벤토나이트의 중금속 흡착에 대한 수리화학적 영향 : 열역학적 및 통계학적 해석

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1. Introduction

Heavy metal ion contamination released in subsurface systems pose a threat to human health and the surrounding environment. Sources of heavy metals include landfill leachate, mining activity, urban runoff, erosion from metal-rich soil, agricultural uses and industrial discharge.

In this study, sorption characteristics of Pb, Cu, Cd, and Zn onto smectite clay was investigated by the batch sorption test in the condition of various pHs and concentrations of groundwater major anions(SO_4^{2-} and HCO_3^-). The high pH-dependence on the sorption and sorption preference (Pb>Cu>Zn>Cd) among heavy metals were mainly explained by the species distribution and the saturation index predicted by the WATEQ4F program.

The Box-Behnken model which is a statistically designed by experimental method was applied to determine relative impact among three variables such as pH, HCO3 contents and heavy metal concentrations on the sorption. SAS program was used to obtain the statistical solution.

2. Methods

A clay material used for the sorption experiment is the Geko Ca-smectite clay, which is a commercial bentonite made by Süd-chemie Korea Co. The Pb, Cd, Zn and Cu were selected as heavy metals for this study. The experiment was designed as two types. Firstly, batch experiment was attempted to investigate the effect of pH and anions on the sorption of heavy metals by smectite clay. Secondly, the statistical designed batch experiments was carried out to model the relative effect among the concentration of heavy metals, pH and bicarbonate content on the sorption of heavy metals. The species distribution of heavy metals in various pHs and anion conditions was calculated by using the thermodynamic program WATEQ4F. The program was also used to predict the saturation state of secondary phases in such solutions.

Key words : surface response analysis, thermodynamic analysis, sorption, species distribution, heavy metals

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The Box-Behnken model which is a statistically designed by experimental method was applied to determine relative influence among three variables such as pH, bicarbonate content and heavy metal concentration on the sorption. This model was efficiently used to show the effects of two or more factors on sorption. The experimental design of the Box-Behnken model has three levels and three variables. In this study three independent variables were pH, bicarbonate and heavy metals. Three levels indicate their concentrations.

The experimental design of Box-Behnken and statistical analysis provide an equation that can be used to predict sorption values (distribution coefficient, Kd or sorption percent, P) within the range of the independent variables:

$$\text{Log [Kd]} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_{12} + b_{22}X_{22} + b_{33}X_{32} + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (1)$$

Experimental data were used to derive b values required to solve the polynomial for any combination of the variables X_1, X_2 and X_3 that lie on or within the response surface of the experimental design. The determined b values are used to draw the response surface of the sorption behavior of heavy metals.

3. Results and Discussion

The pH-dependence on the sorption of heavy metals by smectite clay was recognized and shows the sorption competition among heavy metals is as a following order: Pb>Cu>Zn>Cd. The sorption percent is characterized by an increasing shape of two steps. First increasing step is the range of pH 1.8 to 3.5 for all heavy metals. Second increasing step is the range of pH 5.5 to 7.0 for Pb and Cu, and pH 5.5 to 9 for Zn, and pH 7 to 10 for Cd. Above pH 9 sorption percent slightly decrease. The sorption percent of Cu and Pb gently increases in the range of pH 1.8 to 5.8, and then sorption percent dramatically increase between pH 5.8 and 7.0. The sorption percent for Zn and Cd shows a low level in the range of pH 1.8 to 6.5, and then it highly increases between pH 6.5 and 8. The sorption competition of heavy metals is divided into two groups. One group is related to Pb and Cu, and the other group is similar sorption shape of Zn and Cd.

Bicarbonate and sulfate are the major anions in natural water. In a high concentration of bicarbonate, all heavy metals are perfectly sorbed by smectite, and then sorption percent dramatically decreases in bicarbonate concentration less than 10^{-2}M. Sorption preference among heavy metals is recognized within a narrow range, and it is Pb, Cu, Cd and Zn in order. Sulfate concentration influences sorption behavior of lead, and rarely other metals. In high sulfate concentration (10^{-1}M), Pb is highly sorbed on smectite clay. Sulfate concentration below 10^{-2}M sorption percent of Pb highly decrease (Fig. 3b). Sorption percent of Cu, Cd and Zn shows the range from 20 to 30% without a distinct variation according to sulfate concentration. Sorption preference among heavy metals is also Pb, Cu, Cd and Zn in order.

It also predicted that high sorption of Pb in 0.1 M sulfate solution is attributed to the precipitation of $PbSO_4$(anglesite). However, sulfate has little effect on the sorption of other metals. The heavy metals were perfectly sorbed in 0.1M bicarbonate solution, and the sorption efficiency significantly decreased in the bicarbonate concentration of 10^{-2}M to 10^{-4}M. The precipitation as carbonate complex of heavy metals was thermodynamically analyzed as major mechanism of sorption. The statistical surface response analysis indicated that relative impact of the variables on the sorption was a following order: concentration of heavy metals, pH, bicarbonate concentration.

4. Conclusions

The high pH-dependence on the sorption and sorption preference (Pb>Cu>Zn>Cd) among heavy metals were mainly explained by the species distribution and the saturation index predicted by the WATEQ4F program. It also predicted that high sorption of Pb in 0.1 M sulfate solution is attributed to the precipitation of $PbSO_4$ (anglesite). However, sulfate has little effect on the sorption of other metals. The heavy metals were perfectly sorbed in 0.1M bicarbonate solution, and the sorption efficiency significantly decreased in the bicarbonate concentration of 10^{-2}M to 10^{-4}M. The precipitation as carbonate complex of heavy metals was thermodynamically analyzed as major mechanism of sorption. The Box-Behnken model which is a statistically designed by experimental method was applied to determine relative impact among three variables such as pH, HCO_3 contents and heavy metal concentrations on the sorption. SAS program was used to obtain the statistical solution. The statistical surface response analysis indicated that relative impact of the variables on the sorption was a following order: concentration of heavy metals, pH, bicarbonate concentration.

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