

## Prediction of the Dynamic Adsorption Behaviors of Uranium and Cobalt in a Fixed Bed by Surface Modified Activated Carbon

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### Abstract

In order to predict the dynamic behaviors of uranium and cobalt in a fixed bed at various influent pH values of liquid waste, the adsorption system was regarded as multi-component adsorption between each ionic species in a solution. Langmuir isotherm parameters of each species were extracted by incorporating equilibrium data with the solution chemistry of uranium and cobalt using IAST. Prediction results were in good agreement with the experimental data, except for a high concentration and pH. Although there was some limitations in predicting the cobalt adsorption, this method may be useful in analyzing a complex adsorption system where various kinds of ionic species exist in a solution.

### 1. Introduction

Various kinds of radioactive fission or corrosion products as well as uranium are simultaneously present in liquid wastes, and exist in several characteristic forms.<sup>1,2)</sup> These are generated during the fabrication and reprocessing of nuclear fuels, decommissioning of alpha contaminated facilities, and other activities.<sup>3)</sup> In particular, because of its long half-life and high radiological toxicity, uranium is considered to be a serious long-term environmental hazard. Cobalt is considered to be one of the key radionuclides contributing to the radiation dose for workers and the public.<sup>4)</sup> Like uranium, a very low concentration of cobalt is allowed in the effluents from a nuclear facility.<sup>5)</sup> In order to avoid the problems arising from the contamination of radioactive nuclides, both ion exchangers and sorbents for improving the removal efficiencies have been used. Numerous experimental studies have also been conducted on the removal of residual uranium and cobalt in radioactive liquid wastes.<sup>6-8)</sup>

The prediction of dynamic behaviors in a practical column process generally depends on the incorporation of the adsorption equilibrium relationship and the transport mechanism with a mass balance. In the adsorption of metal ions from aqueous solutions, solution pH may significantly affect the extent of the adsorption.<sup>9)</sup> Therefore, surface complexation models are useful to quantify the metal ion adsorption onto a hydrous solid surface.<sup>10)</sup> While the use of the complexation hypothesis in correlating metal ion adsorption data has been found to be useful, this approach also has its deficiencies. On considering the prediction of the adsorption

behaviors in a continuous-flow column operation, an equilibrium model to calculate the adsorption amount of a specific ion over a wide range of variables should be combined with a transport model in a column operation. In this case, the large number of parameters, presented in the surface complexation models, often make it difficult to obtain a stability of the numerical solution, and to ascertain the true physical significance of these parameters. In this study, the theoretical approach for analyzing the effect of the pH on the dynamic behaviors in a fixed bed packed with surface-modified activated carbon was performed using generalized adsorption model. Isotherm parameters of each uranium species were estimated by the combination of equilibrium data with solution chemistry using the minimizing routine. Based on this method, the trend of the breakthrough curves with the variation of the influent solution pH could be predicted.

## 2. Experimental

The granules of activated carbon, obtained from Han-il Green Tech. Co., were ground, sieved to give an average particle size of 0.85mm from the sieve openings. Some of the pre-treated activated carbons were oxidized by heating in 7 N nitric acid solution at a temperature of 80 ~90 °C for 10 hours in a volumetric flask.<sup>6,8)</sup> Fixed bed runs were confined to the oxidized and activated carbons. The adsorption experiments in the fixed bed were carried out using a glass column of 0.01m inside diameter and 0.3 m in length. Pretreated adsorbents were packed into the column and sustained by glass beads. A micro-metering pump was used to maintain the constant down-flow of 2 ml/min. Effluent from the column was collected periodically by a fraction collector, and the pH of the collected samples was directly measured, except for the over-night runs.

## 3. Theoretical Approach

Dynamic model for uranium adsorption in fixed beds packed with oxidized and activated carbon was formulated. The generalized equations consist of the transport equation and the mass balance equation for the adsorbed component in a multi- component system. The techniques of orthogonal collocation for finite elements combine the classical procedure of orthogonal collocation with the high accuracy of the finite element method. Owing to the system stiffness, its integration is made by means of a stiff solver : LSODI of the International Mathematics and Science Library (IMSL).

## 4. Results and Discussion

### 4.1. Extraction of Isotherm Parameters for Each Species

For the convenience of a simple calculation, it is assumed that the competitive adsorption of three components are as follows ;  $\text{UO}_2^{2+}$  and  $\text{UO}_2(\text{OH})^+$  as a monomer,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  as a dimer, and  $(\text{UO}_2)_3(\text{OH})_5^+$  as a trimer at around pH 6 or below. Therefore, the total adsorption amount of uranium is the sum of each component adsorption amount. In considering the above

assumptions, an uranium adsorption system in an aqueous solution would be regarded as the multi-component adsorption of each uranyl hydroxyl species. Once we obtain the equilibrium pH and the total adsorption amount from the equilibrium experiments over a wide range of pH, the equilibrium parameters of each uranyl hydroxyl species can be calculated by the combination of the solution chemistry of the uranium with the pH variation with IAST(Ideal Adsorption Solution Theory).<sup>11)</sup>

The Langmuir equation is adopted for calculating the equilibrium adsorption amount of each uranyl hydroxyl species with a variation of the pH. A mutual competitive adsorption between each species is represented by IAST. For an uranium adsorption system, the isotherm parameters for each ionic species (monomer, dimer and trimer) are listed in Table 1. For cobalt, the isotherm parameters of each species are confined to the adsorption system for activated carbon, as listed in Table 1.

#### 4.2. Prediction of Dynamic Adsorption Behaviors

When the competitive adsorption of each ionic species was not considered, the large discrepancies between the prediction and experimental data are observed, with the exception of the breakthrough curve at  $pHi=3$  ( $pHi$  : influent solution pH). These results may come from the inaccurate calculation of the adsorption amount with the variation of the pH.

Table 1. Langmuir isotherm parameters of each uranyl species and cobalt ions calculated by IAST

System Species	As-received activated carbon		Oxidized carbon	
	$q_m(\text{mol}/\text{m}^3)$	$B(\text{m}^3/\text{mol})$	$q_m(\text{mol}/\text{m}^3)$	$B(\text{m}^3/\text{mol})$
U(monomer)	$2.2 \times 10^{-2}$	7.42	0.268	65.2
U(Dimer)	$5.1 \times 10^{-2}$	23.8	0.35	50.2
U(Trimer)	$1.14 \times 10^{-1}$	103	0.67	30.0
$\text{Co}^{2+}$	$4.8 \times 10^{-2}$	1.06	-	-
$\text{Co}(\text{OH})^+$	$9.4 \times 10^{-2}$	$1.1 \times 10^5$	-	-

Fig. 1 represents a comparison of the experimental data with the model prediction, which was obtained by introducing the competitive adsorption of each uranyl hydroxyl species based on the isotherm parameters in Table 1. For the cobalt adsorption system, dynamic behavior of cobalt on activated carbon was satisfactorily predicted by considering the competitive adsorption of each species, as shown in Fig. 2.

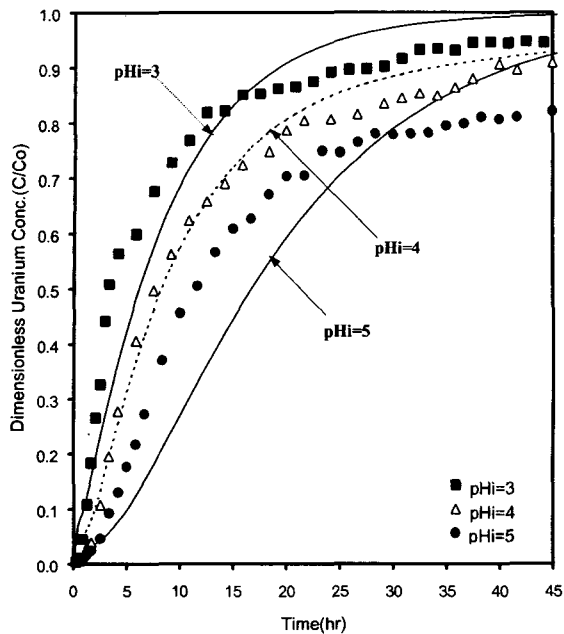


Fig. 1. Prediction of the experimental data of uranium adsorption on oxidized carbon in fixed bed [ $C_0=0.84 \text{ mol/m}^3$ ,  $\text{pHi}=3, 4, 5$ ].

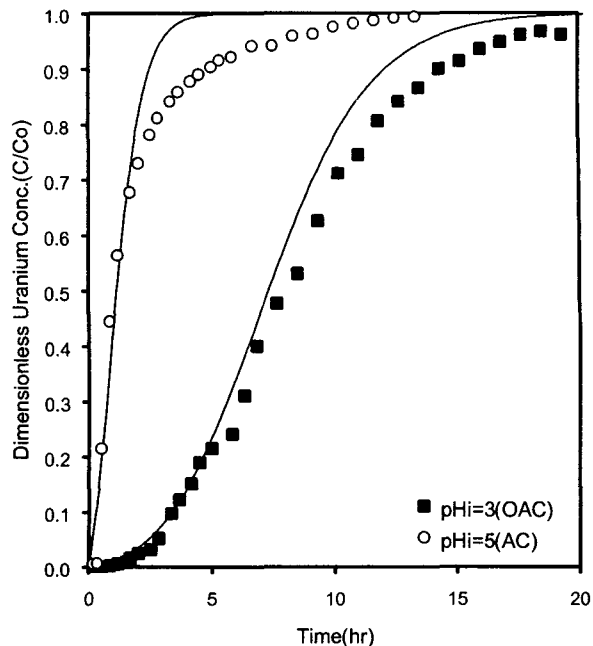


Fig.2. Prediction of experimental data of cobalt adsorption on activated carbon in fixed bed [ $C_0=0.21 \text{ mol/m}^3$ ,  $\text{pHi}=3$ , and 5].

Agreement between the experimental and prediction curves was fairly good, with the exception of the breakthrough curve at  $\text{pHi}=5$ . This deviation at  $\text{pHi}=5$  may come from a sharp pH variation inside the column compared to that at  $\text{pHi}=3$  and 4.

However, because the isotherm parameters of each ionic species in oxidized carbon-cobalt adsorption system could not be obtained, the method adopted in this study has a relative limitation in predicting the dynamic behaviors, as a associated with a simple system. However, at the low pH ranges, the prediction result gives a good fit with the experimental data. As a whole, the prediction method adopted in this study for predicting dynamic behavior incorporated with a pH influence may be applied to a complex system where various kinds of species exist in a solution.

## 5. Conclusions

While a surface complexation model is useful for predicting the adsorption behaviors of a metal ion, the use of an excessively large number of parameters can rule it out for a practical consideration, especially a column operation. Therefore, for describing the adsorption equilibrium and correlating the isotherm data, an alternative approach for representing the equilibrium data considering the pH effect on the metal adsorption was suggested using a generalized Langmuir equation. In an uranium adsorption system, the competitive adsorption of three kinds of uranyl hydroxyl species were considered. Based on the results from the equilibrium studies, the equilibrium isotherm parameters of each uranyl hydroxyl species were

extracted by the combination of the solution chemistry of the uranium with the pH variation with IAST. Experimental breakthrough curves at various influent pHs was satisfactorily predicted by introducing the competitive adsorption of each uranyl hydroxyl species, with the exception of the breakthrough curve at pH 5. Although some limitation in predicting the cobalt adsorption system was observed, this method may be useful for analyzing a complex adsorption system where various kinds of ionic species exist in a solution.

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## **References**

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