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Equilibrium Sorption of Heavy Metals (Pb, Cu, Zn, Cd) onto Scoria

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Abstract

Scoria is a bomb-sized, generally vesicular pyroclast that is red or black in color and light in weight. In this study, scoria from Cheju was examined for the use as a sorbent. It is composed of plagioclase, olivine, hornblende, pyroxene, and glass, with an average composition of 49.84% SiO_2, 14.07% Al_2O_3, and 9.14% Fe_2O_3.

Studies on kinetic isotherm sorption of Zn(Ⅱ) onto scoria under various parameters such as initial zinc concentration, particle size, and adsorbent/adsorbate ratio were carried out using an agitated batch. The results suggest that the smaller scoria size and the larger adsorbent/adsorbate ratio produce the higher degree of Zn(Ⅱ) removal. More effective removal also appears at lower initial Zn concentration. The sorption behavior of Zn(Ⅱ) onto scoria seems to be mainly controlled by cation exchange.

Studies on equilibrium isotherm sorption of other heavy metals (Pb, Cu, Cd) onto scoria were also conducted and compared with those onto powdered activated carbon (PAC) and non-organic matter scoria (NOS). The results suggest that the Cheju scoria has the slightly higher sorption capability than PAC and NOS, and the order of the effective sorption onto scoria and PAC is Pb > Cu > Zn > Cd. The monometal sorption onto scoria is more stronger than the competitive sorption.

Key words : Sorption, Heavy metals, Scoria, Cation exchange

1. Introduction

Heavy metal release from wastewater is a serious environmental problem, and therefore various wastewater treatment techniques have been developed. Among the techniques, sorption technique is most attractive. Though activated carbon, silica gel, and activated alumina are still popular as adsorbents, they are limitable because of expensive costs. Thus, considerable researches are recently focussed on the search of inexpensive adsorbents especially developed from various natural materials such as smectite, magnetite, goethite, granite, tuff, sand, clay minerals, etc.

Scoria consists of vesicular, fine to coarse fragments, which are red or black in color and light in weight, and is widespread in and around the volcanic cones in Cheju Island. The material has a potential use in industry, e.g., manufacturing of lightweight concrete, heating-insulating material, low-cost fillers in paint, filter material, and absorbents.

The aim of this study is to assess the sorption behavior of scoria using kinetic and equilibrium sorption isotherm (monometal and competitive) batch tests under various conditions, in order to evaluate the removal efficiency of heavy metals (Pb, Cu, Zn, Cd).

2. Materials and methods

Powder X-ray diffraction (XRD) and SEM-EDX analyses indicated the mineralogy of scoria, consisting mainly of plagioclase, olivine, hornblende, and pyroxene. The XRF data also revealed the composition of 49.84% SiO_2, 14.07% Al_2O_3, and 9.14% Fe_2O_3.

Though size reduction and subsequent sieving we have prepared four size fractions ranging from 2 ㎜ to <100 ㎛. The smaller size fraction (<100 ㎛) with the highest specific surface area was used for all the experimental works in this study. Sorption experiments were performed within 15-ml polypropylene centrifuge tubes. The absorbates were made of metal-chlorides (ACS grade) and distilled water and were adjusted by adding HCl to pH 3. Then, the solution was allowed to equilibrate without further pH adjustments. The samples were equilibrated for at least 24 hour by bath agitation at 150 rpm and 25℃. After equilibration, solid-solution separation was achieved by centrifugation at 3,000 rev./min for 10 minutes and the supernatant was acidified with HCl and was analyzed for cations by ICP-AES.

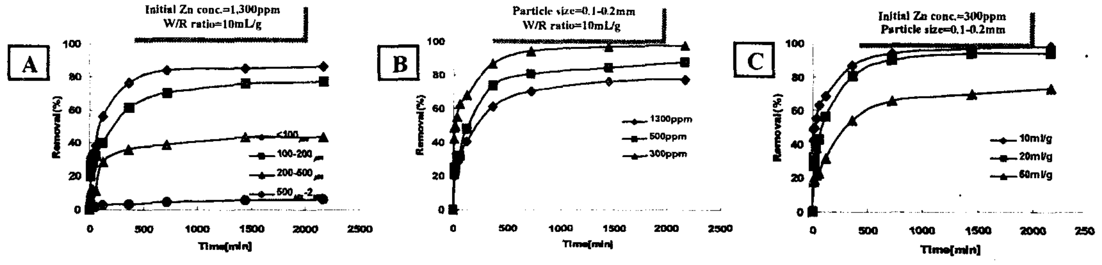

Fig. 1. Effects of particle size (A), initial concentration (B), and the amount of absorbent (C) on the absorption of zinc ion onto scoria (temp. = 25℃, initial pH = 3).

3. Results

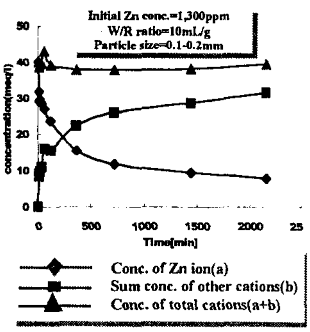

Fig. 2. The concentration (meq/l) of zinc ion and other cations (Ca, Mg, etc) in the solution, determined by ICP-AES analysis.

The removal (absorption) curves for Zn(Ⅱ) in kinetic isotherm are given in Fig. 1. The results generally follow the expected absorption behavior; i.e., the greatest absorption occurred at the smaller size (A), the larger amounts of scoria (C), and the lower initial concentration of absorbate (B). The sorption capacity of non-porous particles is generally proportional to the total surface area related to the particle diameter, because the kinetics of diffusion-controlled processes in porous particles are directly related to particle size (Papelis et al., 1995). In Fig. 1(B), it is noteworthy that although the fractional uptake represented as a fraction of total zinc ion concentration decreases with increasing concentration, the total zinc ion sorbed is actually increasing. Similarly, the percentage of zinc removal increases with the increasing scoria amount (Fig. 1(C)) but the amount of sorbed Zn(Ⅱ) per unit quantity of scoria actually decreases with the increasing scoria amount.

When zinc ion was removed onto scoria, other cations (mostly, Ca and Mg) were concurrently released into solutions. Variations of the concentrations of Zn(Ⅱ) and other cations in solution are shown in Fig. 2, demonstrating that Zn uptake is accompanied by the

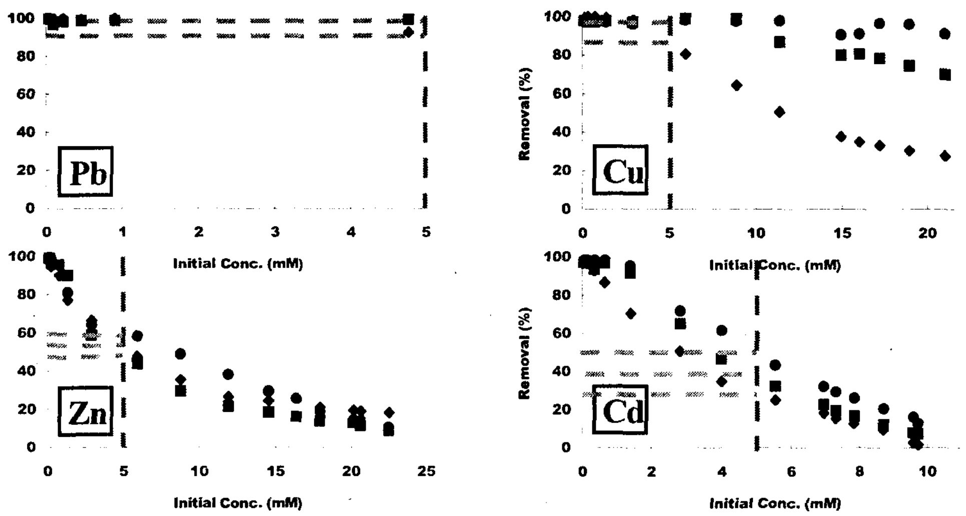

Fig. 3. The removal of divalent mono-metal ions (Pb, Cu, Zn, Cd) onto PAC (◆), NOS (■), and scoria (●).

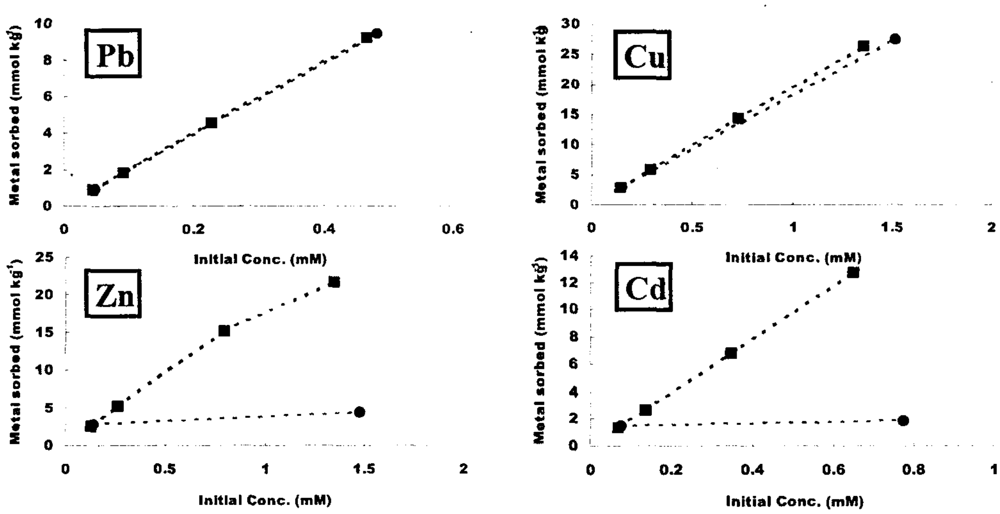

Fig. 4. Monometal (■) and competitive (●) sorption isotherm at 25℃, showing the retention of metals by scoria.

stoichiometric release of other cations. This trend agrees with the cation-exchange equilibrium. Fig. 3 depicts the removal of divalent metal ions (Pb, Cu, Zn, Cd) onto PAC, NOS, and scoria.

It is observed that the removal efficiency is slightly higher for scoria than those for PAC and NOS. The order of increasing removal efficiency onto absobents was Pb ≥ Cu > Zn > Cd. Fig. 4 compares the monometal vs competitive sorption isotherms onto scoria at 25℃. The affinity of metals on the scoria surface follows the order of Pb ≥ Cu > Zn > Cd, which is in agreement with their hydrated radii (Pb < Cu < Zn < Cd). The sorbed amount for Zn and Cd ions was much smaller in competitive isotherm than in monometal isotherm.