

# Removal of Zn(II) ion from aqueous solutions by using scoria as a sorbent

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## 1. Introduction

Zinc occurs in the nature as sulfide, carbonate, silicate, and oxide. In natural water, zinc is generally in the form of the divalent cation  $Zn^{2+}$  as well as in the form of fairly weakly bound complexes. Human activities introduce zinc ion to the hydrosphere in many ways. The zinc complexes in the aqueous environment are accumulated not only in aquatic organisms but also in human body ultimately through physico-chemical and/or biological processes. In human body, zinc is an essential trace nutrient, a constituent of many enzymes, and coenzymes for a number of systems, but concentrated zinc can motivate disorders. Thus, the USEPA and the Canadian Department of the Environment suggested the drinking water standard for zinc as  $5 \text{ mg L}^{-1}$ . For those reasons, various technologies have been developed for a cleanup of water and wastewater contaminated with zinc ion. The conventional treatment of zinc-containing wastewater usually involves the application of physico-chemical processes. Among the techniques, sorption was used as a most practical method.

In this paper, we used the scoria from the Jeju island a sorbent to remove the zinc ion from aqueous solution. The main objectives of this study are: (1) to estimate the affinity of zinc ion onto the Jeju scoria; (2) to investigate the effects of particle size, initial sorbate concentration, sorbate/sorbent ratio, and pH on the removal of zinc ion from the solution; (3) to understand the sorption mechanism; (4) to compare the sorption capacity of the Jeju scoria with that of powdered activated carbon (PAC); and (5) to evaluate the consistency between experimental data and theoretical adsorption capacity using adsorption isotherms.

## 2. Materials and methods

### 2.1. Sorbent and sorbate

Scoria was taken from the Jeju island, Korea. Prior to the sorption experiment, the Jeju scoria was first washed with distilled water many times to remove any dust and other water-soluble impurities and dried at room temperature. Then, the scoria was broken into small sizes and then was sieved into four fractions ( $<0.1$ ,  $0.1-0.2$ ,  $0.2-0.5$ ,

0.5–2.0 mm). Before the experiments, each fraction was stored in desiccator cabinets.

All chemicals used were of analytical reagent grade with the highest quality. Hydrated zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ),  $\text{NaOH}$ , and  $\text{HNO}_3$  were purchased from Aldrich. Stock solution (20 mM) of Zn(II) was prepared by dissolution of 2.9749 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 500 mL of deionised/distilled water, and then the Zn(II) solutions for the following experiments were prepared by appropriate dilution process.

## 2.2. Sorption experiments: kinetics and equilibrium

Studies on the kinetics of Zn(II) sorption were carried out using batch experiments within acid-washed, 50-mL polypropylene centrifuge tubes. 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  $\text{g}^{-1}$ . 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  $\mu\text{m}$  cellulose nitrate membrane filter paper, and the supernatant was acidified with  $\text{HNO}_3$  and then was analyzed for cations by ICP–AES (model: Perkin Elmer ELAN 3000).

A set of ten centrifugal tubes (each 15 mL) was prepared and each tube had different pH values and initial zinc concentrations. The set of samples was agitated for at least 24 h at 150 rpm and 25°C. The equilibration time was determined through preliminary kinetic sorption experiments. The data obtained were then fitted to the Langmuir and the Freundlich adsorption isotherms.

## 3. Results

### 3.1. Kinetics of sorption reaction

Various sorption parameters controlling the removal efficiency (%) of Zn(II) by the Jeju scoria were determined empirically. The effects of particle size, initial sorbate

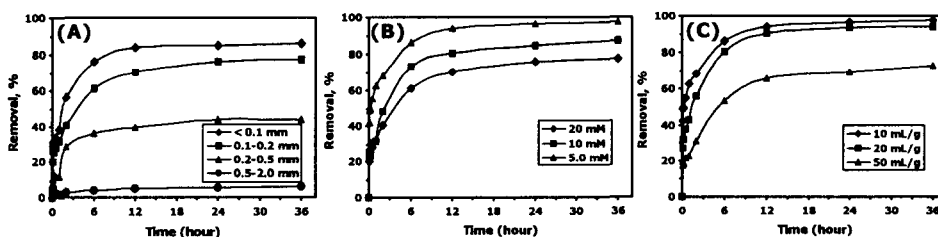


Fig. 1. Effects of the particle size (A), the initial sorbate concentration (B), and the sorbate/sorbent ratio (C) on the sorption of Zn(II) onto the Jeju scoria (temp. = 25°C,  $\text{pH}_i = 3$ ).

Table 1. Rate constant of adsorption ( $K_{ad}$ ) values for the sorption of Zn(II) onto the Jeju scoria with various conditions at temp. = 25°C, and  $pH_{ini}$  = 3.

No.	Size of scoria (mm)	Initial Zn(II) concentration (mM)	Sorbate/sorbent ratio (mL g <sup>-1</sup> )	$K_{ad}$ (X 10 <sup>-3</sup> )	R <sup>2</sup>
1	0.1-0.2	20	10	3.13	0.9951
2	0.2-0.5	20	10	2.89	0.8995
3	0.5-2.0	20	10	1.51	0.9741
4	< 0.1	20	10	4.92	0.9978
5	0.1-0.2	10	10	3.29	0.9715
6	0.1-0.2	5	10	3.68	0.9958
7	0.1-0.2	5	20	3.87	0.9967
8	0.1-0.2	5	50	2.66	0.9930

concentration, and sorbate/sorbent ratio on the Zn(II) removal are shown in Fig. 1. The removal efficiency increased with decreases in particle size (Fig. 1(A)), initial sorbate concentration (Fig. 1(B)), and sorbate/sorbent ratio (Fig. 1(C)).

The Lagergren rate equation was used to describe the rate of sorption (Table 1), which shows that the value of the rate constant ( $K_{ad}$ ) for each condition tends to increase with decreases in particle size, initial sorbate concentration, and sorbate/sorbent ratio.

To understand the sorption mechanism for the removal of Zn(II) onto the Jeju scoria, the concentration of zinc ion, other cations (including hydrogen ion) were analyzed and examined. Fig. 2 shows the sum of concentrations (meq L<sup>-1</sup>) of zinc and hydrogen ions, the sum of other cations (Ca(II) + Mg(II) + Na(I) + K(I)), and the total cations in solution at contact time  $t$ . The result indicates that the sum of concentrations of released cations is equivalent with that of sorbed zinc and hydrogen ions during the reaction. Consequently, the cation-exchange reaction is likely the dominant mechanism for the sorption of Zn(II) onto the Jeju scoria.

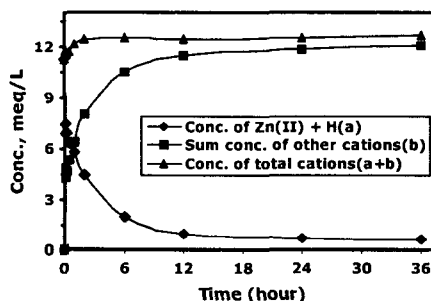


Fig. 2. The sum of concentrations (meq L<sup>-1</sup>) of zinc and hydrogen ions, and other cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>) in the solution, determined by ICP-AES analysis (temp. = 25°C,  $pH_{ini}$  = 3, particle size = 0.1-0.2 mm, initial zinc ion concentration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

### 3.2. Equilibrium of sorption reaction

The equilibrium isotherm for the sorption of Zn(II) was determined by agitating 0.5 g sorbent (0.1-0.2 mm in particle size) with 10 mL of Zn(II) solutions of various concentrations at 25°C for 24 h.

The solution pH showed a significant effect on the sorption of Zn(II) onto the Jeju

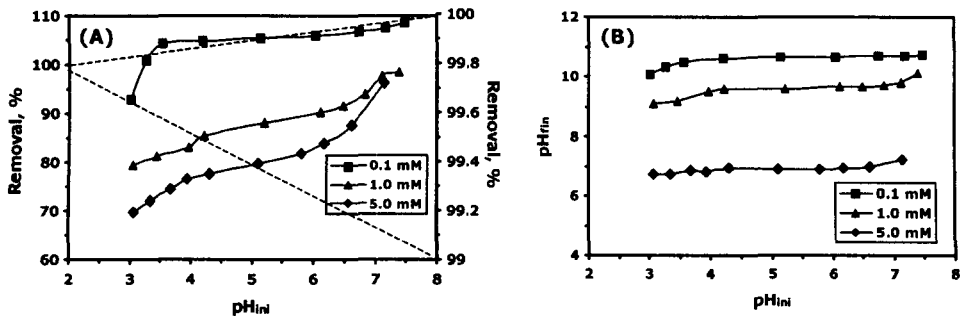


Fig. 3. Effect of the initial pH on the sorption of Zn(II) onto the Jeju scoria: (A) the removal percentage versus the initial pH, and (B) the final pH versus the initial pH (temp. = 25°C, particle size = 0.1-0.2 mm, sorbate/sorbent ratio = 20 mL g<sup>-1</sup>, and contact time = 24 h).

scoria. Removal of the zinc ion as a function of initial pH (pH<sub>ini</sub>) is presented in Fig. 3. The sorption of Zn(II) increased with an increase in pH<sub>ini</sub> for all the initial Zn(II) concentrations (Fig. 3(A)). These results are consistent with a typical characteristic of cation sorption. In addition, the variation of the final value of pH (pH<sub>fin</sub>) as a function of pH<sub>ini</sub> is also shown in Fig. 3(B).

To evaluate the fraction of Zn(II) removed by precipitation as a function of pH, the experiments were performed at the absence of sorbent in identical pH conditions. The results are presented in Fig. 4. Zn(II) removal at low pH condition was inhibited due to

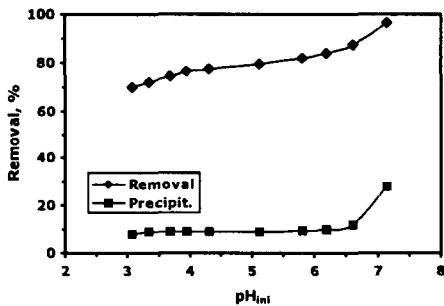


Fig. 4. Contribution of precipitation on the removal of Zn(II) onto the Jeju scoria (temp. = 25°C, particle size = 0.1-0.2 mm, sorbate/sorbent ratio = 20 mL g<sup>-1</sup>, initial zinc ion concentration = 5.0 mM, and contact time = 24 h).

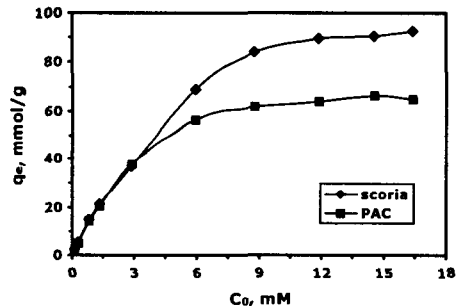


Fig. 5. Sorption capacities of the Jeju scoria and PAC for Zn(II) (temp. = 25°C, pH<sub>ini</sub> = 3, particle size of scoria = 0.1-0.2 mm, particle size of PAC = <0.03 mm, sorbate/sorbent ratio = 20 mL g<sup>-1</sup>, and contact time = 24 h).

Table 2. Langmuir and Freundlich isotherm constants for the sorption of Zn(II) onto the Jeju scoria and PAC at pH<sub>ini</sub> 3 and 25°C.

Sorbent	Langmuir			Freundlich		
	$Q$ (mmol g <sup>-1</sup> )	$b$	$R^2$	$K_r$ (mmol g <sup>-1</sup> )	$1/n$	$R^2$
scoria	96.15	1.651	0.9880	41.51	0.3734	0.9864
PAC	67.11	2.328	0.9979	29.68	0.3997	0.9722

the competition with hydrogen ions for sorption sites, whereas it was enhanced at high pH condition due to the formation of hydroxide precipitation.

The sorption capacity ( $\text{mmol g}^{-1}$ ) of the Jeju scoria for Zn(II) was compared with that of powdered activated carbon (PAC). The PAC has been considered as one of the most effective sorbents. The results are shown in Fig. 5. The plot indicates that the sorbate has occupied all the available sorption sites of PAC and was no longer sorbed at high concentrations. Thus, the results show that the zinc sorption capacity of the Jeju scoria is better than that of PAC. In addition, the sorption capacities of both the sorbents were determined from adsorption isotherms. Table 2 represents the isotherm parameters with correlation coefficients, based on the Langmuir and Freundlich models. Although both isotherms showed an excellent linear correlation, the results show that the Langmuir isotherm model is better to fit with the observed data. The Jeju scoria has the better adsorption capacity and affinity than PAC, based on the  $Q$  and  $K_f$  values (Table 2).

**Keywords:** Scoria; Zinc removal; Sorption; Cation exchange; PAC; Langmuir and Freundlich isotherms

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