3$ ppb, ocean volume $\sim 1.37 \times 10^9$ km³), which is roughly about thousand times larger than the estimated conventional uranium reserves [1]. Utilizing uranium from seawater thus opens up the possibility of virtually unlimited supply of nuclear fuel. However, harvesting uranium from seawater is currently very expensive compared to conventional mining requiring a dedicated adsorbent material and extraction technique. Many types of adsorbent materials have been developed over the past 50 years, and the most recognizable is amidoxime based materials which is known to have high affinity in chelating uranyl ions from seawater [2]. However, the fabrication cost of amidoxime based materials was high which lead to high uranium extraction cost. In recent studies, use of porous carbon materials combined with the electrosorption technique was shown to have high selectivity for uranium separation from seawater [3-4]. The objective of this research is to study electrosorption isotherm of activated carbon electrode at +0.4 V (vs Ag/AgCl) of applied potential that was reported in the previous study [4]. Tasks performed in the study includes material characterization using several technique (SEM, FT-IR, BET and Pore Analyzer and CV analysis) and batch-mode electrosorption studies to investigate the maximum capacity of the fabricated activated carbon electrode. Electrosorption isotherm were modelled using both Langmuir and Freundlich isotherm and electrosorption kinetic were evaluated using Pseudo-first-order and Pseudo-second-order.

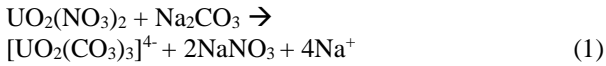
2. Methods and Results

2.1 Fabrication of Activated Carbon Electrode

Activated carbon electrode (ACE) were fabricated by slurry coating on a stainless steel gauze, drying and thermally cross-linking process. Carbon slurry was prepared by mixing activated carbon powder (DARCO® 100, Sigma Aldrich) with poly-vinylidene fluoride (PVdF, M.W. = 534,000, Sigma Aldrich) in an N,N-Dimethylacetamide (NND, 99%, Sigma Aldrich) solution. The PVDF polymer content was 50 wt% of the activated carbon electrode. The mixture was vigorously stirred at room temperature until it reaches homogeneity. The slurry was then casted onto a stainless steel gauze (40 mesh woven with 0.25mm diameter wire, Type 304, Alfa Aesar) and allowed to dry at 80 °C for 6 hours to form a carbon electrode. The carbon electrode was further dried in an 80 °C vacuum oven for 2 hours to remove all the organic solvents remaining in the micropores of the electrode. A detailed fabrication process of activated carbon electrode (ACE) was also given elsewhere [3-4].

2.2 Synthesize of Uranyl Tricarbonate complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ Solution

Uranium tricarbonate solution was synthesized using Eq.1. A 1000 ppm of uranium tricarbonate solution was prepared by mixing 1000 ppm of uranium nitrate standard solution (AccuStandard ICP-66N-5) with sodium carbonate (Sigma Aldrich, ACS reagent, $\geq 99.5\%$). The mixture was shaken at 3300 rpm for 15 minutes using a vortex mixer (WiseMix, VM-10). The 1000 ppm of the synthesized uranium tricarbonate solution then was diluted to the desired concentration with an addition of ultrapure water obtained from water purification system (Human Power I). The acidity of the solution was determined to be in the range of pH 10.0, measured using a pH/Ion meter (F72, Horiba Scientific). A standard buffer agent, TRIS (Sigma Aldrich, $\geq 99.9\%$) was added to the solution to ensure the acidity of the uranium tricarbonate solution will not drop below pH 9.0. It is imperative to maintain the pH of the solution since uranium tricarbonate species was reported to exist around pH 8.0 [5], and become more dominant above pH 9.0 [6].



2.3 Characteristic of Activated Carbon Electrode

The morphology of the fabricated activated carbon electrode (ACE) was observed by Scanning Electron Microscope (SEM S-4800, Hitachi) to determine the physical structure of the fabricated activated carbon electrode as shown in Fig. 1. It is clearly shown that the structure of the activated carbon electrode is a continuous, irregular network-like porous material.

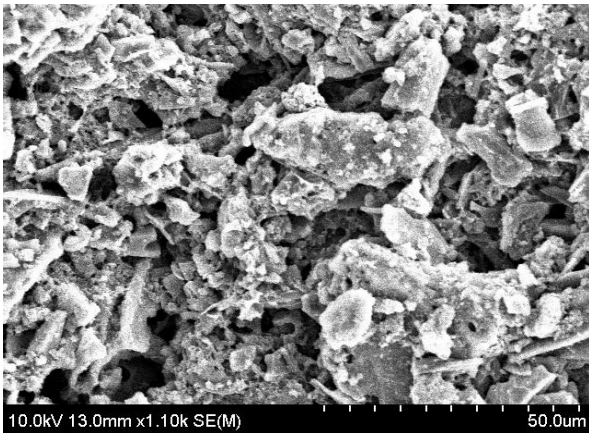


Fig.1. SEM image of activated carbon electrode shows the surface structure of the activated carbon electrode.

The molecular interactions of the fabricated activated carbon electrode were analyzed using Fourier Transformed Infrared Spectroscopy (FT-IR 4100, JASCO), through Attenuated Total Reflectance (ATR) technique. Fig.2 shows the result of FT-IR spectra scan from 0 – 1800 cm^{-1} of wavenumber. The peak of C–(CO)–N of NND at 1186 cm^{-1} and the peak of –CF₂ of PVdF at 1181 cm^{-1} have shifted to lower wavenumber, 1159 cm^{-1} in PVdF-NND-AC mixture indicating strong physical crosslinking by intermolecular hydrogen bonding interaction between oxygen atom in carbonyl functional group from NND with fluorine atoms on vinylidene structure from PVdF. In addition, the –CH₂ rocking or –CF₂ asymmetry stretching peak at 873 cm^{-1} , –CF₂ symmetry stretching peak at 1066 cm^{-1} also shifted to a lower wavenumber, 864 cm^{-1} and 1047 cm^{-1} , respectively. The peak of –N–(CH₃) deformation experiencing insignificant changes indicates that the amide functional group in NND did not take part into the physical interaction. The cross-linking reaction of PVdF-NND-AC is illustrated in Fig.3.

The BET specific surface area of the activated carbon electrode was determined by nitrogen (99.99% purity) adsorption/desorption at 77.3 K using a surface area and porosity analyzer (Tristar II 3020 Micrometrics Inc.). Prior to the analysis, the activated carbon electrode was degassed under vacuum at 378.2 K for 6 hours. The BET

surface area for the carbon electrode was 50 m^2/g and the total pore volume reached 0.1 cm^3/g with the average pores size of 5.0 nm. It indicates that the pore size can be categorized as mesopores. Mesopores are known to be beneficial in the adsorption of ions compared to micropores due to the electric double layer overlapping effects [7]. Therefore, the activated carbon electrode fabricated in this study is judged to be suitable for electroadsorption purposes.

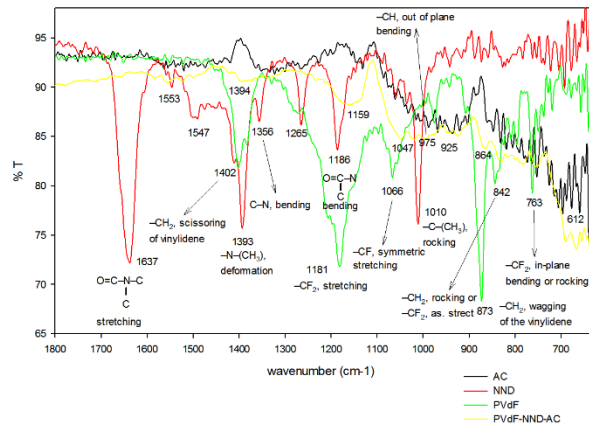


Fig.2. FT-IR spectrum of the NND, AC, PVdF and PVdF-NND-AC.

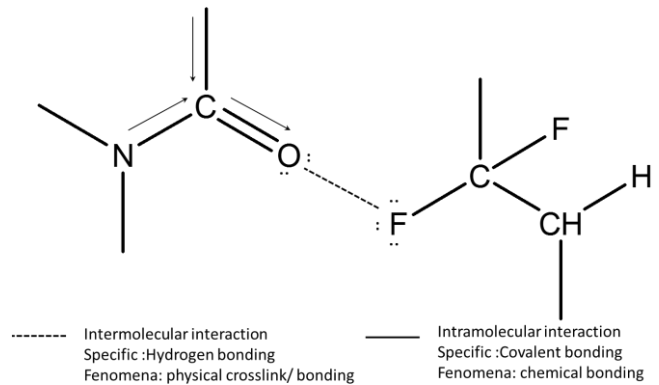


Fig. 3. Cross-linking reaction mechanism of PVdF-NND-AC.

The electrochemical properties of the fabricated carbon electrode was examined through cyclic voltamogram (CV) analysis using 3-electrode system. The activated carbon electrode was inserted into the specimen holder with an exposed surface area of 2.00 cm^2 . A platinum wire (A-002233 Biologic) and a saturated Ag/AgCl (RE-1S Biologic) were used as counter electrode and reference electrode, respectively. The voltage potential of the tested activated carbon electrode was controlled using SP150 Biologic potentiostat. CV measurement of the activated carbon electrode was investigated in the potential range of -0.4 V to 1.0 V at a scanning rate of 20 mV/s . Fig.4 shows the cyclic voltamogram result obtained from the electroadsorption and desorption of $[\text{UO}_2(\text{CO}_3)_3]^{+}$ on the activated carbon electrode. A steady increase of the current in the CV is caused by rapid response of ions with increasing potential.

Apparently, there was no evident oxidation/reduction peak in cyclic voltamogram curves in the applied potential range, which indicated that the ions were removed from the solution by formed electrical double layer rather than electrochemical reaction [8].

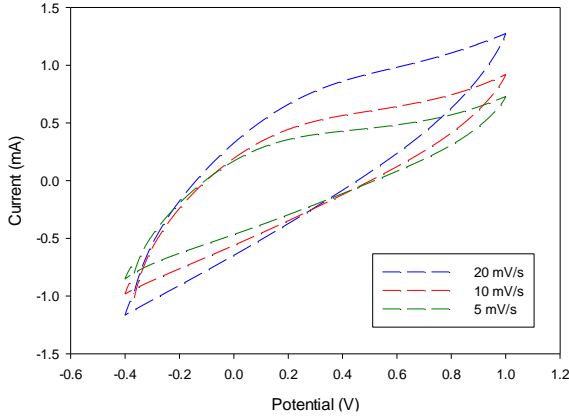


Fig. 4. Cyclic voltamogram of activated carbon electrode in 1 ppm $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ aqueous solution at different scan rate.

2.4 Electrosorption isotherm at +0.4 V

The electrosorption behavior of the fabricated activated carbon electrodes at +0.4V (vs Ag/AgCl) were investigated through batch-mode electrosorption experiment at various solution concentration. Ag/AgCl was used as the reference electrode while the platinum wire was used as the counter electrode. All the electrodes were connected to SP150 Biologic potentiostat. Electrosorption was measured for 5 hours at 25 °C under a constant positive voltage potential of 0.4V (vs. Ag/AgCl) applied to the working electrode and the electrosorption experiments were conducted for 5 hour. The initial concentration of uranyl tricarbonate complex solution were 0.2 $\mu\text{g/L}$, 0.8 $\mu\text{g/L}$, 1.0 $\mu\text{g/L}$, 10.8 $\mu\text{g/L}$, 13 $\mu\text{g/L}$, 100 $\mu\text{g/L}$ 500 $\mu\text{g/L}$, 3000 $\mu\text{g/L}$ and 5000 $\mu\text{g/L}$ respectively.

The amount of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ adsorption per unit mass of activated carbon electrodes was calculated using Eq.2.

$$m_u = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_t are the initial uranium concentration and the uranium concentration after electrosorption at time t in ($\mu\text{g/L}$), V is the volume of the solution (L) and W is the mass of adsorbent used (g) at time, t . The data obtained from experiment were further analyzed using Freundlich and Langmuir isotherm.

$$\text{Freundlich: } q_e = K_f C_e^{1/n} \quad (2)$$

$$\text{Langmuir: } q_e = \frac{Q \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (3)$$

where q_e is the amount of adsorbed $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ in $\mu\text{g-U/g-ACE}$, K_f is Freundlich constant related to electrosorption capacity of adsorbent, C_e is the equilibrium concentration of adsorbate in solution ($\mu\text{g/L}$) and $1/n$ is the tendency of the adsorbate to be adsorbed. The maximum amount of adsorbed $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ in $\mu\text{g-U/g-ACE}$ and the Langmuir constant related to binding energy were denoted as Q and b respectively.

Fig. 5 displays both the experimental and modelled electrosorption isotherms of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ on activated carbon electrodes. The values of the parameters are listed in Table 1. It was found that the activated carbon electrode is not yet reached the maximum adsorption capacity at the highest tested solution concentration. The adsorption capacity still shows an increasing trend with the increase of the equilibrium concentration. This result is similar to what was reported in the previous study [3-4], indicating that the pores structure in activated carbon electrode were not fully occupied by $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ions. The fabricated activated carbon electrode is capable of absorbing more $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ions due to high porosity structure. Also, the results suggested that the adsorption capacity of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ on activated carbon electrodes improved with the increase in the concentration. The calculated Freundlich and Langmuir isotherms were almost identical to each other as both were found to fit the experimental data well especially in the low concentration region.

2.5 Electrosorption kinetic

The kinetic of electrosorption reactions in the uranyl solution were investigated at +0.4 V (vs Ag/AgCl) with the initial concentration of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ fixed at 100 $\mu\text{g/L}$. Two model equation including pseudo-first-order and pseudo-second-order were used to fit the experimental data as follows.

$$\text{Pseudo - First - Order: } \log(q_e - q) = \frac{k_1 t}{2.303} \quad (4)$$

$$\text{Pseudo - Second - Order: } \frac{t}{q_t} = \frac{1}{q_2 q_e^0} + \frac{t}{q_e} \quad (5)$$

Here k_1 is the pseudo-first-order adsorption rate (min^{-1}), k_2 is the pseudo-second-order adsorption rate [$\text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$], q_e and q_t are the amount of of adsorbed $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ at equilibrium and time t , in $\mu\text{g-U/g-ACE}$ respectively. The results of experiment and data fitting are shown in Fig. 6 and Table 2, respectively. It was found that the pseudo-second-order kinetic equation can fit the experimental data better than the pseudo-first-order kinetic equation with higher value of the correlation coefficient (R^2). It is clearly indicated that the electrosorption of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ on the fabricated activated carbon electrodes followed pseudo-second-order kinetic model.

Table 1. The isotherm parameters of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ electro sorption on activated carbon electrodes at +0.4V (vs Ag/AgCl).

| $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ | Freundlich | | |
|-------------------------------------|-----------------|-----------------------|-------|
| | K_f | K_f | R^2 |
| +0.4 V | 13.06 | 13.06 | 1 |
| | Langmuir | | |
| | Q | b | R^2 |
| | 1×10^6 | 1.34×10^{-5} | 1 |

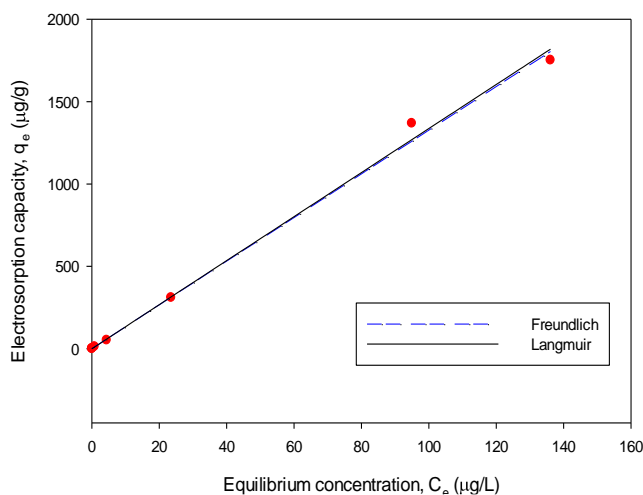


Fig.5. The electro sorption isotherm of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ on activated carbon electrode at +0.4 V (vs Ag/AgCl) of applied potential.

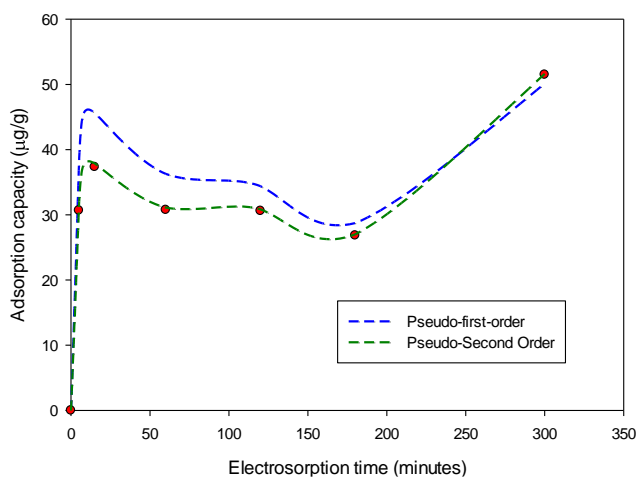


Table 2. The electro sorption parameters of pseudo-first-order and pseudo-second-order kinetic at +0.4V

| Co (µg/L) | Pseudo-first-order | | |
|-----------|---------------------|----------------|----------------|
| | qe | k1 | R ² |
| 100 | 1.30 | 0.0004 | 0.63 |
| | Pseudo-second-order | | |
| | qe | K ₂ | R ² |
| | 0.67 | 0.022 | 0.67 |

3. Conclusion

The main objective in this study is to investigate the maximum electro sorption capacity of the fabricated carbon electrode at +0.4 V (vs Ag/AgCl) of applied potential. However, at this stage, the maximum electro sorption capacity could not be determined through this preliminary result because only low concentration region (equilibrium concentration) has been tested. It is clear that the electro sorption capacity increase with the increasing of electrolyte concentration. The investigated activated carbon electrode still not reach the maximum adsorption capacity in the test condition. The morphology analysis confirmed that the fabricated activated carbon electrode has a porous structure, where BET analysis has revealed that the size of the pores can be categorized in mesopores region which is the optimum condition for electro sorption purposes. Other than that, the FT-IR analysis has enough evident that the molecular interaction of the activated carbon electrode involves the intermolecular interaction (physical crosslink/bonding) and stable for electro sorption application. The FT-IR finding was also supported by CV analysis which reveal that uranyl tricarbonate complex ions $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ were removed through electro sorption process rather than electrochemical reaction. However, further investigation are required in order to obtain the maximum adsorption capacity of the fabricated activated carbon electrode with the higher concentration of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ shall be used and tested at various of applied potential.

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