Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.5127

Investigation on Zn adsorption/coprecipitation mechanisms on MnO_2 under neutral pH conditions

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Birnessite (MnO_2) is known as a great adsorbent for trace metals because it has a layered structure resulting in a higher specific surface area and many vacancy sites than other Mn oxides. It shows a high affinity to especially Zn and Cd and uptakes by forming a surface complexation on the vacancy site under a neutral pH condition (pH<6); which is a lower pH condition than to form hydroxides (pH<8). Different uptake mechanisms of these metals on MnO_2 surface are estimated between adsorption and coprecipitation processes; however, there are many unclear points of the Zn removal mechanism and adsorption capacity in these processes. In this study, we investigated the removability of Zn on MnO_2 in adsorption and co-precipitation reactions at different Zn/Mn molar ratios (0.05-2.0) at pH 6. Sorption isotherm showed higher Zn removal in the co-precipitation reaction (0.20 mmol-Zn/mmol-Mn) than the adsorption reaction (0.10 mmol-Zn/mmol-Mn). Furthermore, the Langmuir model was the best fit for the experimental values in both adsorption and coprecipitation reactions, demonstrating single-layer adsorption of Zn on the MnO_2 surface. The XRD analysis result showed an increase of the lattice parameter *c* of MnO_2 after the adsorption reaction, which indicates Zn could form a surface complexation in the layers (001) and (002). Besides, other peaks than MnO_2 have not been confirmed in the adsorption process at all Zn/Mn molar ratios, whereas new peaks derived from hetaerolite ($ZnMn_2O_4$) were found in the coprecipitation reaction, which peak intensity was the highest at 0.25 Zn/Mn. This finding indicates that hetaerolite formation is also one of the possible reasons to enhance the Zn removal capacity in the co-precipitation reaction at pH 6. Based on our experimental results and thermodynamic model, the addition of MnO_2 about 10 times molar of Zn in acid mine drainage is required to remove it efficiently at pH 6 in the adsorption process. When the concentration of Zn and Mn is significantly high in which is difficult to add MnO_2, Zn would be effectively removed in the neutral pH by co-precipitation process with an oxidizing agent and/or Mn-oxidizing bacteria.