Modified Freundlich Sorption of Cesium and Strontium on Wyoming Bentonite

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Sorptions of cesium and strontium on natural Wyoming bentonite have been investigated. A modified two-stage Freundlich sorption model was proposed on the basis of such primary factors as temperature, pH value and nuclide concentration which influence the sorption behavior of bentonite. The dominant sorption mechanism of bentonite was observed here to be an ion-exchange reaction, while physical adsorption functioned in a minor role.

Introduction

The sorption of cesium and strontium on geomedia has been the focus of a great number of previous investigations (Berry et al., 1988; Erton et al., 1988; Meyer et al., 1984; Walton et al., 1994; Westvik et al., 1982). The assumption of linear sorption isotherm has been the basis of most of these investigations. The concentrations of radionuclides may substantially influence the sorption. The assumption of linear isotherm has been indicated by many studies (Del Deddio, 1991; Polzer and Fuentes, 1988) to possibly be modified if the nuclide concentration becomes higher than the tracer level. Various well-known sorption isotherms, i.e. Langmuir, modified Langmuir and Freundlich isotherms, have been used in earlier studies for describing the sorption of soils (Aksoyoglu et al., 1991; Bornemiza and Lianos, 1967; Sposito, 1980; Polzer and Fuentes, 1991). The sorption of Zn\textsuperscript{2+} on clay minerals, including bentonite, has been previously examined by Fujiyoshi et al. (1992), and the experimental results were fitted by traditional Freundlich isotherm. A possibility is revealed in this work which could introduce the nonlinear isotherm into the study on the sorption behavior of bentonite. On the other hand, a two-stage modified Freundlich isotherm has been applied on the mordenite sorption by Liang and Hsu (1993). The results of Cs\textsuperscript{+} and Sr\textsuperscript{2+} sorption on natural bentonite may also be fitted more closely in the present study by modified Freundlich isotherm.

Experimental

Natural Wyoming MX-90 bentonite was used in this study. Batch experiments developed by Relyea et al. (1980) were employed. The ratio of volume of solution to mass of bentonite (V/m) was 30(cm\textsuperscript{2} g\textsuperscript{-1}).

The initial pH values of solutions were regulated by additions of HCl and NaOH. Bentonite was indicated in previous studies to exhibit a rather wide range of pH buffering effects, from pH\textsubscript{m} = 3 to pH\textsubscript{m} = 12. The pH values of solution in equilibrium condition were maintained at ca 8.7 in the pH buffering region. Three different pH\textsubscript{m} values were therefore selected for this study, i.e. pH\textsubscript{m} = 2.8 and 12. Carrier-free forms of \textsuperscript{137}Cs and \textsuperscript{85}Sr, with the concentration of 0.1 \textmu Ci cm\textsuperscript{-3}, were used as a radiotracer. The concentrations of the carriers varied from 10\textsuperscript{-7} to 0.2 M for cesium and 10\textsuperscript{-7} to 0.1 M for strontium. The respective chemical species of the carriers were CsNO\textsubscript{3} and Sr(NO\textsubscript{3})\textsubscript{2}. Test temperatures were set at 25\textdegree and 90\textdegree C. Four samples carried out under the same experimental condition. The size of the particles of MX-90 bentonite powder was <325 mesh (43 \mu m), with an average diameter of 17.5 \mu m. The equilibrium period of time for batch studies was 7 days. The solutions were separated by previous centrifuge and ultra fine filtration. The centrifugal force was 13,000 g over a duration of 15 min, and then the solutions were filtered by a membrane with a pore size of 0.22 \mu m. Well-type NaI counting systems were employed for residual activity measurement, and the counting efficiency was estimated at about 50%. A typical counting time was set at 300 s.

Results and Discussion

The sorptions of Cs and Sr on bentonite in various concentrations of nuclides were determined experimentally; the results are illustrated in Figs 1 and 2, respectively. The traditional Freundlich sorption isotherm is written as

\[
S = K \cdot C^{1/n}
\]
in which \( S \), equivalents of solute sorbed (\( \mu \text{eq g}^{-1} \)); \( C \), solute concentration in equilibrium (\( \mu \text{eq mL}^{-1} \)); \( K \), curve-fitting parameters (\( \text{mL g}^{-1} \)); \( n \), intensity of sorption.

The intensity of sorption is an empirical parameter denoting the capacity of sorption; its value generally exceeds unity. The customary Freundlich isotherm is based on the assumption that ions are infinitely

Fig. 1. Modified Freundlich sorption isotherm of Cs\(^{+}\).

Fig. 2. Modified Freundlich sorption isotherm of Sr\(^{2+}\).
accumulated on the sorbent surface; this assumption is, however, impossible to confirm for bentonite. The concentration gradient between solution and bentonite surface and the distribution of counter-ion influence the sorption ability. On the other hand, as Muurinen et al. (1986) and Gast (1972) indicated, the primary interaction occurring between bentonite and Cs and/or Sr is an ion-exchange reaction, and the numbers of reactive sites where reactions take place are finite. The electric field on the bentonite surface has been shown by Bolt (1982) to become nonlinear if the cation concentration rises. All the above-mentioned reasons limit the validity of the linear isotherm applied in a higher cation concentration environment. A modified Freundlich model is proposed here for predicting the sorption behavior of bentonite as a combination of two related conventional Freundlich models

\[
S = K_H \cdot C^{ln_H} + K_s \cdot C^{ln_s} \tag{2}
\]

in which \(K_H\), the fitting parameter in the region of high concentration (mL g\(^{-1}\)); \(K_s\), the fitting parameter in the region of low concentration (mL g\(^{-1}\)); \(n_H\), the intensity of sorption in the region of high concentration; \(n_s\), the intensity of sorption in the region of low concentration.

The data fit proposed for the modified Freundlich model according to equation (2) is given in Table 1. Temperatures, initial pH values of solutions, carrier concentrations and chemical species of nuclide are the four primary factors which influence the sorption of bentonite. Temperature is indicated by experimental data to be apparently not a dominant factor in the sorption property of bentonite. The excellent thermal stability of bentonite has been proven within the temperature range from 25 to 90\(^\circ\)C through these data. The \(pH_{\text{max}}\) of solution has a more significant influence on sorption. The intensity of sorption of Sr\(^{2+}\) in a higher concentration region, \(n_{\text{Sr}^{2+}}\), increases as the \(pH_{\text{max}}\) values of solution increase. Three possible reasons may be introduced for this phenomenon:

1. the surface of a bentonite particle may be charged more negatively at a higher \(pH_{\text{max}}\) for enhancement of the sorption;
2. the formation of partially soluble precipitation \(\text{Sr(OH)}_2\) occurs in an extremely basic solution, and this reaction gradually becomes important in higher carrier \(\text{Sr}^{2+}\) concentrations; and
3. the rate of dissolution of the bentonite framework structure increases when the solution is strongly basic.

The influence of \(pH_{\text{max}}\) on the sorption of Cs\(^+\) is apparently not so great as on that of \(\text{Sr}^{2+}\); it causes only a slight increase in the basic solution.

The intensity of sorption is expected to follow the relationship between cesium and strontium owing to the charge-dependent characteristics of the ion-exchange and adsorption reaction in the region of high concentration. The intensities of sorption at various pH values are listed in Table 2. These data have been fitted by a two-step least-square method. The optimum linear fit is determined by the least-square errors of both curves. Several interesting results are discovered: (1) Both the intensity of sorption in the region of low concentration, \(n_{\text{Cs}}\) and \(n_{\text{Sr}}\), are near unity when the initial carrier concentration of solution is \(<0.01\) M. The assumption of linear isotherm is confirmed by this result to still be applicable in a low nuclide concentration condition. The traditional governing equation for nuclide migration is based on the assumption of a linear isotherm. The apparent diffusion coefficient \(D_{\text{nu}}\) is also assumed to be independent of the concentration gradient. The proposed modified Freundlich isotherm provides a more detailed model for future theoretical developments. (2) The values of \(n_{\text{Cs}/n_{\text{Sr}}}\) decrease from roughly 1.7 to 1 with the increase of \(pH_{\text{max}}\) for the possible reasons mentioned above. (3) The substantial differences occurring between \(n_{\text{Cs}}\) and \(n_{\text{Sr}}\) may be owing to several reasons. The sorption theory of traditional Freundlich isotherm, linear isotherm, and
traditional Langmuir isotherm is based on the assumption of the existence of infinite reactive sites on the sorbent surface, and each sorption reaction occurs independently. This assumption is valid while the nuclide concentration is extremely small. But the energy state, activity and ion distribution near the bentonite surface have changed as the nuclide concentration increases. The modification of Gouy-Chapman theory (Grahame, 1947; Bolt, 1955) predicts that nuclides concentrate locally near the sorbent surface. This condensation reduces the chemical potential of solution and the thickness of the diffuse layer, and then influences the sorption behaviors of nuclides.

Conclusion

A modified Freundlich sorption isotherm was proposed here for describing the characteristics of bentonite sorption. This model was fitted into two ranges of concentration, large and small. The linear sorption model was feasible in the latter, whereas another typical Freundlich isotherm became feasible in a greater concentration. The great differences occurring between the values of $n_f$ and $n_l$ could be accounted for by the diffuse double layer theory. The carrier concentrations were observed to influence the thickness of the diffuse layer, reducing the solution chemical potential and activity, and finally transform the energy state of sorbent surface.

References


