Equilibrium Adsorption of Manganese Using Mordenite

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1. Introduction

The acid mine drainage is acidic wastewater containing heavy metal sulfates, generated through the oxidization of metal sulfides at the surface of mineral deposit with water or air, and polluting the ecological systems. To improve this environmental issue, the treatment of the acid mine drainage with natural zeolites has been studied. However, natural zeolites generally contained several metal ions and so on as impurities to make adsorption equilibrium more complicated [2].

In this study, commercially available synthetic zeolite of Mordenite was used as adsorbent and the adsorption equilibrium was measured to treat with the model acid mine drainage containing manganese ion.

2. Experimental

The synthetic zeolite of Mordenite was used, purchased from Wako Pure Chemical Industries (HS-690, Powder, Hydrogen Mordenite). **Table 1** shows the conditions of adsorption equilibrium measurement. In advance, the zeolite was kept at 383K for more than 24 hrs in order to dehydrate. To measure the cation exchange capacity (CEC) of the zeolite, 4g of zeolite was contacted with 30mL of 1M aqueous ammonium acetate (NH_4OAc) solution and shaken for 5 minutes. After phase separation using centrifuge, fresh 30mL NH_4OAc solution was added to the solid phase and this operation was repeated 10 times, based on the Method-9801 by the US Environmental Protection Agency. The solutions were prepared by dissolving $MnSO_4 \cdot 5H_2O$ and deionized water. The specified amounts of zeolite and solution were contacted at 300 K for 240 hrs to be equilibrated.

The liquid phases were analyzed by pH meter(Horiba,F-74) and ICP-AES(SPS7800, SII Nano Technology) to determine the pH and metal concentration, respectively.

Table.1 Experimental condition of Batch adsorption

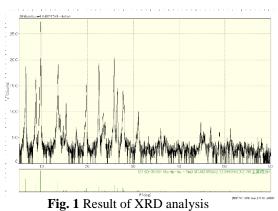| pH of feed solution	[-]	2-5
Volume of feed solution	[L]	50×10^{-3}
Initial concentration of Mn	[mol/L]	9.1×10^{-4} -1.8×10^{-2}
Mass of zeolite	[g]	2.5
Contacting time	[hours]	240
Temperature	[K]	300

3. Results and discussion

Material balance of batch adsorption is shown as,
$$C_{i,0}V_0 + q_{i,0} S_0 = C_i V + q_i S \quad (1)$$
where C_i V, S, and q_i are the concentration of component i , volume of the solution, mass of zeolite and adsorbed amount of component i per unit mass of zeolite. The subscript of 0 stands for the initial conditions. It was assumed that there was no change in the volume of the solution and mass of zeolite before and after the experiment. The Langmuir model for multicomponent adsorption is expressed as,

$$q_i = \frac{q^* K_{L,i} C_i^{1/n_i}}{1 + \sum_k K_{L,k} C_k^{1/n_k}} \quad (2)$$

q^* and $K_{L,i}$ are the saturated adsorption amount and the Langmuir parameter of component i. The n_i is the charge number of component i.

Fig. 1 shows the result of XRD analysis. It was confirmed that the zeolite used was pure mordenite, and there was no other component. The CEC was measured as 6.94×10^{-4} mol/zeo-g, lower than that of the ideal pure mordenite (22×10^{-4} mol/zeo-g). The zeolite was originally treated by acid solution, and this should lower the CEC of the zeolite[4].

Fig. 1 Result of XRD analysis

Fig. 2 shows the changes in pH before and after adsorption equilibrium measurement. The pHs at equilibrium become lower than initial when intial pHs were 3 and 5. The pHs at equilibrium were almost constant, ranged from 2.6 to 2.8 in the cases that the initial pHs were 3 and 5. The hydrogen ion in the mordenite might have been exchanged with Mn^{2+} ion and this made the pH lower. When the initial pH was set at 2, the equilibrium pH was the same as the initial one. The H^+ concentration was so high that the amount
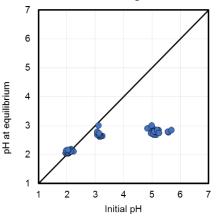

Fig. 2 Change of pH at initial and equilibrium

of the H^+ desorbed was negligible.

Fig. 3 shows the molar concentrations of the metal ions at equilibrium, desorbed from the zeolite. Although Na, K, Mg and Ca were detected, their concentrations were much lower than those of H^+ or Mn^{2+} and the effects of these ions on H^+ or Mn adsorption must be small.
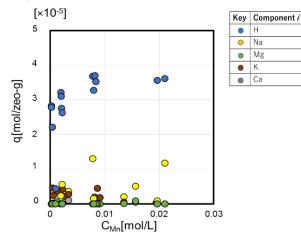

Fig. 3 Concentrations of cations at equilibrium

Fig. 4 shows the charge numbers of the cations due to adsorbed on and desorbed from the zeolite. The charge numbers of adsorbed ion, Mn^{2+}, were almost balanced with those of desorbed ions, H^+, Na^+, K^+, Mg^{2+} and Ca^{2+}. However when initial pH=2, the charge numbers were not balanced. This might be because when initial pH=2, the concentration changes of H^+, Na^+, K^+, Mg^{2+} and Ca^{2+} were so small, the amount of the desorbed ion could not be appropriately calculated.
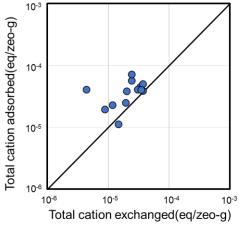

Fig. 4 cation balance of the batch adsorption

Fig.5 shows the adsorption isotherms of Mn with mordenite and natural zeolite from Bogor[1][2]. The q_i of Mn increased as C_{Mn} and pH increased. The q_i of Mn with mordenite were much lower than those with Bogor zeolite. The equilibrium pH was much lower with mordenite and H^+ should be competitively adsorbed. In the cases of low initial pH, adsorption amount of Mn was lower. Here it was assume that only cations of H^+ and Mn^{2+} existed in the system, q* was equal to 6.94×10^{-4} mol/L, corresponding to the CEC, and all sites on the mordenite before adsorption run were occupied by only H^+. Then, the adsorbed amounts of H^+ on the
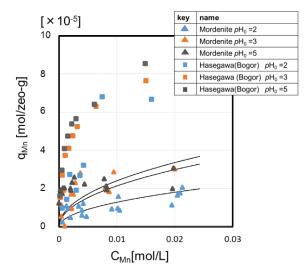

Fig. 5 Adsorption isotherms of manganese

mordenite at adsorption equilibrium were estimated, and the Langmuir parameters of H^+ and Mn^{2+} were determined, as shown in **Table 2**. The value of $K_{L,H}$ was not affected by the initial pH. When initial pH=3, 5 the value of $K_{L,Mn}$ become the same value. This might because when initial pH=3, 5, pH at the equilibrium was almost same. The q_i of Mn^{2+} could be roughly predicted with these parameters by considering the adsorption of H^+.

Table 2 Langmuir parameter

	$K_{L,H}$	$K_{L,Mn}$
Initial pH=2	20000	300
Initial pH=3,5	20000	120

4, Conclusion

XRD pattern showed that the zeolite was pure mordenite and the cation exchange capacity was measured as 6.94×10^{-4} mol/zeo-g. Mordenite could remove the manganese in the solution and it lowered the pH. Manganese in the solution was exchanged with H^+ in the zeolite to reduce the pH. The initial pH of the solution affected the adsorption of Mn and the amount of Mn adsorbed decreased as pH decreased. In the case of binary systems of hydrogen and manganese ions, it was confirm that the Langmuir model could predict the adsorption isotherms of manganese with the consideration of hydrogen adsorption.

References

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