The Removal Kinetics of Mn and Co from the Contaminated Solutions by Various Calcium Carbonate Surfaces

(다양한 방해석 표면에 대한 Mn과 Co 흡착 기작)

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Abstract

Removal characteristics of Mn and Co was studied from the contaminated solutions via surface reaction with various calcium carbonate (calcite). Synthetic calcium carbonates which has different surface morphology as well as surface areas were prepared by a spontaneous precipitation method and used. Mn and Co removal behavior by the different solid surface demonstrate characteristic sorption behaviors depend on the type of calcite used, such as surface area or surface morphology. Calcium carbonate crystals (mostly calcite) which exhibit complicated surface morphology (c-type) shows strong sorption affinity for Mn and Co removal via sorption than on the a-type or b-type calcite crystals of less complicated surfaces. The applicability of two kinetic models, the pseudo-first-order kinetic equation and the Elovich kinetic model was examined on these sorption behavior. Elovich kinetic model was found more suitable to explain the very early stage adsorption kinetics, while the pseudo-first-order kinetic equation was successfully fitted for the adsorption kinetics after 50 hours.

key word : Calcite, Spontaneous precipitation, Surface morphology, Pseudo-first-order, Elovich

1. Introduction

Knowledge of the factors that control pollutant metals removal process by mineral surfaces has important applications in many geo-environments. The surface sorption behavior of common metal ions such as Co and Mn on carbonate minerals is of considerable importance in calcarious aquifer. The geochemical behavior of those metal ions has been the subject of extensive study not only because of pure scientific interest but because it has proved useful in understanding removing process of pollutant metal ions by the calcium carbonate mineral surfaces.

In this study, the removal kinetics of two metal ions, Mn and Co, as the pollutant metals on calcium carbonate surface was studied and the kinetics of their interaction was quantitatively

measured. A special comparison is given to the effect of surface characteristics on controlling the initial fast adsorption reaction. The removal rate of Mn and Co on three types of calcite was compared and analyzed using two adsorption kinetic models, the pseudo-first-order kinetic equation and the Elovich kinetic model.

2. Materials and Method

2.1. The calcite sorbent

The sorbent calcite crystals were prepared by a spontaneous precipitation method. Solutions of three different supersaturating conditions of 0.02, 0.2, and 0.4 mol/dm^3, for both total calcium concentration, $[Ca]_T$, and total carbonate concentration, $[CO_3]_T$ were used to precipitates calcite crystals of different surface morphology. The calcite precipitation was prepared by mixing two concentrated solutions of $CaCl_2 \cdot 2H_2O$ and $(NH_4)_2CO_3$ in a 1000ml glass reaction vessel, which was immersed in a temperature controlled water bath at 25°C and 1atm pressure, and continuously stirred by rotating the propeller at 250-300 rpm.

2.2. Adsorption of Mn and Co on calcite

Adsorption experiments of manganese and cobalt were conducted on synthetic calcite precipitates. The known amount of $CaCO_3(aq)$ in equilibrium with $CaCO_3(s)$ was added to a acid-soaked 250ml polypropylene bottles at pH 8.27 and atmospheric $PCO_2(g)$. New calcite precipitates were added to the reaction bottle to yield 3.75g/L. Every experiment was duplicated twice to confirm the accuracy of the experiment. The calcite-solution mixture was gently shacked for 2 hours in a temperature controlled water bath at 25°C and allowed sitting for 24 hours open to air. Then, either $MnCl_2$ or $CoCl_2$ stock solutions of 10^{-6} mol/dm^3, concentration was added to yield the final manganese and cobalt concentration of 10^{-8} mol/dm^3.

3. Result and Discussions

XRD and SEM analyses confirmed that the $CaCO_3$ precipitates prepared from three different supersaturating solution conditions were mostly pure calcite crystals with less than 1% of vaterite present. The calcite precipitates obtained from 0.02 mol/dm^3, 0.2 mol/dm^3, and 0.4 mol/dm^3 supersaturating solutions were designated as a-, b-, and c-type calcite, respectively.

The precipitated calcite crystals, a-, b-, and c-type, clearly exhibited different surface morphology. The a-type calcite exhibited simple rhombohedral cleavage, while b-type calcite consisted of intergrowths of more numerous, smaller and thinner crystallites (Fig. 1). The b-type calcite exhibited a periodic growth and partial agglomeration of small platelets.

The mean size analysis and the BET surface area measurements showed that each calcite crystal had a mean size of 6.1µm, 5.8µm, and 7.2µm and surface area of 1.03m^2/g, 1.57 m^2/g, and 0.92 m^2/g for the a-, b-, and c-type calcite respectively.

The removal of Mn and Co was carefully examined to study the effect of surface factors on various calcite surfaces. The removal kinetics of Mn and Co on the a-, b-, and c-type calcite surface was examined by the pseudo-first-order kinetic equation and by the Elovich kinetic model. Fig. 2 shows the theoretical pseudo-first-order kinetic equation and Elovich kinetic model plotted against the experimental data point of manganese and cobalt adsorption on a-, b-, and c-type calcite. The overall adsorption kinetics of manganese and cobalt were well fitted by the pseudo-first-order kinetic equation and the Elovich kinetic model.
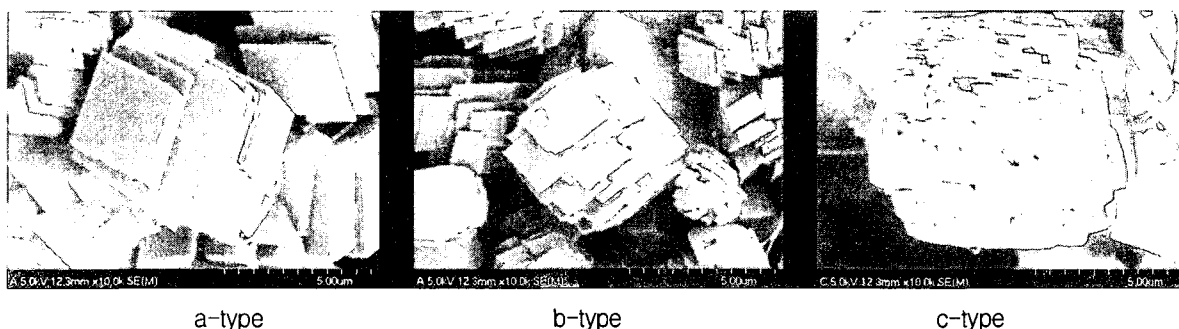

a-type   b-type   c-type

Fig. 1. SEM photographs of three types of synthetic calcite crystals grown by instantaneous nucleation method. (a) a-type calcites: grow in 0.02 mol/dm^3 CaCl$_2$·2H$_2$O solution (b) b-type calcites: in 0.2 mol/dm^3 CaCl$_2$·2H$_2$O, (c) c-type calcites: in 0.4 mol/dm^3 CaCl$_2$·2H$_2$O.
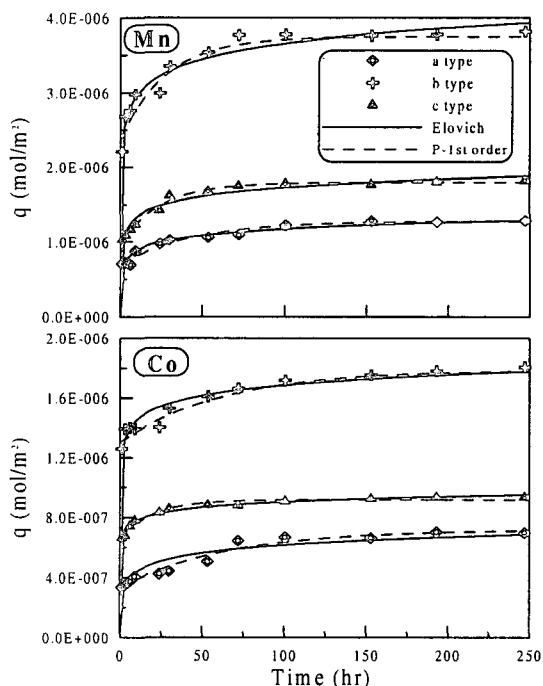

Fig. 2 Adsorption kinetics of Mn, Co on various synthetic calcites. Adsorption kinetics was analyzed by the Elovich model (solid line) and by the pseudo-first-order kinetic equation (dotted line). The adsorption kinetics was analyzed based on unit surface areas of each calcite.

The initial stage of adsorption kinetics is not well fitted and lower than the experimental data points. During 9 to 50 hours, the theoretical pseudo-first-order kinetic lines became fairly straight. Compare to this, the pseudo-fist-order kinetic equation is successfully fitted for the adsorption after 50 hours. The Elovich kinetic model successfully described the adsorption kinetics of Mn and Co especially for the initial adsorption period (Fig. 2). The theoretical Elovich kinetic model fitted well for all experimental data plots especially for the very initial stage adsorption up to 50 hours. The kinetics of adsorption and the amounts of adsorbed metal ion concentration during very early stage demonstrated several important features. It implies preferred adsorption capacity of solid surfaces, and the density of high-energy surface sites on solid. Driven by growth rate, the highly active high-energy surface sites were easily occupied by the foreign ion during initial adsorption process.

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