

*Electronic Supplementary Information*

**An Effective One-pot Method for Preparing Covalently  
Bonded Nanocomposite Soft Magnetic Beadlike Microgels  
and Its Evaluation as Adsorbent for Removal of Toxic  
Heavy Metals from Aqueous Solution**

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## Materials and reagents

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (AR) was obtained from Tianjin Damao Chemical Reagent Company, China.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (AR) and ammonium peroxydisulfate (AR) were from Yantai Shuangshuang Chemical Industry Co. Ltd., China. Acrylic acid (AA, AR) and acrylamide (AM, AR) were from Tianjin Kaixin Chemical Industry Co. Ltd., China. Attapulgite (industrial grade) was from Yutai Xinyuan Technology Co. Ltd., China. Span-80 (AR), Tween-60 (AR) and liquid paraffin (CR) were from Tianjin Guangfu Fine Chemical Research Institute, China. KH-570 (industrial grade) was from Jiangsu Chenguang Silane Co., Ltd, China. HCl (AR) was from Xinyang Great Wall Chemical Industry Plant, China. Self-made secondary distilled water has been used throughout the experiments.

## Preparation of multi-functional $\text{Fe}_3\text{O}_4$ nanoparticles and attapulgite nanorods

Typically,<sup>1</sup>  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (26 g) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (10 g) were dispersed in 400 mL distilled water, heated to 70 degree centigrade under  $\text{N}_2$  atmosphere, followed by adding 100 mL aqueous ammonia drop by drop. The sample was then stirred at 75 degree centigrade for 1 h after aqueous ammonia was added, and further stirred at 85 degree centigrade for 0.5 h. The obtained mixture was acidified in 0.1 mol/L HCl aqueous solution to release hydroxyl groups on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles, washed with distilled water until neutralized, then followed by filtration with air pump to get a water dispersion of  $\text{Fe}_3\text{O}_4$  nanoparticles with solid content around 25 wt%.

Attapulgite was baked at 180 degree centigrade for 6 h to remove organic

impurities, grinded in HCl aqueous solution for 3 h to release hydroxyl groups on the surface of attapulgite nanorods,<sup>2</sup> washed with distilled water until neutralized, then followed by filtration with air pump to get a water dispersion of attapulgite nanorods with solid content around 25 wt%.

The obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles aqueous dispersion and attapulgite nanorods aqueous dispersion were mixed at a mass ratio of 1:1, and dispersed into liquid paraffin with the mixture of Span-80 (sorbitan monooleate) and Tween-60 (polyoxyethylene sorbitan monostearate) as emulsifier, in which the mass ratio of the total amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods to liquid paraffin was 1:3. KH-570 of one third mass of the total amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods was then added into the above-obtained water-in-oil emulsion, stirred at room temperature for 0.5 h, followed by heating at 40 degree centigrade for 6 h to get a water-in-oil emulsion of multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods.

#### **Preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles/poly(acrylic acid-co-acrylamide)/attapulgite nanorods composite soft magnetic beadlike microgel adsorbent**

The mixture of AA and AM at a mass ratio of 1:1 was dispersed into liquid paraffin with the mixture of Span-80 and Tween-60 as emulsifier, in which the mass ratio of the total amount of AA and AM to liquid paraffin was 1:3. The mixture was pre-emulsified for 1 h, then added into the water-in-oil emulsion of multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods, and stirred for 0.5 h. Ammonium

peroxydisulfate was added into the reactor, stirred at room temperature for 0.5 h, then 60 degree centigrade for 2 h and followed by 80 degree centigrade for 3 h in N<sub>2</sub> atmosphere. Through the bridge of “—C=C—” in KH-570, AA and AM were polymerized in-situ onto the surface of multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods. The resulting microgels were separated from liquid phase, and washed with ether, ethanol and distilled water in sequence to develop a Fe<sub>3</sub>O<sub>4</sub> nanoparticles/poly(acrylic acid-co-acrylamide)/attapulgite nanorods composite soft magnetic beadlike microgel adsorbent.

### **Optimization of the formulation**

With the adsorption capacity to Pb(II) and Cu(II) as the objective function, the effects from the ratio of the total mass of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods to the total mass of AA and AM, the mixed ratio of Span-80 and Tween-60, the mass percentage of APS in the total mass of AA and AM, and the mass ratio of oil phase to water phase on the properties of the adsorbents were investigated based on series of orthogonal experiments and single factor experiments. The optimized formulation of the adsorbent was summarized in Table S1.

### **Characterization and analysis**

The unmodified Fe<sub>3</sub>O<sub>4</sub> nanoparticles and raw attapulgite clay were separately purified and dispersed ultrasonically in distilled water for 2 h, and then deposited on copper grids covered with perforated carbon film. On the other hand, the prepared

water dispersions of the multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the multi-functional attapulgite nanorods were separately diluted with distilled water to a certain concentration, then deposited on copper grids covered with perforated carbon film, respectively. The morphologies of these 4 samples were imaged with a transmission electron microscope (TEM, JEM-1200 EX/S (JEOL Ltd., Japan)).

The adsorbents were thoroughly swollen in distilled water, then dried in a freeze dryer. The freeze-dried adsorbents were dissected in halves, and then the section planes were characterized with a field emission scanning electron microscope (SEM, S-4800 (HITACHI, Tokyo, Japan)).

The adsorbents were immersed in ammonia water at pH 8-9 for 72 h, followed by extraction in distilled water for 24 h to remove un-grafted poly (acrylic acid-co-acrylamide). The purified adsorbents were soaked in ethanol, and thoroughly dried in a vacuum oven at 70 C. The amount of copolymers grafted on the surface of multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and attapulgite nanorods was evaluated by a thermogravimetric analyzer (TGA 2050 (TA Instruments, USA)).

The adsorbents were frozen at -20 °C for 2 h, then heated at 60 °C for 2 h. This freeze-heat cycle was repeated for 5 times to investigate the temperature resistance of the adsorbents.

The swollen adsorbents were stirred in distilled water at 5000 rpm for 2 h to study the resistance to shear flow.

The magnetic hysteresis, saturation magnetization and coercivity of the unmodified Fe<sub>3</sub>O<sub>4</sub> nanoparticles, the multi-functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the

prepared adsorbents were separately evaluated with vibrating sample magnetometer system (VSM, Lakeshore 7400 (Lake Shore Cryotronics Inc., USA)) at room temperature in the range from -12000 oe to 12000 oe.

Fe<sub>3</sub>O<sub>4</sub>/poly(acrylic acid-co-acrylamide)/attapulgate sample, Cu(II)-absorbed sample (prepared by immersing in 100 mg /L Cu(II) solution of pH 4 at room temperature for 3 h) and Pb(II)-absorbed sample (prepared by immersing in 100 mg /L Pb(II) solution of pH 6 at room temperature for 3 h) were compared with an Avatar 360 FT-IR instrument (Nicolet, USA) in the range of 300-4000 cm<sup>-1</sup> by the KBr pellet technique.

#### **Absorption selectivity to different metal ions**

The accurately weighted adsorbent in the range from 0.0500 g to 0.1000 g was added into 50 mL solution containing 5 mg of Pb(II), Cu(II), Ni(II), Hg(II), Zn(II) and Cd(II) each, and stirred for 3.0 h. The concentrations of the remained ions were measured respectively by a fire atomic absorption spectrometer (AA 240 FAAS (Varian, USA)) to evaluate the adsorption capacity of the adsorbent to different metal ions.

#### **Absorption capacity to Pb(II) and Cu(II) as a function of pH level**

Six 100 mg /L Pb(II) specimens were prepared with aq. HCl solutions of pH at 1, 2, 3, 4, 5 and 6, and the accurate concentration of Pb(II) (represented as  $C_0$ , mg/L) in each specimen was measured with FAAS. Six adsorbents in the range from 0.0500 g

to 0.1000 g were accurately weighed (represented as  $W$ , g), and respectively added into 50 mL above-prepared Pb(II) solutions and stirred for 3 h, then the concentration of the remaining Pb(II) (represented as  $C_t$ ) in the upper liquid phase of each specimen was measured with FAAS. The absorption capacities of the adsorbent to Pb(II) (represented as  $A_{\text{Pb(II)}}$ , mg/g) at different pH values were calculated with following formula (1).

$$A_{\text{Pb(II)}} = 0.05 * (C_0 - C_t) / W \quad (1)$$

The absorption capacities to Cu(II) ( $A_{\text{Cu(II)}}$ ) at different pH values were studied in the same way.

### **Absorption capacity to Pb(II) and Cu(II) as a function of time**

A 100 mg /L Pb(II) solution of pH at 6 was prepared, and the accurate concentration of Pb(II) in the solution was measured with FAAS. 12 specimens were prepared by adding accurately weighed adsorbents in the range from 0.0500 g to 0.1000 g to the Pb(II) solutions of 50 mL each. These specimens were stirred and sampled at 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 24 h, 36 h, 48 h and 60 h, respectively. Correspondingly, the concentration of the remaining Pb(II) in each sample was measured with FAAS. The absorption capacity to Pb(II) as a function of time was calculated with formula (1). A 100 mg /L Cu(II) solution of pH at 4 were prepared, then the absorption capacity to Cu(II) as a function of time was studied in the same way.



## **The dosage of adsorbent that can bring the Pb(II) (0.5 g/L) up to the national standard of USA's EPA**

A 500 mg /L Pb(II) solution of pH at 6 was prepared, and the accurate concentration of Pb(II) in the solution was measured with FAAS. 6 specimens were prepared by adding accurately weighed adsorbents (around 0.3000, 0.4000, 0.5000, 0.6000, 0.7000 and 0.8000 g respectively) to the Pb(II) solutions of 50 mL each. These specimens were stirred and sampled at 8 h. Correspondingly, the concentration of the remaining Pb(II) in each sample was measured with FAAS. The absorption capacity to Pb(II) was calculated with formula (1) to investigate the dosage of adsorbent that can bring the Pb(II) (0.5 g/L) up to the national standard of USA's EPA.

## **Adsorption kinetics of adsorbent to Pb(II) and Cu(II)**

The absorption capacity to Pb(II) at pH of 6 and the absorption capacity to Cu(II) at pH of 4 at different adsorption time were studied based on the pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model with the formulas (2)~(4), respectively.

The linear equation of the pseudo-first-order model is the following:

$$\frac{1}{q_t} = \frac{k_1}{q_e \cdot t} + \frac{1}{q_e} \quad (2)$$

Where  $k_1$  ( $\text{h}^{-1}$ ) is the rate constant of pseudo-first-order adsorption;  $q_t$  (mg/g) is the amount of adsorbed Pb(II) or adsorbed Cu(II) at time  $t$  (h), and  $q_e$  (mg/g) is the amount of adsorbed Pb(II) or adsorbed Cu(II) at equilibrium.

The linear equation of the pseudo-second-order model is described as the

following:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where  $k_2$  (g/(mg·h)) is the rate constant of pseudo-second-order adsorption.

The linear equation of the intra-particle diffusion model is the following:

$$\ln q_t = \ln k_i + \frac{1}{2} \ln t \quad (4)$$

Where  $k_i$  (mg/(g·h<sup>1/2</sup>)) is the rate constant of intra-particle diffusion adsorption.

### **Adsorption isotherm of adsorbent to Pb(II) and Cu(II)**

5 accurately weighed adsorbent in the range of 0.0500~0.1000 g was respectively added into each of 50 mL Pb(II) solutions of 20, 40, 60, 80 and 100 mg/L (pH 6.0), then stirred at a given temperature for 72 h. The accurate concentrations of Pb(II) before and after adsorptions were measured with FAAS, and then the absorption capacities to Pb(II) of different initial concentrations at a given temperature were calculated with formula (1). The adsorption isotherm to Pb(II) was studied based on Langmuir model with formula (5) and Freundlich model with formula (6), separately. The adsorption isotherm of adsorbent to Cu(II) was investigated with the same procedure.

The linear equation of Langmuir model can be written as the following:

$$\frac{C_e}{q_e} = \frac{1}{k_L \cdot q_L} + \frac{C_e}{q_L} \quad (5)$$

Where  $q_e$  and  $C_e$  are the concentrations of the adsorbed ions (Pb(II) or Cu(II)) and the ions (Pb(II) or Cu(II)) in the solution at equilibrium respectively;  $q_L$  and  $k_L$

are the monolayer adsorption capacity to Pb(II) or to Cu(II) and equilibrium constant for the adsorption respectively.

The linear equation of Freundlich model can be written as the following:

$$\ln q_e = \ln k_F + \frac{1}{n_F} \ln C_e \quad (6)$$

Where  $k_F$  and  $n_F$  are constants.

### **Acidity dependence for desorption of Pb(II) and Cu(II) in adsorbent**

With the same procedure described above, the adsorption capacities with adsorption time of 8 h to Pb(II) (pH 6) and to Cu(II) (pH 4) for 5 specimens of each ion were evaluated. These Pb(II)-saturated or Cu(II)-saturated samples, filtrated from above 10 specimens, were wiped with filter paper to remove the residual solution on the surface, then added into 50 mL aqueous HCl of 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L respectively and stirred for 3 h. The concentrations of the eluted Pb(II) or Cu(II) in liquid phases of the samples were measured by FAAS and represented as  $C_d$ . The desorption ratios (represented as  $R_d$ ) were calculated with the formulas (7).

$$R_d = [C_d / (C_0 - C_i)] \times 100\% \quad (7)$$

### **Desorption time for complete elution of Pb(II) and Cu(II) form adsorbent**

With the same procedure described above, the adsorption capacities with adsorption time of 48 h to Pb(II) (pH 6) and to Cu(II) (pH 4) for 6 specimens of each ion were evaluated. These Pb(II)-saturated or Cu(II)-saturated samples from the 12 specimens were wiped with filter paper. 6 Pb(II)-saturated samples were added into

50 mL aqueous HCl of 0.4 mol/L, and the other 6 Cu(II)-saturated samples were added into 50 mL aqueous HCl of 0.2 mol/L, then sampled at 20, 40, 60, 80, 100 and 120 min respectively for both Pb(II) and Cu(II). The concentrations of the eluted Pb(II) or Cu(II) in liquid phases of the samples were measured by FAAS. The desorption ratios of Pb(II)-saturated samples in 0.4 mol/L aqueous HCl and those of Cu(II)-saturated samples in 0.2 mol/L aqueous HCl at different time were calculated with the formulas (7).

### **Regeneration of adsorbent**

The adsorption capacities with adsorption time of 48 h to Pb(II) (pH 6) and to Cu(II) (pH 4) were evaluated. The desorption rates of Pb(II)-saturated samples in 0.4 mol/L aqueous HCl for 100 min and the desorption rates of Cu(II)-saturated samples in 0.2 mol/L aqueous HCl for 60 min were calculated. 10 cycles of adsorption-desorption were investigated to evaluate the regeneration of the adsorbent.

All the FAAS data were the averages of three measured values with the deviations less than 5%.

**Table S1.** The formulation of the adsorbent

Preparation process	Materials	Amount (g)
Step 1: Preparation of multi-functional Fe <sub>3</sub> O <sub>4</sub> nanoparticles and attapulgite nanorods	Fe <sub>3</sub> O <sub>4</sub> nanoparticles (Solid content: 25%)	4.0
	Attapulgite nanorods (Solid content: 25%)	4.0
	Liquid paraffin	24.0
	Span-80	0.20
	Tween-60	0.20
Step 2: Pre-emulsification	KH-570	0.67
	AA	5
	AM	5
	Span-80	0.25
	Tween-60	0.25
Step 3: Preparation of the adsorbent	Liquid paraffin	30.0
	Multi-functional Fe <sub>3</sub> O <sub>4</sub> nanoparticles and attapulgite nanorods	All obtained
	Pre-emulsion	All obtained
	Ammonium peroxydisulfate	0.1

## References

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