

## Supporting information for:

### **Probing into acid/base chemistry and adsorption mechanisms of hydrolysable Al(III) species and clays system in aqueous solution**

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## **Experimental**

### **Materials**

The bentonite used in this study was obtained from a mineral processing plant, India. The kaolin (analytical grade) was purchased from Tianjin Chemical Reagent Technologies Co., Ltd, China. Both the clay samples were further dried at 105 °C for 24 h. Unless specifically noted, all reagents used in the experiments were analytical grade and were used without further purification. A stock solution of Al(III) was prepared by dissolving 13.90 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  into ultrapure water and then diluted to 1000 mL, acquired a 1000  $\text{mg} \cdot \text{L}^{-1}$  of Al(III) solution with keeping pH 3.5. Working solutions of Al(III) were prepared from the stock solution by dilution with ultrapure water. The initial pH of the solution was adjusted by 0.1 M  $\text{HNO}_3$  or 0.1 M NaOH.

### **Adsorption isotherm experiments**

The isotherm experiments were conducted using a batch equilibration approach at three different temperature (25, 35, and 45 °C), and the 250 mL Erlenmeyer flasks containing the clays and metal solution were shaken in a thermostatic rotary shaker, operating at 150 rpm. The concentration of clay is 8  $\text{g} \cdot \text{L}^{-1}$  for bentonite and 100  $\text{g} \cdot \text{L}^{-1}$  for kaolin, and the initial concentration of Al(III) ions was varied from 10 to 100  $\text{mg} \cdot \text{L}^{-1}$  with pH 3.5. The thermodynamic parameters were calculated from the isotherm results.

## **Results**

### **Adsorption isotherm**

Al(III) adsorption isotherms on two clay minerals at three different temperatures are shown in Fig. 1S, and the adsorption isotherm data are listed in Table 1S. The experimental data are best fitted to Langmuir-Freundlich model.

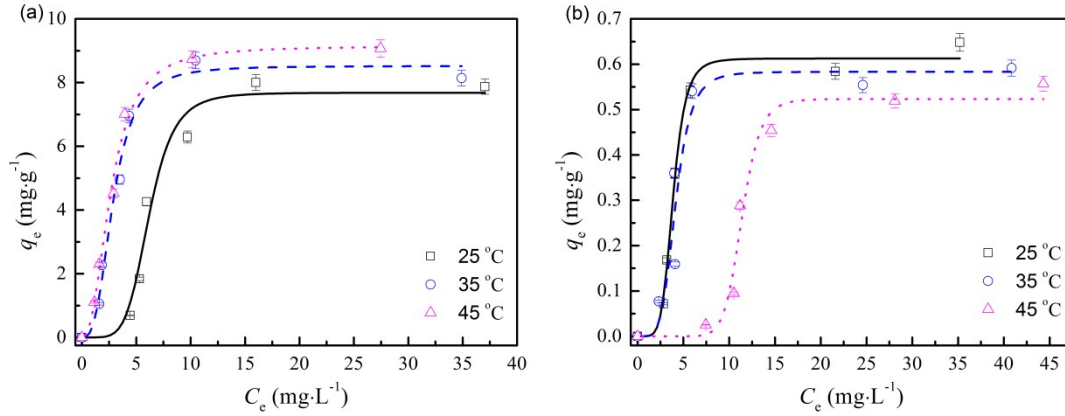


Fig. 1S. Adsorption isotherms of Al(III) on (a) bentonite and on (b) kaolin. The lines are Langmuir-Freundlich model simulation.

Table 1S. Adsorption isotherm data for adsorption of Al(III) on the two clays

| Clay minerals | T/°C | Langmuir-Freundlich model |          |          |       |
|---------------|------|---------------------------|----------|----------|-------|
|               |      | $q_m$                     | $K_{LF}$ | $n_{LF}$ | $R^2$ |
| Bentonite     | 25   | 7.68                      | 0.16     | 5.45     | 0.936 |
|               | 35   | 8.52                      | 0.35     | 2.94     | 0.969 |
|               | 45   | 9.14                      | 0.37     | 2.38     | 0.984 |
| Kaolin        | 25   | 0.61                      | 0.26     | 5.66     | 0.983 |
|               | 35   | 0.58                      | 0.24     | 4.93     | 0.799 |
|               | 45   | 0.52                      | 0.09     | 11.42    | 0.942 |

### Adsorption thermodynamics

The thermodynamic parameters for Al(III) adsorption process, free Gibbs energy ( $\Delta G$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ), enthalpy ( $\Delta H$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ), and entropy ( $\Delta S$ ,  $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) can be calculated from the temperature dependent adsorption isotherms using the following equations (Bhattacharyya and Gupta, 2011; Futralan et al., 2011):

$$\Delta G = - RT \ln K \quad (1)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

where  $K$  is the Langmuir equilibrium constant same as  $b$ ,  $R$  is the universal gas constant ( $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$ ), and  $T$  is the solution temperature (K). The plot of  $\ln K$  vs  $1/T$  is linear with the slope and the intercept giving values of  $\Delta H$  and  $\Delta S$ . The results can be found in Table 2S.

Table 2S. Thermodynamic data for adsorption of Al(III) on clay minerals

| Clay minerals | $\Delta H$ | $\Delta S$ | $\Delta G$ |       |       |
|---------------|------------|------------|------------|-------|-------|
|               |            |            | 25 °C      | 35 °C | 45 °C |
| Bentonite     | 32.86      | 0.10       | 4.52       | 2.70  | 2.60  |
| Kaolin        | -42.93     | -0.15      | 3.36       | 3.65  | 6.44  |

## References

Bhattacharyya, K.G. and Gupta, S.S. 2011. Removal of Cu(II) by natural and acid-activated clays: An insight of adsorption isotherm, kinetic and thermodynamics. *Desalination* 272(1-3), 66-75.

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