

Supporting information on

**Effect of humic acid on nickel(II) sorption to Ca-montmorillonite by batch and
EXAFS techniques study**

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Figure Captions

Fig. SI-1 XRD pattern of Ca-montmorillonite sample.

Fig. SI-2 FTIR spectrum of Ca-montmorillonite sample.

Fig. SI-3 Sorption isotherms of Ni(II) on Ca-montmorillonite in the presence/absence of HA. $C[\text{HA}]_{\text{initial}} = 10 \text{ mg/L}$, $m/V = 0.5 \text{ g/L}$, $I = 0.001 \text{ mol/L CaCl}_2$, $T = 20 \pm 1 \text{ }^\circ\text{C}$, $\text{pH} = 6.40 \pm 0.05$.

Fig. SI-4 Effect of HA initial concentration on Ni(II) sorption on HA-montmorillonite hybrids. $C[\text{Ni(II)}]_{\text{initial}} = 10 \text{ mg/L}$, $\text{pH} = 6.40 \pm 0.05$, $m/V = 0.5 \text{ g/L}$, $I = 0.001 \text{ mol/L CaCl}_2$, and $T = 20 \pm 1 \text{ }^\circ\text{C}$.

XRD and FTIR Characterization of Ca-montmorillonite. The XRD pattern of the Ca-montmorillonite is shown in Figure SI-1 and the crystallographic parameters are evaluated by measuring the (001) and (060) peaks. The peaks marked by (M) are the reflections indicative of 2:1 swelling clay, which confirms the characteristics of the montmorillonite type. The other peaks are impurities corresponding to quartz. Ca-montmorillonite exhibits a diffraction peak of the (001) plane at $2\theta = 5.74^\circ$, which corresponds to its basal spacing of 15.1 Å. The (060) reflection at $2\theta = 61.81^\circ$ indicates that Ca-montmorillonite has a dioctahedral structure.

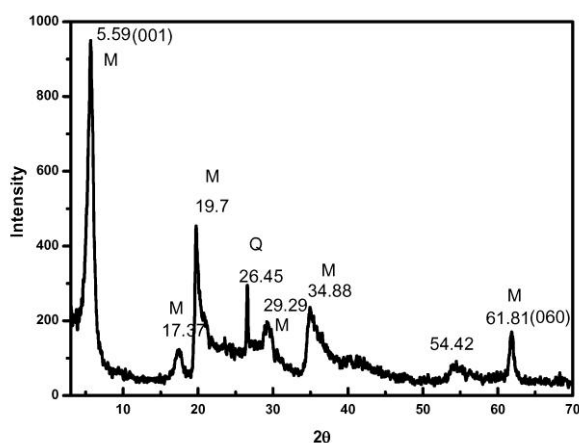


Fig. SI-1 XRD pattern of Ca-montmorillonite sample.

Figure SI-2 shows the FTIR spectrum of Ca-montmorillonite. The broad bands at 3621 and 3424 cm^{-1} are due to the O-H stretching vibration of the silanol (Si-OH) groups and H-OH vibration of water molecules adsorbed on the solid surface. The spectral band at 1642 cm^{-1} reflects the bending H-OH bond of water molecules, which is retained in the matrix. The strong band at 1032 cm^{-1} represents the Si-O-Si groups of the tetrahedral sheet. The spectral band at 912 cm^{-1} reflects the stretching vibration of Al-O-(OH)-Al. The bands at 838, 519 and 467 cm^{-1} are due to the deformation and bending modes of the Si-O bond (1). The FTIR analysis indicates that there are a large number of silanol (SiOH) and aluminol (AlOH) groups on Ca-montmorillonite surfaces.

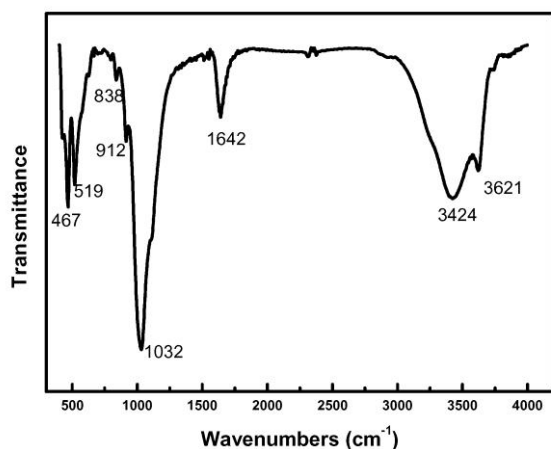


Fig. SI-2 FTIR spectrum of Ca-montmorillonite sample.

Batch Sorption. The sorption isotherms of Ni(II) on Ca-montmorillonite in the presence and absence of HA are investigated at $\text{pH } 6.40 \pm 0.05$ in 0.001 mol/L CaCl_2 solutions (Figure SI-3). One can see that sorption isotherm of Ni(II) on HA-montmorillonite hybrids is much higher than that of Ni(II) on bare montmorillonite, this is in agreement with the results shown in Figure 1A. The positive effect of HA on Ni(II) sorption can be explained by strong complexation of Ni(II) with the surface adsorbed HA, and suggests a surface-binding of Ni(II) via HA as “bridge” between the solid surface and Ni(II) ions. In order to gain a better understanding to the mechanism and to quantify the sorption data, the Langmuir model is adopted to simulate the results. The Langmuir equation ($C_s = \frac{K_L Q_m C_{eq}}{1 + K_L C_{eq}}$, C_{eq} is the equilibrium Ni(II) concentration in the aqueous solution (mg/L), C_s is the amount of Ni(II) adsorbed on solid) is applied to calculate the maximum sorption capacity Q_m (mg/g) and the energy of sorption K_L (L/mg). The Langmuir constants are obtained by fitting the sorption equilibrium data, and the results indicate that the Langmuir model fits the sorption of Ni(II) on Ca-montmorillonite successfully. The maximum sorption capacities (Q_m) of Ni(II) are 57.47 mg/g on HA-montmorillonite hybrids and 47.17 mg/g on bare montmorillonite at pH 6.40. It can be seen that the maximum sorption capacity of Ni(II)

on HA-montmorillonite is higher than that of Ni(II) on bare montmorillonite, indicating that the presence of HA enhances the sorption of Ni(II) to HA-montmorillonite hybrids.

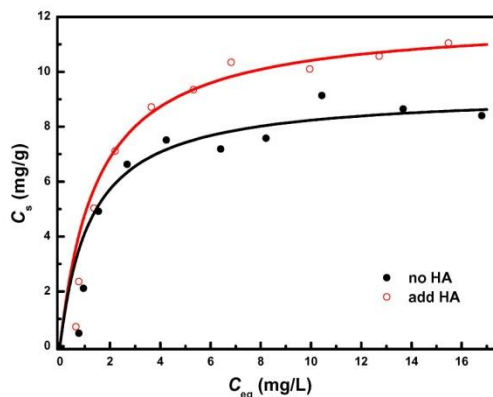


Fig. SI-3 Sorption isotherms of Ni(II) on Ca-montmorillonite in the presence/absence of HA. $C[\text{HA}]_{\text{initial}} = 10 \text{ mg/L}$, $m/V = 0.5 \text{ g/L}$, $I = 0.001 \text{ mol/L CaCl}_2$, $T = 20 \pm 1 \text{ }^\circ\text{C}$, $\text{pH} = 6.40 \pm 0.05$.

Figure SI-4 shows the sorption percentage of Ni(II) from solution to HA-montmorillonite hybrids as a function of HA initial concentrations at $\text{pH} 6.40 \pm 0.05$ in $0.001 \text{ mol/L CaCl}_2$ solutions. One can see that Ni(II) sorption on HA-montmorillonite hybrids increases with increasing HA concentrations in the ternary system, which indicates that the surface complexation of Ni(II) with surface adsorbed HA is stronger than that of Ni(II) with montmorillonite surface functional groups. At higher concentration of HA, more HA macromolecules are adsorbed on montmorillonite and thereby provides more functional groups (such as carboxylic and phenolic groups) to bind Ni(II) on HA-montmorillonite (2).

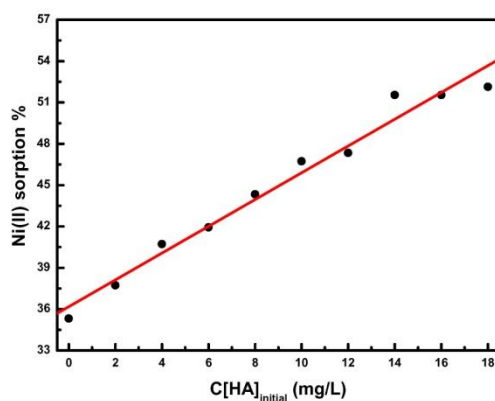


Fig. SI-4 Effect of HA initial concentration on Ni(II) sorption on HA-montmorillonite hybrids.

$C[\text{Ni(II)}]_{\text{initial}} = 10 \text{ mg/L}$, $\text{pH} = 6.40 \pm 0.05$, $m/V = 0.5 \text{ g/L}$, $I = 0.001 \text{ mol/L CaCl}_2$, and $T = 20 \pm 1 \text{ }^\circ\text{C}$.

Literature Cited

- 1 Tan, X.L.; Hu, J.; Zhou, X.; Yu, S.M.; Wang, X.K. Characterization of Lin'an Montmorillonite and Its Application in the Removal of Ni^{2+} from Aqueous Solutions. *Radiochim Acta* **2008**, *96*, 487-495.
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