



Mechanism investigation and surface complexation modeling of zinc sorption on aluminum hydroxide in adsorption/coprecipitation processes



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HIGHLIGHTS

- Zn(II) removal by adsorption and coprecipitation with Al(OH)₃ was studied.
- Zn(II) removal mechanism was mainly surface complexation.
- Surface precipitation of Zn–Al LDH partly occurred by coprecipitation.
- Quantitative DLM model was constructed for Zn(II) removal with Al(OH)₃.

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ABSTRACT

The sorption mechanism of dilute Zn [initial Zn(II) concentration up to 40 mg dm⁻³] on aluminum hydroxide was investigated. Adsorption and coprecipitation at pH 7 were compared. The adsorption process gave a Langmuir-type isotherm and the zeta potential of Zn(II)-adsorbed aluminum hydroxide decreased linearly with increasing sorption density of Zn on aluminum hydroxide. The adsorption mechanism is therefore mainly surface complexation. In contrast, in the coprecipitation process, a Brunauer–Emmett–Teller like isotherm was obtained; the slope of the zeta potential versus Zn(II) sorption density decreased when the initial Zn/Al molar ratio was greater than 0.5. The X-ray diffraction pattern of Zn(II)-coprecipitated aluminum hydroxide changed from that of poorly crystalline gibbsite to a Zn–Al layered double-hydroxide (LDH) when the initial Zn/Al molar ratio was greater than 0.5, showing that surface complexation was the main sorption mechanism, but surface precipitation of Zn–Al LDH was also involved when the initial Zn/Al molar ratio in the coprecipitation process was greater than 0.5. A quantitative diffuse-layer model was constructed. The aluminum hydroxide exchange capacity was set at 0.61 mol mol⁻¹ Al⁻¹, based on the experimentally determined surface area, 340 m² g⁻¹. Surface complexation coefficients for H⁺, OH⁻, and Zn(II) adsorption on aluminum hydroxide were determined by fitting to the experimental adsorption results. The obtained parameters were in excellent agreement with those previously reported for a database of gibbsite adsorption equilibrium constants. The pH edge for Zn(II) removal by aluminum hydroxide was successfully reproduced by the constructed model.

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1. Introduction

Zn is an essential nutrient for living organisms because it is involved in many aspects of cellular metabolism, supports human growth, and is required for a proper sense of taste and smell [1,2].

Abbreviations: LDH, layered double-hydroxide; DLM, diffuse-layer model; AMD, acid mine drainage; XRD, X-ray diffraction; ICP-AES, inductively coupled plasma atomic emission spectroscopy.

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Many nutritionists recommend a daily intake of Zn to maintain a steady state in the human body [3]. However, elevated concentrations result in growth inhibition and toxicity. Many researchers have investigated Zn toxicity at high concentrations in plants [4], fish [5], and humans [6]. The upper limit for Zn and its compounds in air, water, food, and other media are regulated worldwide [7]. Although the World Health Organization has not set any guidelines for Zn in drinking water, as it does not pose a health threat, the US Environmental Protection Agency has set a non-mandatory National Secondary Drinking Water Standard of 5 mg dm⁻³ [8]. In Japan, effluent standards for Zn at point sources, including

wastewater treatment plant discharges into public water, were set at 2 mg dm^{-3} in 2006 [9].

There is a wide range of physicochemical treatment methods for Zn removal from wastewater, such as membrane filtration, adsorption, ion exchange, reverse osmosis, chemical precipitation, and solvent extraction [10,11]. Biological treatment methods have also been investigated to achieve required reductions in the amounts of chemicals used, low operating costs, and removal of toxic sludge [12]. Electrochemical treatment methods such as electrowinning, electrodialysis, electrodeionization, and electrocoagulation have also been proposed for recycling Zn from wastewater [13].

Zn treatment by coprecipitation with hydroxides is the most economic and commonly used procedure, especially for wastewater contaminated with large amounts of dilute concentrations of Zn. Acid mine drainage (AMD) is an example of such wastewater [14,15]. In Japan, there are a large number of closed/abandoned mines that contain AMD contaminated by several tens of milligrams per cubic deciliter of Zn. Neutralization and hydroxide coprecipitation require large amounts of neutralizer and flocculating agents, as well as substantial amounts of energy for many years [16]. Large volumes of sludge containing heavy metal hydroxides are also generated. To reduce the amounts of costly chemicals used and waste generation, better designs for AMD treatment are needed, because AMD treatment will be necessary for many years [17].

AMD is mainly treated using ferrihydrite coprecipitation during neutralization [18]. AMD usually contains Al ion and forms aluminum hydroxide during neutralization. Aluminum hydroxide is a good adsorbent for Zn, but the mechanism of Zn uptake by aluminum hydroxide during coprecipitation is not clearly understood.

The objective of this study is quantitative modeling of Zn uptake by aluminum hydroxide in coprecipitation/adsorption processes, to enable optimum design of treatment processes for large amounts of wastewater such as AMD. To accomplish this, the sorption mechanism of Zn on aluminum hydroxide in coprecipitation/adsorption processes was investigated experimentally using sorption isotherms, zeta potential measurements, and X-ray diffraction (XRD) analysis. The results of a series of experiments investigating metal ion uptake mechanisms in adsorption/coprecipitation processes have already been published for arsenate uptake by ferrihydrite [19], arsenate uptake by aluminum hydroxide [20], fluorine uptake by aluminum hydroxide [21], silicate uptake by aluminum hydroxide [22], and boron uptake by magnesium hydroxide [23].

A surface complexation model was constructed for Zn removal by aluminum hydroxide in adsorption/coprecipitation processes, based on experimental information obtained from the series of experiments mentioned above. In this study, a diffuse-layer model (DLM) was used as the surface complexation model because it is the simplest and involves fewer parameters than other surface complexation models [24]. Wastewater is a complex system with many coexisting ions and large fluctuations in composition, but the simplest model involving the fewest parameters can be used for optimum design of wastewater treatment [25]. Many researchers have confirmed that the DLM can be applied to adsorption phenomena of metal ions with ferric/aluminum hydroxides in complex suspensions [26,27]. The constructed model was validated using Zn removal data from experiments on the pH dependence of aluminum hydroxide adsorption.

2. Materials and methods

2.1. Standards and reagents

All chemicals and solutions used were of analytical grade and were purchased from Kanto Chemicals Inc., Tokyo, Japan. The

Zn(II) and Al(III) solutions were prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively. For all experiments, the pH and ionic strength were adjusted by addition of 0.1 M HNO_3 , KOH , and KNO_3 . The ionic strength was fixed at 0.1. All experiments were conducted at 25°C .

2.2. Coprecipitation experiments

The coprecipitation experiments involved the formation of aluminum hydroxide in the presence of Zn ions. Al(III) and Zn(II) solutions were initially combined at pH 3 to maintain the ionic states of both Al(III) and Zn(II). The pH and ionic strength were then adjusted to the target level. The initial Zn concentration was fixed at 10, 25, or 40 mg dm^{-3} (0.15 , 0.38 , or $0.61 \text{ mmol dm}^{-3}$), and the Al concentration was varied to give initial Zn/Al molar ratios from 0.015 to 2.

The suspension was then agitated using a magnetic stirrer, while controlling the pH within ± 0.5 (accomplished by adding a few drops of 0.1 M KOH), for 1 h. It was then filtered through a $0.1\text{-}\mu\text{m}$ membrane filter. The filtrates were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Seiko Instruments Inc., SPS-7800, Chiba, Japan) to determine the residual concentrations of Zn and Al.

2.3. Adsorption experiments

Adsorption experiments were conducted using the same conditions as for the coprecipitation experiments, but the aluminum hydroxide suspensions and Zn solutions were prepared separately at twice the initial concentrations of Zn(II) and Al(III). The pH values and ionic strengths of both solutions were adjusted to the target levels, and equivalent amounts of them were then combined and agitated for 1 h. The pH was kept at the target value within ± 0.5 by the addition of a few drops of 0.1 M KOH during agitation. After agitation, the suspension was filtered through a $0.1\text{-}\mu\text{m}$ membrane filter, and the filtrate was analyzed using ICP-AES to determine the concentrations of Zn and Al, using the procedure described in Section 2.2. In all the adsorption experiments, freshly precipitated aluminum hydroxide was used to avoid changes caused by aging.

2.4. Zeta potential measurements

The zeta potentials of the precipitates in the suspensions were measured using an electrophoresis light-scattering spectrophotometer (Zetasizer Nano, Malvern, Worcestershire, UK). For the zeta potential measurements, the initial Al concentration was adjusted to 20 mg dm^{-3} and the initial Zn concentration was varied according to the target Zn/Al molar ratio. The suspensions produced in the coprecipitation and adsorption experiments were dispersed in an ultrasonic bath for 5 min prior to filtration. The suspensions were then quickly poured into a capillary cell to measure the zeta potentials of the precipitates.

2.5. XRD analysis

The filter residues from the coprecipitation and simple adsorption experiments were analyzed using XRD (RINT Ultima III, Rigaku, Inc., Tokyo, Japan). For XRD analysis, the initial Al concentration was adjusted to 20 mg dm^{-3} and the initial Zn concentration was varied according to the target Zn/Al molar ratio. The filter residues from the coprecipitation and adsorption experiments were freeze-dried at -45°C and 10 Pa for at least 24 h to avoid crystallization or mineralogical transformation.

Powder XRD patterns were obtained using a copper target ($\text{Cu K}\alpha$), a crystal graphite monochromator, and a scintillation detector.

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