Enhanced Oxidative and Adsorptive Capability towards Antimony by Copper-doping into Magnetite Magnetic particles

Zenglu Qi,^{ab} Huachun Lan,^a Tista Prasai Joshi,^{ab} Ruiping Liu,*^a Huijuan Liu^a and Jiuhui Qu^a

^aKey Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail:liuruiping@rcees.ac.cn
^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author. E-mail:liuruiping@rcees.ac.cn



Fig. S1 XPS Cu 2p spectra of Cu-doped Fe₃O₄ before and after Sb(III) adsorption



Fig S2 Adsorption performance of non-doped Fe_3O_4 and Cu-doped Fe_3O_4 towards low level (a) Sb (III) and (b) Sb (V) (initial centration of 50 µg L⁻¹)



Fig. S3 The species distribution of (A) Sb(III) and (B) Sb (V) over a wide pH range from 2.0 to 12.0



Fig. S4 The adsorption of (a) Sb(III) and (b) Sb (V) onto Fe_3O_4 and Cu-doped Fe_3O_4 at different IS of 0.01 M and 0.1 M over wide pH range. $([Sb(III)]_0 = [Sb(V)]_0 = 50 \text{ mg } \text{L}^{-1}$, adsorbents doses = 0.2 g L⁻¹)



Fig. S5 Iron (red line) and Copper (green line) release into solution in the antimony adsorption process and the adsorbent amount was 200 mg/L [(A) Fe₃O₄ adsorption Sb(III); (B) Fe₃O₄ adsorption Sb(V) ; (C) Cu-doped Fe₃O₄ adsorption Sb(III); (D) Cu-doped Fe₃O₄ adsorption Sb(V) and solid symbol represents IS = 0.1 M KNO₃ ; hollow solid symbol represents IS = 0.01 M KNO₃]



Fig. S6 Effect of co-existing anions at different concentrations on the adsorption of Sb(III) and Sb(V) ($[Sb(III)]_0 = [Sb(V)]_0 = 50 \text{ mg } \text{L}^{-1}$, adsorbents doses = 0.2 g L⁻¹, pH = 7.0, The dash lines correspond to their removal efficiency in control systems)



Fig. S7 FTIR spectra for Fe_3O_4 and Cu-doped Fe_3O_4 before and after exposure to either Sb(III) and Sb(V). (The transmittance infrared spectrum of these adsorbents in the 4000-400 cm⁻¹ region before and after interaction with 50 mg/L Sb(III) and Sb(V) at pH 7.0. The band near to 1630 cm⁻¹ existing in all samples was ascribed to the deformation of water molecules, which indicated the presence of physisorbed water on these adsorbents and very small peaks at 2860 cm⁻¹ and 2937 cm⁻¹ are observed in each case, which confirms that these peaks are due to the trace amount of physically adsorbed ethylene glycol (-CH₂- stretching) on the adsorbents' surface during nanoparticle synthesis. For the original Fe₃O₄ and Cu-doped Fe₃O₄, three peaks at 1130, 1049, and 979 cm⁻¹ were due to the bending vibration of the hydroxyl group associated with Fe and the peak at 595 or 590 cm⁻¹ is attributed to Fe-O bond vibration)



Fig. S8 Fe 2p XPS spectra for Cu-doped Fe_3O_4 and Fe_3O_4 before and after Sb removal

The magnetic force (F_m) acts on magnetic particles could be expressed as follows:

$$F_m = V \cdot M(H) \cdot \frac{dH}{dx}$$
(S1)

Where V is the volume of the magnetic particle, M(H) is the magnetization of the magnetic particle in a magnetic intensity (H), and dH/dx is the magnetic gradients. [From **eqn (S1)** we can know, it is not easy to remove a magnetic particle with relatively less magnetized or extremely small size]

Sample	Composition (at.%)		
	Cu	Fe	0
non-doped Fe ₃ O ₄	0.00	37.04	47.04
Cu-doped Fe ₃ O ₄	7.31	16.96	40.74

Table S1 XPS result of surface elemental compositions of non-doped Fe $_3O_4$ and Cu-doped Fe $_3O_4$