Supporting Information

Millimeter-sized Mg-Al-LDHs nanoflakes impregnated magnetic alginate beads (LDHs-n-MABs): A novel bio-based sorbent for removal of fluoride in water

Chao Gao [†,‡,§], Xin-Yao Yu[‡,§], Tao Luo[‡], Yong Jia[‡], Bai Sun[‡], Jin-Huai Liu[‡], and Xing-Jiu Huang*[,†,‡]

[†]Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P.R. China.

[‡]Nano-materials and Environmental Detection Laboratory, Hefei Institute of Physical Sciences, Chinese Academy of Sciences, Hefei, 230031, P.R. China.

[§]These two authors contributed equally to this work.

*Address correspondence to X.-J. Huang

E-mail: xingjiuhuang@iim.ac.cn (X.J.H)

Tel.: +86-551-5591142; fax: +86-551-5592420.

Adsorption capacity:

Adsorption capacity was calculated from the relationship:

$$q_e = \frac{(C_0 - C_e)\ V}{m} \tag{1}$$

Where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e represent the initial and equilibrium F^- concentrations (ppm), V (L) is the volume of solution and m (g) is the weight of the adsorbent.

Adsorption isotherms:

The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent adsorption energies, and no interaction between adsorbed species.

The Langmuir adsorption isotherm can be represented in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where q_m and K_L are Langmuir constants, representing the maximum adsorption capacity of adsorbents (mg/g) and the energy of adsorption, respectively. The values of q_m and K_L can be calculated from the slope and intercept of plots of $\frac{C_e}{q_e}$ versus C_e.

Freundlich isotherm is based on an exponential distribution of adsorption sites and energies. It is derived to model multilayer adsorption and adsorption onto heterogeneous surfaces. The linear form of Freundlich adsorption model is as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{3}$$

Where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The values of n and K_F can be obtained by a plot of $\ln q_e$ against $\ln C_e$.

Temkin isotherm takes into account the adsorbing species-adsorbent interactions. The linearized form of the Temkin isotherm is:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (4)$$

Where $B_1 = RT/b$, T is the absolute temperature in K, R the universal gas constant, 8.314 J mol^{-1} K^{-1}, K_T the equilibrium binding constant (L mg^{-1}) and B_1 is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ yields a straight line from which the isotherm constants B_1 and K_T can be determined.

Table S1. Thermodynamic parameters for fluoride adsorption onto LDHs-n-MABs.

T (K)	K_d	ΔG^0 (KJ/mol)	ΔS^0 (J/mol K^{-1})	ΔH^0 (KJ/mol)
293	11.01	-5.844	-138.45	-46.185
313	2.42	-2.297		
333	1.15	-0.375		

Table S2. Mg/Al/Fe in the LDHs-n-MABs. (Unit: mg/ (mg adsorbent))

Adsorbents	Mg	Al	Fe
Adsorbent before adsorption	0.115	0.058	0.021
Adsorbent after adsorption	0.113	0.053	0.022
Adsorbent after one cycle regeneration	0.116	0.057	0.023

Table S3. Physio-chemical parameters of real groundwater

Parameter	Value
pH	8.52
Fluoride, mg/L	3.02
Total organic carbon	22.23
Total hardness	0.108
Chloride, mg/L	119.6
Nitrate, mg/L	10.76
Sulfite, mg/L	4.74
Sodium, mg/L	395.2
Potassium, mg/L	2.46
Total iron, mg/L	0.25
Manganese, mg/L	0.02
Calcium, mg/L	3.24
Magnesium, mg/L	7.92
Zinc, mg/L	0.02
Alumina, mg/L	0.12

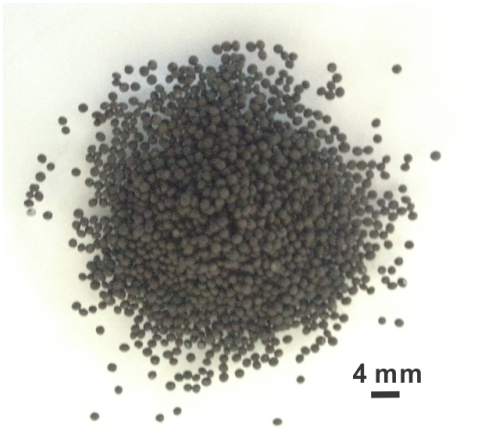

Fig. S1. Photograph of the dry beads.

Fig. S2. Photograph for the magnetic separation of the beads from solution under an external magnetic field.

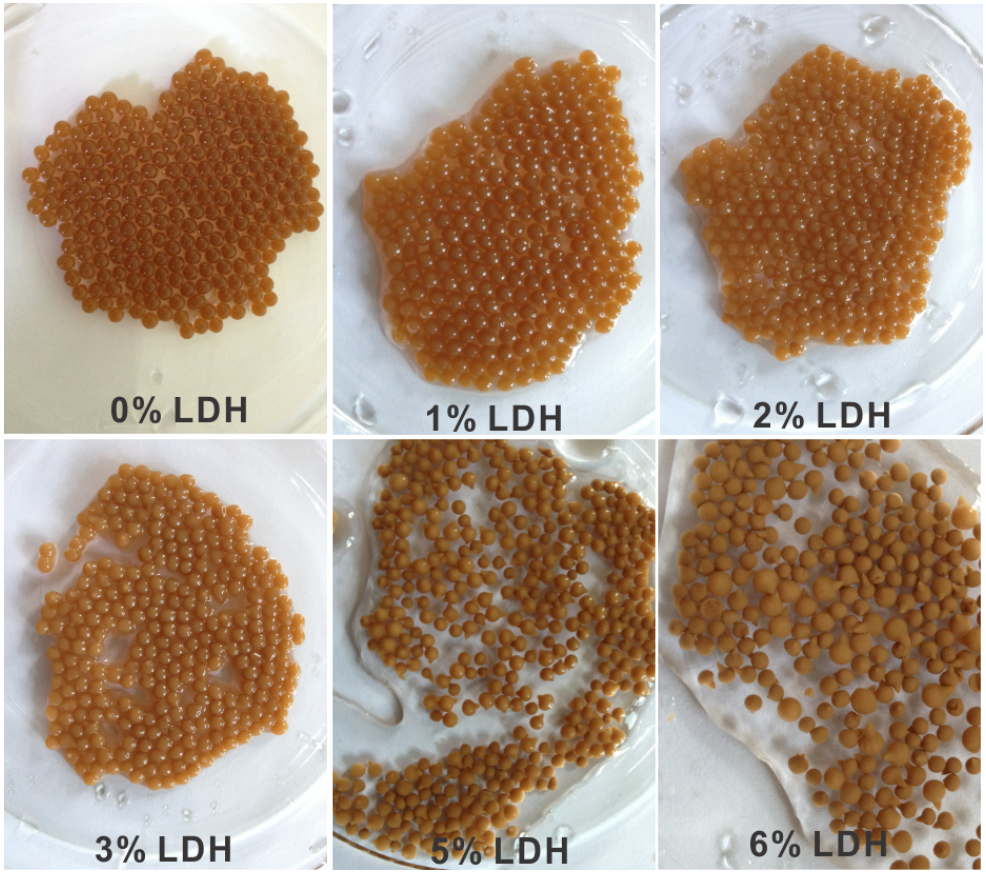

Fig. S3. Photograph for the beads with different content of LDHs.

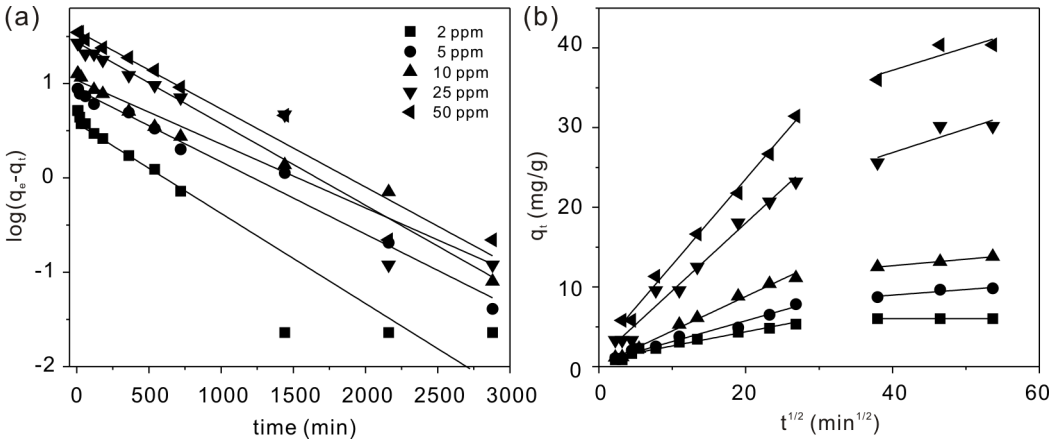

Fig. S4. The pseudo-first-order kinetic (a) and intra-particle (b) model fitting of the adsorption kinetics studies demonstrated in Figure 4(a).

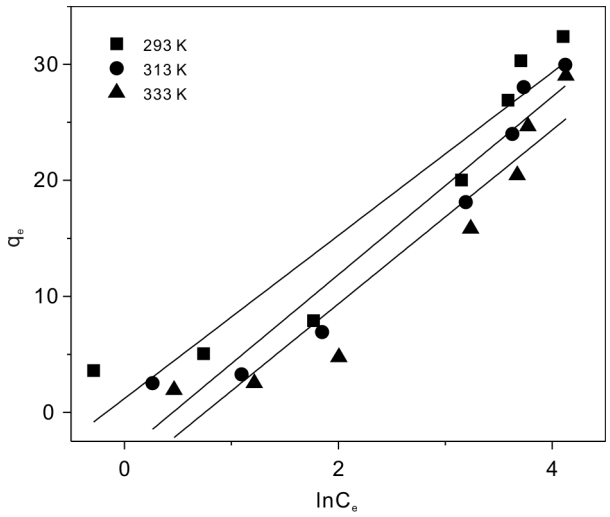

Fig. S5. Temkin isotherm fitting results of fluoride adsorption onto LDHs-n-MABs.

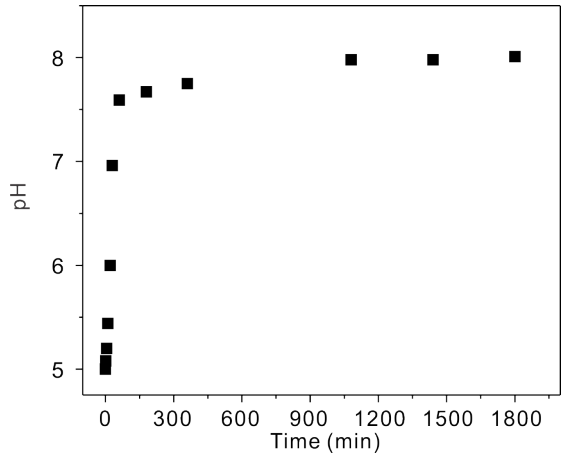

Fig. S6. pH variation during the adsorption.