Synthesis of magnetic mesoporous silica microspheres with accessible carboxyl functionalized surfaces and radial oriented large mesopores as adsorbents for removal of heavy metal ions

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S1 Adsorption equilibrium experiments

The equilibrium adsorption capacity of adsorbent described the heavy metal ions removal ability of the synthesized adsorbent. In this work, 10 mg of adsorbent was added in 10 mL of Cd(II), Cu(II), and Pb(II) solution at concentrations (1 ~ 1000 mg L^{-1}) for 2 h at room temperature. After adsorption, the supernatant was collected through magnetically separated for about 10 min and then the concentration of final heavy metal ions was measured using atomic absorption spectroscopy (AAS). The equilibrium adsorption capacity of adsorbent was defined as follows:

$$qe = \frac{(C_o - C_e) \times V}{M}$$

Where q_e stands for adsorption capacity (mg g⁻¹), C_0 and C_e are the initial and equilibrium concentrations of the adsorbates (mg L⁻¹), respectively, V is the volume of solution (L), and M is the mass of adsorbent (g).

S2 Adsorption isotherm models

The Langmuir isotherm model, Freundlich isotherm model and Temkin isotherm model were used to describe the adsorption process and investigate the mechanism of adsorption. The Langmuir isotherm model was based on the assumption that the adsorption process was a mono-molecular layer adsorption. The Freundlich isotherm model could be applied to nonideal sorption on heterogeneous surfaces as well as multi-layer sorption. The three models could be respectively defined as follows:

$$q_{e} = \frac{K_{L} \cdot C_{e}}{1 + a_{L} \cdot C_{e}}$$
 S(2)

$$q_e = K_F \cdot C_e^{n_F}$$
 S(3)

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln (C_e)$$
 S(4)

Where q_e is the equilibrium amount of adsorbate adsorbed (mg g⁻¹), C_e is the adsorbate concentration at equilibrium (mg L⁻¹), K_L (L g⁻¹) and a_L (L mg⁻¹) are the Langmuir isotherm parameters, respectively, K_F (L g⁻¹) is the Freundlich parameter, n_F is the heterogeneity factor, A is the Temkin isotherm constant (L g⁻¹), b is the Temkin constant related to heat of sorption (J mol⁻¹), R is the gas constant (8.3145 J mol⁻¹ K⁻¹), and T is the absolute temperature (K), B = RT/b. respectively.

S3 Effect of pH

To measure the influence of pH on the adsorption performence, the adsorption experiments were carried out under different pH (2 ~ 8) adjusted by 1 M HCl or NaOH. 10 mg of adsorbent was added in 10 mL of 500 mg L⁻¹ heavy metal ions solution for 2 h at room temperature. After adsorption, the supernatant was also collected through magnetically separated for about 10 min and then the concentration of final heavy metal ions was measured. The removal efficiency of heavy metal ions, R, was defined as follows:

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$
 S(5)

where R is the removal efficiency of the heavy metal ions, C_0 and C_e are the initial and equilibrium concentration of the adsorbate (mg L⁻¹), respectively.

S4 Adsorption kinetics

To study relationship between adsorption time and heavy metal ions removal ability, the adsorbed amount of heavy metal ions versus time was investigated. The adsorption time was varied from 0 to 120 min and the initial heavy metal ions concentration was selected as 500 mg L^{-1} , and 10 mg of adsorbent was added in 10 mL of Cd(II), Cu(II), and Pb(II) solution. After adsorption, the supernatant was collected by centrifugation and then the concentration of final heavy metal ions was measured. The adsorption ability of adsorbent at time t was defined as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{M}$$
 S(6)

Where q_t is the amount of the adsorbed adsorbates at time t (mg g⁻¹), C₀ and C_t (mg L⁻¹) are the concentrations of adsorbates initially and at time t, respectively, V is the volume of solution (L), and M is the mass of adsorbent (g).

To examine the adsorption rates and study the possible adsorption mechanism, the pseudo-first-order kinetic model and the pseudo-second-order kinetic model were investigated, respectively. The lineal form of pseudo-first-order kinetic model and the pseudo-second-order kinetic model could be respectively defined as follows:

$$\ln(\mathbf{q}_{e} - \mathbf{q}_{t}) = \ln \mathbf{q}_{e} - \mathbf{k}_{1}t$$
 S(7)

$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{k}_2 \cdot \mathrm{q}_{\mathrm{e}}^2} + \frac{\mathrm{t}}{\mathrm{q}_{\mathrm{e}}} \tag{8}$$

Where q_t is the amount of the adsorbed adsorbates at time t (mg g⁻¹), q_e is the amount of the adsorbates at equilibrium (mg g⁻¹), k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min⁻¹), and k_2 is the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹).



Fig. S1 SEM images of Fe₃O₄ (a), Fe₃O₄@SiO₂ (d) and Fe₃O₄@SiO₂@mSiO₂ (g) microspheres (a), TEM images of Fe₃O₄ (b), Fe₃O₄@SiO₂ (e) and Fe₃O₄@SiO₂@mSiO₂ (h) microspheres. Size distribution histogram of Fe₃O₄ (c), Fe₃O₄@SiO₂ (f) and Fe₃O₄@SiO₂@mSiO₂ (i) microspheres calculated from SEM images.



Fig. S2 XRD patterns of the Fe_3O_4 (a) and the $Fe_3O_4@SiO_2@mSiO_2$ -COOH (b) microspheres.



Fig. S3: Comparison of the experimental and fitted adsorption isotherms on the Fe₃O₄@SiO₂@mSiO₂-COOH microspheres: (A) Cd(II), (B) Cu(II) and (C) Pb(II).

Table S1 Comparison of adsorption capacity (mg g⁻¹) for removal of Cd(II), Cu(II), and Pb(II) on the Fe₃O₄@SiO₂@mSiO₂-COOH microspheres with other absorbents.

Adsorbents	Cd(II)	Cu(II)	Pb(II)
Fe ₃ O ₄ /cyclodextrin polymer ^[1]	27		64
magnetic Fe_3O_4 yeast treated with EDTA ^[2]	47		99
iron oxide coated sewage sludge ^[3]	14	42	17
Cibacron Blue F ₃ GA-attached ^[4]	38	9	86
Carboxyl Functional Magnetite ^[5]	45	44	74
EDTA functionalized magnetic graphene oxide ^[6]		301	508
poly (itaconic acid)-grafted crosslinked chitosan ^[7]			1320
graphene oxide with 3-aminopyrazole ^[8]	285		



Fig. S4 FTIR spectrum of the structure of $Fe_3O_4@SiO_2@mSiO_2$ -COOH microspheres after multiple reuses.

Sample	Pore size	BET surface area	Pore volume	
	(nm)	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	
Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -COOH	11.03	165	0.17	
Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -COOH after reuse	10.65	139	0.14	

Table S2 The pore structure change of $Fe_3O_4@SiO_2@mSiO_2$ -COOH microspheres after multiple reuses.

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