

Adsorption of $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_3(\text{OH})]^{2-}$ onto $\delta\text{-MnO}_2$

DAISUKE KAWAMOTO^{1*}, MAO KAWABATA¹

AND AKANE MIYAZAKI¹

¹Faculty of Science, Japan Women's University, 2-8-1
Mejirodai, Bunkyo-ku, Tokyo, Japan

* e-mail: kawamotod@fc.jwu.ac.jp

Adsorption of two predominant Pd(II) complex ions in seawater, i.e., $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_3(\text{OH})]^{2-}$ onto $\delta\text{-MnO}_2$ was studied in order to understand Pd concentration in marine ferromanganese oxide from seawater. Adsorption experiment was performed at 25 °C by mixing K_2PdCl_4 solution and suspension of $\delta\text{-MnO}_2$ so to obtain 0.10 mmol/dm³ Pd and 1.0 g/dm³ $\delta\text{-MnO}_2$. These mother solutions contain 0.56 mol/dm³ NaCl and their pH were adjusted to 4.0 or 7.5 by using NaOH solution or HCl. According to the literature, Pd species at pH 4.0 and 7.5 are calculated to $[\text{PdCl}_4]^{2-}$ (89 %) and $[\text{PdCl}_3(\text{OH})]^{2-}$ (96 %), respectively. After the adsorption experiments were started, pH of the reacting suspension was kept at pH 4.0 or 7.5 by adding NaOH solution or HCl. An aliquot of the suspension was taken out and filtered with 0.20 μm membrane filter with appropriate intervals. The Pd concentration of the filtrate was determined by ICP-AES. To examine chemical state of Pd species adsorbed on $\delta\text{-MnO}_2$, the Pd K-edge XA spectrum for that was measured at SPring-8.

$[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_3(\text{OH})]^{2-}$ showed clearly different adsorption behaviour onto $\delta\text{-MnO}_2$. While $[\text{PdCl}_4]^{2-}$ was hardly adsorbed onto $\delta\text{-MnO}_2$, approximately 60% of $[\text{PdCl}_3(\text{OH})]^{2-}$ adsorbed within 24 h. Since pH_{pzc} of $\delta\text{-MnO}_2$ is approximately 4, the surface net charge of that at pH 4.0 and pH 7.5 is zero and negative, respectively. Therefore, it was considered that while $[\text{PdCl}_4]^{2-}$ was hardly adsorbed onto the uncharged surface of $\delta\text{-MnO}_2$, $[\text{PdCl}_3(\text{OH})]^{2-}$ was adsorbed onto the negatively charged surface of that. This indicates that $[\text{PdCl}_3(\text{OH})]^{2-}$ was adsorbed specifically onto $\delta\text{-MnO}_2$. To examine whether the chemical state of $[\text{PdCl}_3(\text{OH})]^{2-}$ is changed due to the specific adsorption, the Pd K-edge XA spectrum for the Pd species adsorbed on $\delta\text{-MnO}_2$ measured. The Pd K-edge XA spectrum for Pd species adsorbed on $\delta\text{-MnO}_2$ showed that the oxidation state of that is bivalent and all of coordination atom of that is oxygen. From these results, it was suggested that the Cl^- which was originally coordinated the $[\text{PdCl}_3(\text{OH})]^{2-}$ was substituted with OH^- and/or H_2O due to the specific adsorption onto $\delta\text{-MnO}_2$.