Supporting information

Performance and characteristics of fluoride adsorption using nanomagnetite graphite-La adsorbent

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1 SEM images and EDX detection

The surface morphology of NG, MGNP, MGLNP and MGLNP loaded with fluoride was shown in Fig. S1. Fig. S1b indicated that lots of nano-Fe_3O_4 particles were successful loaded on the NG. In Fig. S1c, the brighter regions correspond to the lanthanum particles,[1] that was confirmed by EDS analysis (Fig. S2).

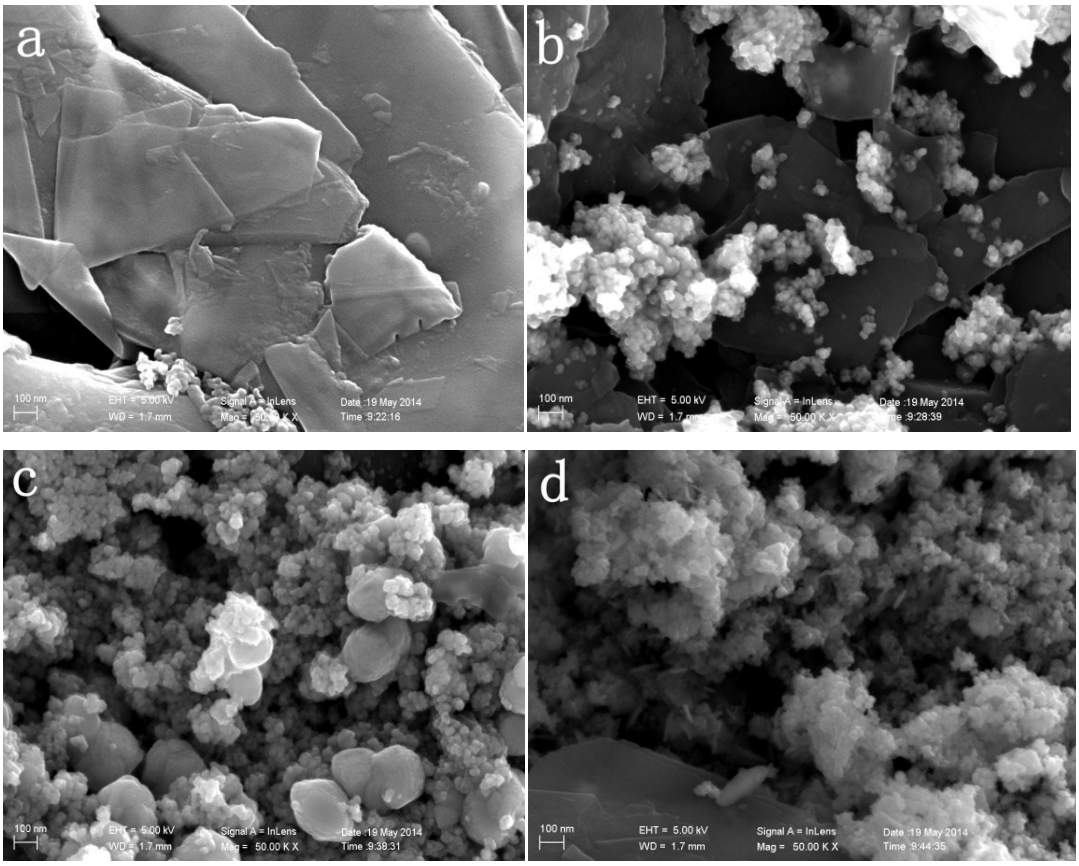

Fig. S1. SEM micrographs: (a) NG; (b) MGNP; (c) MGLNP and (d) F^- loaded MGLNP.

Fig. S2c showed that the γ-Fe_2O_3 and La ions are successfully immobilized on the surface of adsorbent.

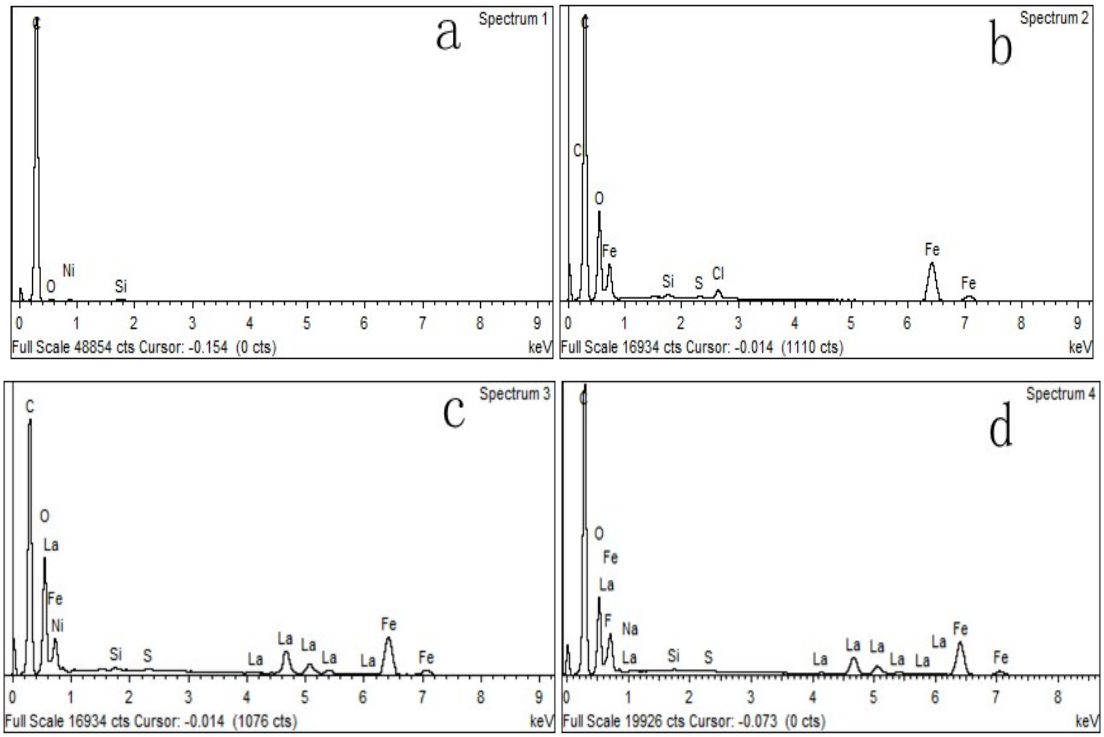

Fig. S2. EDX images: (a) NG; (b) MGNP; (c) MGLNP and (d) F^- loaded MGLNP.

2 XRD patterns

X-ray diffraction patterns of all the samples were investigated by a X-ray diffractometer, Model D8, BRUKER AXS, using Cu Kα radiation (α = 0.15425 nm) in the range of 2θ from 10° to 90°. The results are displayed in Fig. S3. In Fig. S3(A), the typical peak of nano-graphite (NG) was identified at 2θ = 26.5°. In Fig. S3(B), the typical peaks of Fe_3O_4 at 2θ = 30.2°, 35.6°, 43.2°, 57.5° and 62.7°[1] indicated that the nano-Fe_3O_4 particles were loaded on the surface of NG. After the MGNP was immersed by saturated $La(NO_3)_3 \cdot 6H_2O$ solution and calcined at 300 °C for 3 h, the nano-Fe_3O_4 particles were transformed into γ-Fe_2O_3, Fig. S3(C) shows the X-ray diffraction of γ-Fe_2O_3-graphite-La (MGLNP), which includes all the peaks of graphite, γ-Fe_2O_3 and La (2θ = 30.1°, 38.2°, 44.8°, 49.8°, 54.7° and 57.4°).[2]

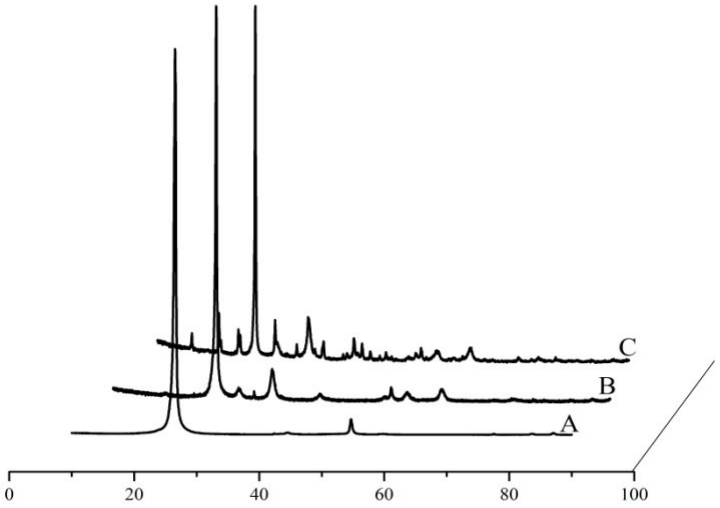

Fig. S3. XRD patterns: (A) NG; (B) MGNP and (C) MGLNP.

3 Cost analysis

On the basis of market investigation, the cost of MGLNP preparation was determined as following:

Tab. S1. Cost analysis of MGLNP adsorbent.

Item	**Price**	**Dose per Kg MGLNP**	**Cost** (US \$·kg^{-1} MGLNP)	**Total price** (US \$·kg^{-1} MGLNP)
Nanographite powder	76.92 US \$·kg^{-1}	0.43 kg	33.08	
$FeCl_2 \cdot 4H_2O$	1.38 US \$·kg^{-1}	0.17 kg	0.24	
$FeCl_3 \cdot 6H_2O$	0.71 US \$·kg^{-1}	0.45 kg	0.32	
Ammonia	0.69 US \$·kg^{-1}	0.98 kg	0.69	
$La(NO_3)_3.6H_2O$	53.85 US \$·kg^{-1}	0.78 kg	42.00	79.71
Concentrated nitric acid	2.46 US \$·L^{-1}	0.58 L	1.40	
Concentrated sulfuric acid	1.08 US \$·L^{-1}	0.98 L	1.06	
Water	0.77 US \$·t^{-1}	0.15 t	0.12	
Electricity	0.10 US \$·kW^{-1}	8 kW	0.80	

The cost of MGLNP could be divided into several items: materials and reagents, water and electricity. In total, the price for MGLNP adsorbent is 79.71 US $\$\cdot kg^{-1}$, which is higher than some low-cost adsorbents derived from either natural or waste sources as show in Tab. S2.[3] However, MGLNP adsorbent had high adsorption capacity of 77.12 $mg\cdot g^{-1}$ at 25 °C, and even remained higher than 75% adsorption capacity after three cycles of fluoride adsorption. Therefore, MGLNP adsorbent had a potential for fluoride removal from drinking water.

Tab. S2. Comparison between various adsorbents used for fluoride removal on the basis of adsorption capacity and cost of used material.

Adsorbent	**Adsorption capacity** ($mg\cdot g^{-1}$)	**Estimated cost** (US $\$\cdot kg^{-1}$)
Activated alumina	2.40	~2.30
Amorphous alumina	3.60	~70.00
Activated carbon (ALC-300)	1.10	~25.00
Calcite	4.37×10^{-5}	~0.11
Clay (bentonite)	7.09	~1.00
Charcoal	7.88×10^{-5}	~0.32
Red mud	6.28×10^{-3}	~0.10
Carbon slurry	4.86	~0.20
MGLNP	77.12	~79.71

4 Stability of the MGLNP

The effects of temperature (25°C, 35°C and 50°C) and pH (4~10) on magnetic separation and equilibrium adsorption capacity have been studied. The corresponding experiments were conducted as below:

Firstly, several 100 ml MGLNP suspensions of 10 $g\cdot L^{-1}$ in the polyethylene bottles were shaken for 8 days at 160 rpm in the air bath thermostat oscillator.

Afterward, the MGLNP in the suspensions was separated under a magnetic field. Fig. S4 presented the magnetic separation results accordingly. As treated with different pH values or temperatures, the MGLNP could be easily separated with magnet, and the black opaque suspension rapidly changed to clear liquid.

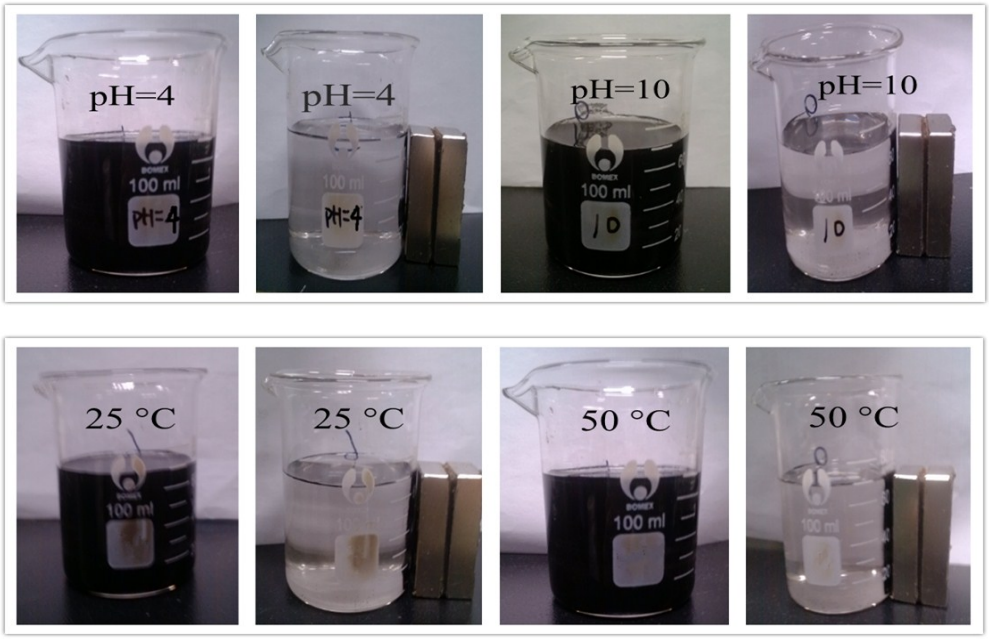

Fig. S4. Magnetic separation of treated MGLNP with different pH values or temperatures.

Subsequently, the magnetically separated MGLNP was dried at 60 °C for 8h. The fluoride adsorption experiments with these dried MGLNPs were carried out according to the procedure in section 2.3 of the manuscript. 20 mg MGLNP adsorbent was dosed into 100 ml F^- solution with the concentration of 9.88 $mg \cdot L^{-1}$, then this suspension was shaken at 160 rpm and 25 °C in the air bath thermostat oscillator. Tab. S3 showed the corresponding equilibrium adsorption capacities (Q_e).

Tab. S3. Equilibrium adsorption capacities of treated MGLNP with different pH values or temperatures.

Q_e for original MGLNP ($mg \cdot g^{-1}$)	Q_e for 8-day treated MGLNP ($mg \cdot g^{-1}$)									
	pH = 4.0	pH = 5.0	pH = 6.0	pH = 7.0	pH = 8.0	pH = 9.0	pH = 10.0	t = 25 °C	t = 35 °C	t = 50 °C
18.10	14.13	16.63	17.27	17.80	17.63	17.77	17.93	18.03	17.97	17.27

As indicated in Tab. S3, most Q_e values of 8-day treated MGLNPs showed slight difference except for the 8-day treated MGLNP with pH = 4.0, which decreased from 18.10 $mg \cdot g^{-1}$ of the original MGLNP to 14.13 $mg \cdot g^{-1}$.

5 The quantitative analysis of the adsorption mechanism

In order to further analysis of defluorination mechanism, the fluoride removal data were estimated through quantitatively calculating the [OH^-] increase and the loaded La^{3+} on the surface of MGLNP. The corresponding result is shown in Tab.3. The quantitative analysis of the adsorption mechanism is provided as following:

Tab. S4. The quantitative analysis of the adsorption mechanism (adsorbent dosage = 200 $mg \cdot L^{-1}$, 25 °C).

Mechanism	Before adsorption	After adsorption	Difference	Adsorption capacity ($mg \cdot g^{-1}$)
F^- ion exchange with OH^-	pH = 6.94	pH = 8.98	$\Delta[F^-] = \Delta[OH^-] =$ 0.18 $mg \cdot L^{-1}$	0.90
Surface La^{3+} complexation with F^-	Loaded La^{3+} = 254.26 $mg \cdot g^{-1}$	Adsorbed F^- = 104.31 $mg \cdot g^{-1}$	q = 104.31 $mg \cdot g^{-1}$	104.31

As indicated in Tab. 3, the calculated F^- adsorption capacity of MGLNP is 105.21 $mg \cdot g^{-1}$, which is higher than the maximal adsorption capacity (Q_m) for fluoride determined with the Langmuir model were 77.12 $mg \cdot g^{-1}$ at 25 °C. This difference could be attributed to a part of La^{3+} loading on the MGLNP without F^- complexation.

Therefore, the calculated adsorption capacity of 104.31mg·g^{-1} was overestimated, and surface La^{3+} complexation mechanism played an important role in the fluoride removal by MGLNP.

Reference

1 L. Gao and L.G. Chen, Microchim Acta, 2013, 180, 423–430.

2 E. Vences-Alvarez, L.H. Velazquez-Jimenez, L.F. Chazaro-Ruiz, P.E. Diaz-Flores and J.R. Rangel-Mendez, J Colloid Interface Sci, 2015, 455, 194-202.

3 S. Jagtap, M.K. Yenkie, S. Das and S. Rayalu, Desalination, 2011, 273, 267-275.