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Sorption kinetics on the removal of zinc ion using scoria

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Abstract

Recently, considerable researches have been focused to find out inexpensive sorbents for removal of heavy metals in aquatic environments. In particular, various natural materials including geologic media have been attractive. In order to evaluate the applicability of the scoria taken from the Jeju island, Korea, to remove Zn(II) from aqueous solutions, the kinetic sorption experiments were performed in this study. The batch-type kinetic sorption tests were carried out under different conditions, such as different initial Zn(II) concentration, particle size of the scoria, and sorbate/sorbent ratio. The results indicated that the removal of Zn(II) by scoria increased with decreases in initial Zn(II) concentration, particle size of the scoria, and sorbate/sorbent ratio. However, the sorption capacity of the scoria decreased with increasing amount of the scoria. The sorption behavior of Zn(II) onto scoria seemed to be mainly controlled by cation exchange.

key word : Scoria, Zinc removal, Sorption, Cation exchange.

1. Introduction

In natural water with a near-neutral pH, zinc occurs in the form of divalent cation (Zn^{2+}) as well as in the form of fairly weak complexes. Human activities may introduce zinc ion to the hydrosphere in many ways. In human body, zinc is an essential trace nutrient, a constituent of many enzymes, and a coenzyme for a number of systems, but concentrated zinc can motivate disorders. For the reasons, various treatment technologies have been developed for a cleanup of water and wastewater contaminated and polluted with zinc ion. The USEPA and the Canadian Department of the Environment suggested the drinking water guideline for zinc as 5 mg L^{-1}. In this research, the Jeju scoria was examined as an economic and efficient sorbent to remove the zinc ion from aqueous solution.

2. Materials and methods

2.1. Sorbent and sorbate

Scoria used as a sorbent in this study was taken from the Jeju island, Korea. The scoria was first washed many times with distilled water to remove any dust and other water-soluble impurities and then dried at room temperature. Then, the size reduction was conducted, as the procedure was important for execution of batch equilibrium experiments because sorption capacity is generally proportional to the total surface area and the total surface area of non-porous particles is also inversely proportional to the particle diameter. Particle size also affects the equilibration time.

All chemicals used were of analytical reagent grade with the highest quality. The stock solution (20 mM) of Zn(II) was prepared by dissolution of $Zn(NO_3)_2 \cdot 6H_2O$ in deionised/distilled water, and then the Zn(II) solutions for each experiment were prepared by appropriate dilution.

2.2. Kinetic sorption experiments

Kinetic Zn(II) sorption studies were carried out in acid-washed 50-mL polypropylene centrifuge tubes using batch experiment. Throughout the study, the contact time was varied from 5 min to 36 h, the sorbent diameter from 2.0 to 0.1 mm, the initial zinc concentration from 5.0 to 20 mM, and the sorbate/sorbent ratio from 10 to 50 mL g^{-1}. Batch kinetic experiments were performed at 150 rpm and 25°C. At each interval of time, solid-solution separation was achieved by filtration through 0.45 μm cellulose nitrate membrane filter paper, and the supernatant was acidified with HNO_3 and then was analyzed for cations by a Perkin Elmer ELAN 3000 inductively coupled plasma atomic emission spectrometry (ICP-AES).

3. Results

Various sorption parameters controlling the removal efficiency were determined empirically. The effects of particle size, initial sorbate concentration, and sorbate/sorbent ratio on the removal of Zn(II) by the Jeju scoria are shown in Fig. 1. The removal of Zn(II) increased with decreases in particle size (Fig. 1(A)), initial sorbate concentration (Fig. 1(B)),

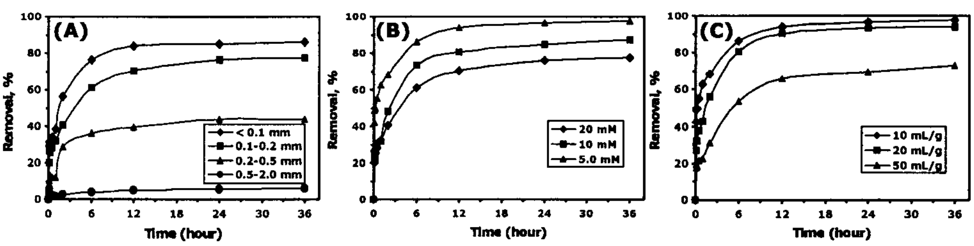

Fig. 1. Effects of the particle size (A), the initial sorbate concentration (B), and the sorbate/sorbent ratio (C) on the sorption of Zn(II) onto the Jeju scoria (temp. = 25°C, pH_{ini} = 3).

and sorbate/sorbent ratio (Fig. 1(C)).

The Lagergren rate equation was used to describe the rate of sorption in liquid/solid system based on the capacity of the solid. The Lagergren plots of the kinetic isotherm data for each system are shown in Fig. 2. The plot of $\log(q_e - q)$ versus time shows a straight line, confirming the applicability of a first-order rate representation for the sorption.

Simply, the sorption represents the change in concentrations of chemicals in the solid phase as a result of mass transfer between solution and solid, and includes all

No.	Size of scoria (mm)	Initial Zn(II) concentration (mM)	Sorbate/sorbent ratio (mL g^{-1})
1	0.1-0.2	20	10
2	0.2-0.5	20	10
3	0.5-2.0	20	10
4	< 0.1	20	10
5	0.1-0.2	10	10
6	0.1-0.2	5	10
7	0.1-0.2	5	20
8	0.1-0.2	5	50

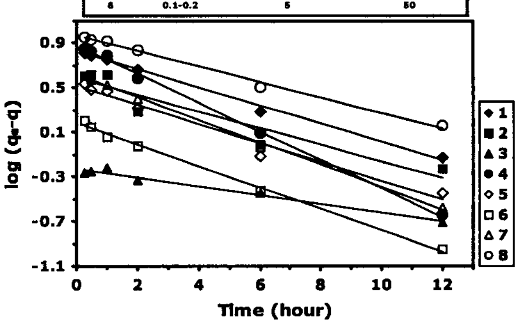

Fig. 2. Lagergren plot for the sorption of Zn(II) onto the Jeju scoria with various conditions at temp. = 25°C, and pH_{ini} = 3.

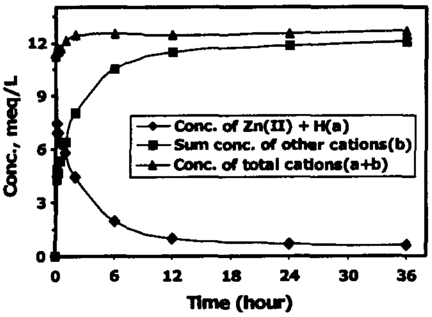

Fig. 3. The sum of concentrations (meq L^{-1}) of zinc and hydrogen ions, and other cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) in the solution, determined by ICP-AES analysis (temp. = 25ºC, pH_{ini} = 3, particle size = 0.1-0.2 mm, initial zinc ion concentration = 5.0 mM, and sorbate/sorbent ratio = 20 mL g^{-1}).

types of removal mechanisms such as adsorption, absorption, and exchange. Surface coordination and in some cases ion exchange are usually the dominant mechanism for the adsorption of heavy metal ions onto charged surfaces. To understand the sorption mechanism for the removal of Zn(II) onto the Jeju scoria, the concentration of zinc ion and other cations were analyzed using ICP-AES, and the concentration of hydrogen was measured by pH meter. Fig. 3 shows the sum of concentrations (meq L^{-1}) of zinc and hydrogen ions, sum of other cations (Ca(II) + Mg(II) + Na(I) + K(I)), and the total cations in solution at contact time, *t*. This result indicates that the sum of concentrations of released cations is equivalent with that of sorbed zinc and hydrogen ions during the reaction. The concentration and percentage of the released metal ions (Ca(II), Mg(II), Na(I), and K(I)) are also shown in Fig. 4. The concentrations of the released cations increased over the contact time (Fig. 4(A)), and the sequence was Ca(II) > Mg(II) > Na(I) > K(I). The percentages of the entire released cations ranged from 89.5% to 92.2% for Ca(II), from 6.29% to 4.88% for Mg(II), from 2.71% to 2.06% for Na(I), and from 2.11% to 1.21% for K(I) during the contact time of

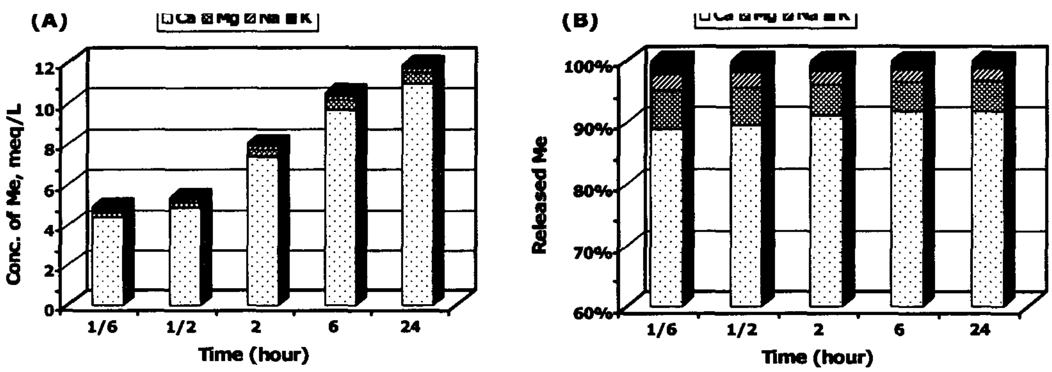

Fig. 4. (A) The absolute and (B) the relative concentration of released metals during the removal of Zn(II) onto the Jeju scoria (temp. = 25ºC, pH_{ini} = 3, particle size = 0.1-0.2 mm, initial zinc ion concentration = 5.0 mM, and sorbate/sorbent ratio = 20 mL g^{-1}).

1/6 h to 24 h (Fig. 4(B)). The correlation between the released metal ions and removed zinc ion are also shown in Fig. 5. The amount of the cations released from the Jeju scoria was linear with the amount of sorbed zinc ion. The slope of the regression line expresses quantitatively the order of exchanged cation, and the sequence is Ca(II) > Mg(II) > Na(I) > K(I). Consequently, we suggest that the cation-exchange reaction is the dominant mechanism for the sorption of Zn(II) onto the Jeju scoria.

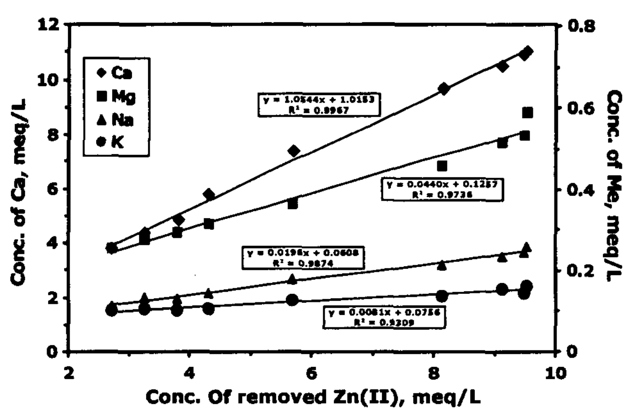

Fig. 5. Concentration of released metals (Ca: left axis; Mg, Na, K: right axis) in the removal of Zn(II) onto the Jeju scoria (temp. = 25ºC, pH_{ini} = 3, particle size = 0.1-0.2 mm, initial zinc ion concentration = 5.0 mM, and sorbate/sorbent ratio = 20 mL g^{-1}).