

CHAPTER V

RESULTS AND DISCUSSION

From the synthesis, the reddish-brown precipitate of goethite was obtained. Goethite characterization (section 3.3) by XRD analysis shows the dominance (110) diffraction peak at 4.17 \AA and (021) diffraction peaks at 2.69 \AA and 2.45 \AA . Potentiometric titrations revealed that the pH_{pzc} of the synthesized goethite was 7.0 ± 0.1 , comparable to the literature values of 7.1 to 8.5 [32-35]. The surface area from the BET measurement was found to be $96.87 \pm 0.2 \text{ m}^2/\text{g}$ which is somewhat higher than that ($70.9 \text{ m}^2/\text{g}$) obtained by Atkinson et al. [31] and McBride [36]. Others have found the surface area of goethite to be in the range of 39 to $86 \text{ m}^2/\text{g}$ [24-27]. The discrepancies are usually due to slightly different conditions of the synthesis. The total concentration of active sites of goethite surface in the suspension, $[\equiv \text{FeOH}]_{\text{tot}}$, was found to be $2.07 \pm 0.06 \text{ mM}$, corresponding to the number of active sites of 0.64 site/nm^2 , which is somewhat higher than that obtained by Lovgren et al. ($1.20 \pm 0.03 \text{ mM}$, 1.68 site/nm^2), as a consequence of the higher value of surface area. Goethite characteristics are summarized in table 5.1.

Table 5.1 Goethite characteristics

| Goethite property | Goethite characteristic |
|--|-------------------------|
| Color | reddish-brown |
| XRD (\AA) | 4.17, 2.69, 2.45 |
| pH_{pzc} | 7.0 ± 0.1 |
| Surface area (m^2/g) | 96.87 ± 0.2 |
| $[\equiv \text{FeOH}]_{\text{tot}}$ (mM) | 2.07 ± 0.06 |
| No. of active site (site/ nm^2) | 0.64 |

A summary of the acid-base and the surface complexation reactions of goethite and the overall equilibrium constants (rounded off to one decimal place) was shown in table 5.2. From the acid-base equilibrium model, the dominant species below and above pH_{pzc} are positively charged ($\equiv \text{FeOH}_2^+$) and negatively charged ($\equiv \text{FeO}^-$), respectively. Each set of $\log \beta_{1,-1}^{\text{int}}$ and $\log \beta_{1,1}^{\text{int}}$ values showed little variations with ionic strengths except for the higher value of $\log \beta_{1,1}^{\text{int}}$ and the lower value of $\log \beta_{1,-1}^{\text{int}}$ obtained in 0.100 M NaNO_3 . These values are, however, more consistent with the result obtained by Lovgren et al.[7].

For the surface complexation with Cu^{2+} and Zn^{2+} , three types of surface complex species were found, the nondeprotonated ($\equiv \text{FeOHCu}^{2+}$ and $(\equiv \text{FeOH})_2\text{Zn}^{2+}$),

Table 5.2 Summary of the equilibrium constants with varying ionic strengths of NaNO₃

| Reactions | Overall equilibrium constant | I=0.001 M | I=0.005 M | I=0.010 M | I=0.100M | I=0.500 M | I=0.10 M (ref)* |
|--|------------------------------------|-----------|-----------|-----------|----------|-----------|-----------------|
| Acid-base reactions: | | | | | | | |
| $\equiv\text{FeOH} \leftrightarrow \equiv\text{FeO}^- + \text{H}^+$ | $\log \beta_{1,-1}^{\text{int}}$ | -9.2 | -9.2 | -9.2 | -9.9 | -9.0 | -9.51 |
| $\equiv\text{FeOH} + \text{H}^+ \leftrightarrow \equiv\text{FeOH}_2^+$ | $\log \beta_{1,1}^{\text{int}}$ | 5.8 | 6.2 | 6.0 | 6.8 | 6.3 | 7.47 |
| Complexation of $\equiv\text{FeOH-H}^+-\text{Cu}^{2+}$ system | | | | | | | |
| $\equiv\text{FeOH} + \text{Cu}^{2+} \leftrightarrow \equiv\text{FeOHCu}^{2+}$ | $\log \beta_{1,0,1}^{\text{int}}$ | n.f. | 5.7 | 6.0 | 4.5 | 4.9 | 8.8 |
| $\equiv\text{FeOH} + \text{Cu}^{2+} \leftrightarrow \equiv\text{FeOCu}^+ + \text{H}^+$ | $\log \beta_{1,-1,1}^{\text{int}}$ | 1.3 | 0.6 | 0.8 | 0.9 | 0.9 | 0.9 |
| $\equiv\text{FeOH} + \text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{FeOCuOH} + 2\text{H}^+$ | $\log \beta_{1,-2,1}^{\text{int}}$ | -8.0 | -7.8 | -5.4 | -7.2 | -6.6 | -6.6 |
| Complexation of $\equiv\text{FeOH-H}^+-\text{Zn}^{2+}$ system | | | | | | | |
| $2\equiv\text{FeOH} + \text{Zn}^{2+} \leftrightarrow (\equiv\text{FeOH})_2 \text{Zn}^{2+}$ | $\log \beta_{2,0,1}^{\text{int}}$ | 8.6 | 8.1 | 9.2 | 8.8 | 8.7 | 10.67 |
| $\equiv\text{FeOH} + \text{Zn}^{2+} \leftrightarrow \equiv\text{FeOZn}^+ + \text{H}^+$ | $\log \beta_{1,-1,1}^{\text{int}}$ | -2.6 | -3.0 | -2.0 | -2.2 | -1.9 | -2.0 |
| $\equiv\text{FeOH} + \text{Zn}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{FeOZn}(\text{OH})_2 + 3\text{H}^+$ | $\log \beta_{1,-3,1}^{\text{int}}$ | -18.0 | -17.9 | -18.2 | -17.5 | -16.4 | -18.2 |

* Lovgren et al. [] , n.f.= not found

Table 5.2 Summary of the equilibrium constants with varying ionic strengths of NaNO₃ (continue)

| Reactions | Overall equilibrium constant | I=0.005 M | I=0.010 M | I=0.100 M | I=0.500 M |
|---|--|-----------|-----------|-----------|-----------|
| <u>Complexation of ≡FeOH-H⁺-Cu²⁺-SO₄²⁻ system</u> | | | | | |
| ≡FeOH+Cu ²⁺ +SO ₄ ²⁻ ↔ ≡FeOHCuSO ₄ | log β _{1,0,1,1} ^{int} | 13.0 | 13.1 | 13.7 | 11.0 |
| ≡FeOH+Cu ²⁺ +SO ₄ ²⁻ ↔ ≡FeOCuSO ₄ ⁻ +H ⁺ | log β _{1,-1,1,1} ^{int} | 8.5 | 8.4 | 9.0 | 6.0 |
| ≡FeOH+Cu ²⁺ +SO ₄ ²⁻ +H ₂ O ↔ ≡FeOCuOHSO ₄ ²⁻ + 2H ⁺ | log β _{1,-2,1,1} ^{int} | 2.5 | 1.8 | 1.7 | 2.2 |
| <u>Complexation of ≡FeOH-H⁺-Zn²⁺-SO₄²⁻ system</u> | | | | | |
| 2≡FeOH+Zn ²⁺ +SO ₄ ²⁻ ↔ (≡FeOH) ₂ ZnSO ₄ | log β _{2,0,1,1} ^{int} | 18.0 | 20.3 | 19.5 | 18.2 |
| ≡FeOH+Zn ²⁺ +SO ₄ ²⁻ ↔ ≡FeOZnSO ₄ ⁻ +H ⁺ | log β _{1,-1,1,1} ^{int} | 12.9 | 13.1 | 12.6 | 11.7 |
| ≡FeOH+Zn ²⁺ +SO ₄ ²⁻ +2H ₂ O ↔ ≡FeOZn(OH) ₂ SO ₄ ³⁻ +3H ⁺ | log β _{1,-3,1,1} ^{int} | -2.5 | -2.5 | -2.5 | -2.5 |

the deprotonated ($\equiv\text{FeOCu}^+$ and $\equiv\text{FeOZn}^+$) and the hydrolyzed species ($\equiv\text{FeOCuOH}$ and $\equiv\text{FeOZn}(\text{OH})_2^-$). The formation of the nondeprotonated species of Zn^{2+} complex system involved two binding sites per Zn^{2+} , while Cu^{2+} binds to a single site. This result can be explained by the lower value of the electronegativity and the larger ionic size of Zn^{2+} compared with Cu^{2+} . The deprotonated and hydrolyzed surface species of Cu^{2+} complex system were more stable than those of Zn^{2+} complex system while the major nondeprotonated surface species was less stable. The same trend of $\log \beta$ values for Cu^{2+} and Zn^{2+} complexation in 0.10 M NaNO_3 was found by Lovgren et al.[7]. The discrepancies in the values of $\log \beta_{1,0,1}^{\text{int}}$ and $\log \beta_{2,0,1}^{\text{int}}$ for nondeprotonated surface species between our results and those of Lovgren et al.[7] are probably due to the differences in surface area and the concentration of the surface active site of the synthesized goethite.

In the presence of SO_4^{2-} ion, The nondeprotonated ($\equiv\text{FeOHCuSO}_4$) and deprotonated ($\equiv\text{FeOCuSO}_4^-$) ternary surface species of Cu^{2+} - SO_4^{2-} complex system were less stable than those of Zn^{2+} - SO_4^{2-} complex system whereas the hydrolyzed ternary surface species ($\equiv\text{FeOCuOHSO}_4^{2-}$) was more stable. This can be explained by the higher value of the hydrolysis constant of Cu^{2+} compared with that of Zn^{2+} ($\log \beta_{\text{CuOH}^+}^{\text{int}} = -8.12$, $\log \beta_{\text{Cu}(\text{OH})_2}^{\text{int}} = -17.15$, $\log \beta_{\text{ZnOH}^+}^{\text{int}} = -9.15$ and $\log \beta_{\text{Zn}(\text{OH})_2}^{\text{int}} = -17.10$). Similar trends were thus found for the $\log \beta$ values of Cu^{2+} , Zn^{2+} , Cu^{2+} - SO_4^{2-} , and Zn^{2+} - SO_4^{2-} complex systems. i.e., the $\log \beta$ values of nondeprotonated > deprotonated > hydrolyzed surface species, and so as their

stability. In addition, the $\log \beta$ values obtained in 0.500 M NaNO_3 were somewhat lower than those obtained in the solutions with ionic strengths below 0.100 M NaNO_3 .

From the distribution diagrams, the adsorption of Cu^{2+} (figures 4.4-4.8) and Zn^{2+} (figures 4.10-4.14) increased with increasing pH, like most metal ions do [12]. Below pH~4-5, adsorption of Cu^{2+} and Zn^{2+} was found to be minimal due to competitive adsorption of proton (protonation) for the surface sites of goethite. As the pH rises, the adsorption of Cu^{2+} increased from 0 to 100 percent within the pH range of 4-7. A slightly narrower range, pH= 4-6 for Cu^{2+} was obtained by Chistophi and Axe [12] in 0.001-0.01 M NaNO_3 . Relative to those of Cu^{2+} , the adsorption edge of Zn^{2+} was shifted to a higher pH range, pH = 5-8. This could indicate that the affinity of Cu^{2+} on goethite surface was greater than Zn^{2+} . Axe, Schwertmann, and Forbes et al. [12,37,38] also found the metal affinities for the goethite surface follow the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$, which is fairly consistent with the order due to the electronegativity of metal ion and the site capacity of oxide surface, each type of which has a characteristic binding energy. The fact that, Cu^{2+} has the smallest ionic size and the greatest electronegativity, thus it is more easily attracted to the goethite surface.

The variation in ionic strengths of solution (0.001-0.500 M NaNO_3) was found to have little effect on the amount of Cu^{2+} and Zn^{2+} adsorbed except in 0.100 and 0.001 M NaNO_3 where the adsorption edges of Zn^{2+} were shifted to lower pH and

covered a wider pH range (pH = 4-8). The results from Lisa et al.[12] showed that no changes in the amount of metal ions (Cu^{2+} , Pb^{2+} , Cd^{2+}) adsorbed with increasing ionic strength (0.001-0.01 M NaNO_3). Dzombak et al.[25] also found that an increase in ionic strength from 0.01-0.10 M NaNO_3 had no noticeable effect on the amount of Cu^{2+} adsorbed. This suggests that the reactions of mineral surface sites with metal ions within the inner layer(0-layer), as illustrated by complexation reactions in table 5.2, are most important in controlling adsorption. That is the metal ions characteristically form the inner-sphere complexes with the surface site, so that their adsorption is largely insensitive to the properties of the solution in the diffuse outer layer such as ionic strengths. These results are also consistent with the spectroscopic studies [13].

The increasing adsorption of Cu^{2+} (figures 4.16- 4.19) and Zn^{2+} (figures 4.20-4.23) on goethite surface at low pH in the presence of SO_4^{2-} ion was successfully modeled using CCM by considering the ternary surface complex species $\equiv\text{FeOHCuSO}_4$ and $\equiv\text{FeOZnSO}_4$. Dzombak and Muhammad [18] also found the same result in their Cu^{2+} - SO_4^{2-} systems in NaNO_3 solution, which is described by the Generalized Two Layer Model (GTLM), considering the Cu^{2+} - SO_4^{2-} ternary surface complex, $\equiv\text{FeOHCuSO}_4$. These results indicated that the formation of the Cu^{2+} - SO_4^{2-} and Zn^{2+} - SO_4^{2-} ternary surface complexes should be responsible for the enhanced adsorption of Cu^{2+} and Zn^{2+} .

Varying ionic strengths of solution hardly affect the species distribution of Cu^{2+} - SO_4^{2-} and Zn^{2+} - SO_4^{2-} complex systems except in 0.500 M NaNO_3 (the highest ionic strength) where the initial amount of free Cu^{2+} and Zn^{2+} in solution at low pH was higher than those in 0.100, 0.010, and 0.001 M NaNO_3 . This result could imply that the concentration of NO_3^- ion may play a significant role in modifying the electrostatic environment at the interface, especially in the diffuse outer layer, and influencing the adsorption of metal ions, thus the formation of the metal-sulfate ternary surface complexes at low pH.