Adsorbed and dissolved As species during the oxidation of As by red mud as a heterogeneous catalyzer

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1. Introduction

The uses of some mine and refinery waste materials are very progressive field for the environmental remediation. This study addresses the adsorption and oxidation behavior of arsenic in contact with calcined red mud as a heterogeneous catalyzer. Its chemical aspect of the red mud is well known, but the catalyst durability should be characterized due to the heterogeneity of the composite metal oxides. In particular, it is not easy to predict the chemical speciation of both adsorbed and dissolved species of As(III) and As(V) during the surface oxidation reaction. Our previous study (Ko et al., 2006 and 2007) reported that the loading order of arsenic, natural organic matter and sorptive material was a significant role in the arsenic speciation during their adsorption and oxidation. However, there are little information about the adsorbed species during the adsorption and oxidation reaction. Then the present study investigated the behavior of adsorbed and dissolved species during the photocatalytic oxidation of As(III) from the chemical extraction and spectroscopic observations.

2. Results and discussion

2.1 As species during the photocatalytic oxidation of As(III)

In the presence of red mud, both oxidation and adsorption reactions were considered as the removal mechanism of arsenic from aqueous solution. The photocatalytic oxidation experiments using UV(Ultraviolet), room light and control system was performed to determine the dissolved and adsorbed species with respect to the various loading concentrations of As(III). The adsorbed species of arsenic was extracted with N_2-purging NaH_2PO_4 extraction solution wrapped with aluminum foil. In the system less than the maximum adsorption amount, the concentration of aqueous As(III) is not significantly detected, compared with that in the system higher than the maximum adsorption amount. In particular, the concentration of the adsorbed As(III) is similar in other systems. In the experimental sets of pure metal oxide, the photocatalytic oxidation efficiency is the order of anatase > hematite > goethite. This is the same order of the maximum adsorption amount of total As in each metal oxide, but the reverse order of the amount of adsorbed As(III). It indicates that the strongly adsorbed As(III) in the specific adsorptive site may be less oxidative than those adsorbed or partitioned with soluble arsenic in the interface of the oxidative site. Arsenic species onto metal oxides could be deduced from soluble arsenic species and partition of arsenic species between the adsorbed and aqueous phases. Also it is true

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that the removal of As(III) in the oxidative system is controlled by the As(V) adsorption. Then, this experimental phenomenon gives the possibility that the oxidation and adsorption of As(III) depends on the specific surface site for the adsorption and oxidation.

2.2 Spectroscopic observation of adsorbed As species

From the SEM(Scanning electron microscopy) analysis, the mineral grains in the red mud was ripened into the large and rounded grains with respect to the reaction timescale. The quantitative SEM-EDX peak area analysis also shows the enhanced adsorption amount of As(III) onto red mud, following the order of the constituent minerals; Fe-associated oxides like goethite, hematite and maghematite > Al-asscoiated oxides > Ti oxides like anatase and titanite. From the XPS (X-ray photoelectron spectroscopy) analysis in the powder mode, the surface metal ions are composed dominantly of Fe, Al, Ti, Ca and Mg. The atomic fraction of As(III) significantly reduced into As(V) to the extent of about 40 to 70% after the photocatalytic oxidation. It is true that the oxidation of As(III) should take place at the solid-liquid interface region since the oxidizing radicals were produced at the metal oxide surfaces. Then, from these experimental observations, the adsorbed As(III) at the surface is not completely oxidized despite the extremely low concentration of As(III) in aqueous solution.

3. Conclusion

The red mud as a heterogeneous catalyzer has both adsorptive and oxidative sites for the photocatalytic oxidation of As(III). Then, due to the favorable photocatalytic oxidation in the oxidative site, the As(III) oxidation could be enhanced in the presence of the excess surface oxidative site. Also the relative strength of As(III) oxidation may depend on the types of oxide minerals.