Magnet-Responsive Silica Microrods as Solid Stabilizer and Adsorbent for Simultaneous Removal of Coexisting Contaminants in Water

Dafan Chen,[†,‡] Yiming Li,[*,†] Mutai Bao,[†] Yajie Hou,[†] Jiafeng Jin,[†] Zichao Yin[†] and Zhining Wang[*,‡]

[†] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, No. 238 Songling Road, Qingdao 266100, P. R. China

[‡] Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, No. 27 Shandanan Road, Jinan 250100, P. R. China

Number of Pages: 14

Number of Figures: 7

Number of Tables: 3

[*] Corresponding author.
E-mail address: liym@ouc.edu.cn (Y. M. Li); wangzhn@sdu.edu.cn (Z.N. Wang).

1. Preparation of materials

1.1. Preparation of SiO_2 particles

Silica microrods were prepared by the method reported by Kuijk et al and He et al.[1-3] 15 g of polyvinylpyrrolidone was added to 150 mL of n-pentanol in a 500 mL conical flask, and sonicated to dissolve. Then 15 mL of ethanol, 4.2 mL of deionized water and 1 mL of 0.18 mol L^{-1} sodium citrate solution were added orderly. After, the resulting mixture was stirred to make the solution uniform. 3.4 mL of NH_4OH and 1.5 mL of TEOS were introduced into the system and then the mixture was stirred again. The conical flask was placed in 30 ℃ thermostatic bath for 24 h. Solid particles obtained by centrifugation at 6000 rpm for 8 min, and washed by ethanol and water for 2 times. The silica microrods were dried in a vacuum freeze dryer for 24 h and then stored in dry form.

The spherical SiO_2 used in the interface adsorption energy calculation was synthesized by the conventional Stöber method.[4] Firstly, 181 mL of ethanol, 64 mL of deionized double distilled water and 5 mL of NH_4OH were mixed. To the aqueous solutions, 70 mmol of TEOS was added. The mixture was shaken at a rotation rate of 100 rpm using a shaker for 2 h at 30 ℃, and white products were formed. They were collected by centrifugation (7000 rpm, 10 min) and washed by repeating redispersion in ethanol for five times. The final precipitates were dried at room temperature.

1.2. Preparation of Fe_3O_4@SiO_2 particles

0.1500 g SiO_2 microrods was dispersed in 50 ml deionized water to obtain the aqueous dispersion. 1.0 mmol L^{-1} HCl was added to the aqueous dispersion to achieve pH = 6.5. 1.05 g of $FeSO_4 \cdot 7H_2O$ was added under a N_2 atmosphere and then stirred overnight. Next, 0.104 g of $NaNO_2$ were added under stirring. Then, 12.5 mL NH_4OH solution were quickly introduced into the system under vigorous stirring. The color of

the mixture became black after 2 h. The whole process was carried out in a N_2 atmosphere. The resulting dispersion was washed with deionized water under a N_2 atmosphere using the magnetic properties. The resulting Fe_3O_4@SiO_2 were also dried in a vacuum freeze dryer for 24 h and then were stored in dry form.[5] The ratio of Fe_3O_4 to SiO_2 in the composite is critical to contaminants removal. In this study, the coating density of R-SiO_2 by Fe_3O_4 was regulated by changing the amount of $FeSO_4 \cdot 7H_2O$ in suspension. According to the mass of $FeSO_4 \cdot 7H_2O$ used, theoretical mass of Fe_3O_4 on R-SiO_2 is calculated. The suitable mass ratio (m_{SiO_2}:$m_{Fe_3O_4}$=1:1.5) was used in this study according to the results of oil removal experiments under different ratios.

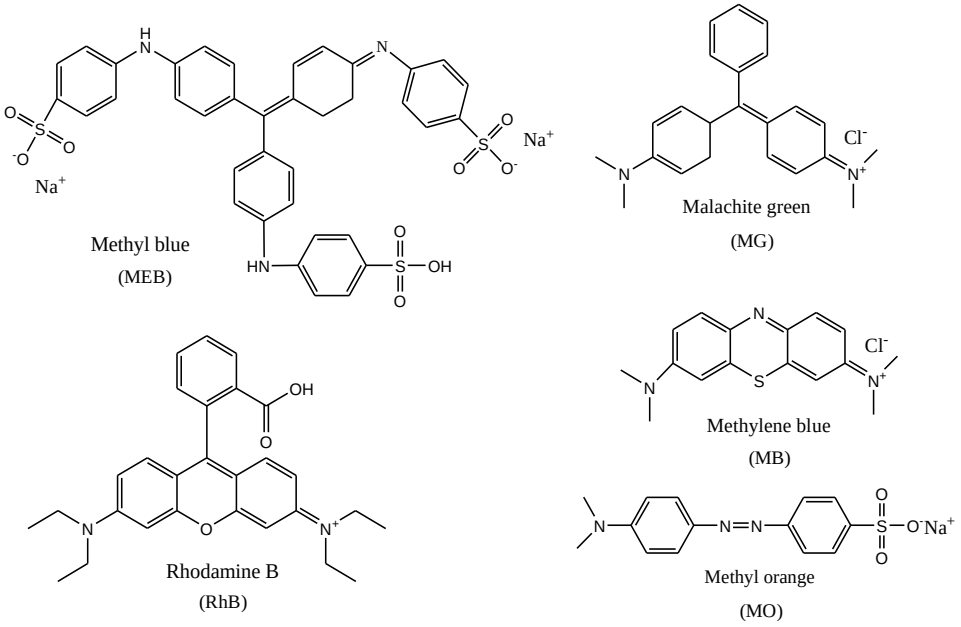

Figure S1. Molecular structure of different dyes.

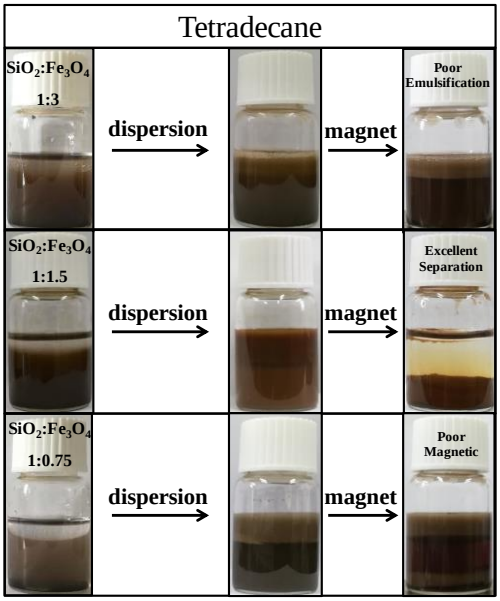

Figure S2. Photographs of tetradecane removal by R-Fe_3O_4@SiO_2 particles synthesized under different mass ratios of SiO_2 and Fe_3O_4. The oil-to-water volume ratio was 1:4 and the concentration of R-Fe_3O_4@SiO_2 was 4 g L^{-1}.

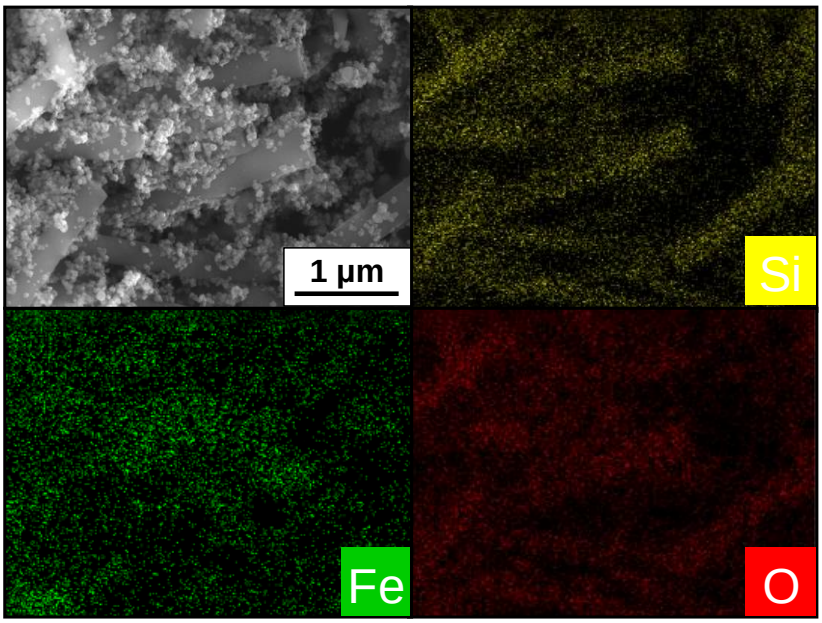

Figure S3. SEM image and corresponding elemental mapping of R-Fe_3O_4@SiO_2.

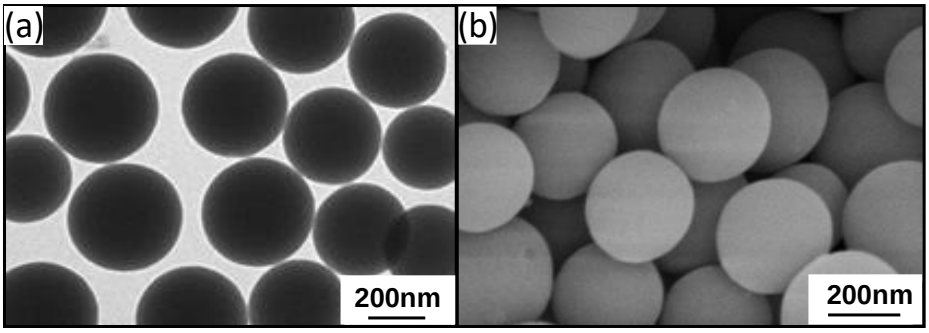

Figure S4. TEM and SEM images of spherical silica nanoparticles (a and b).

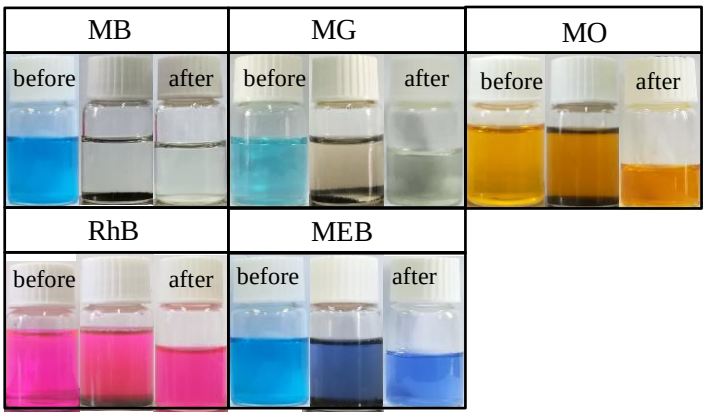

Figure S5. The photographs of removing different dyes from polluted water (C_0 =10 mg L^{-1}).

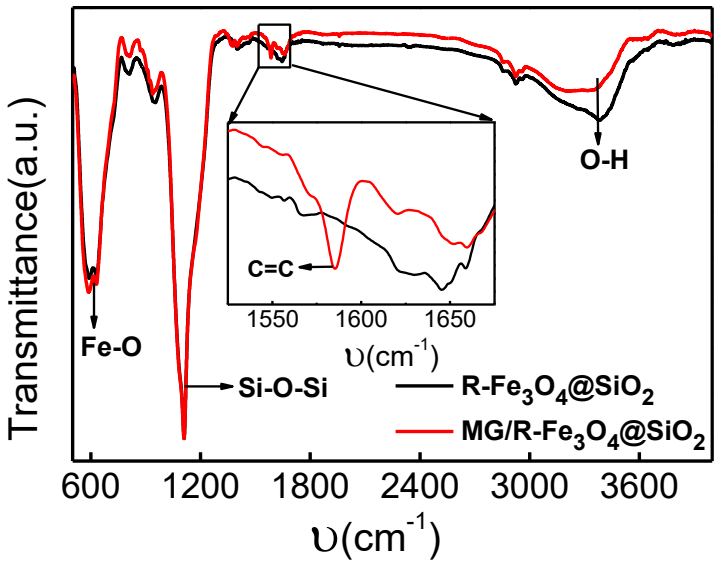

Figure S6. The FT-IR spectra before and after MG adsorption on R-Fe_3O_4@SiO_2.

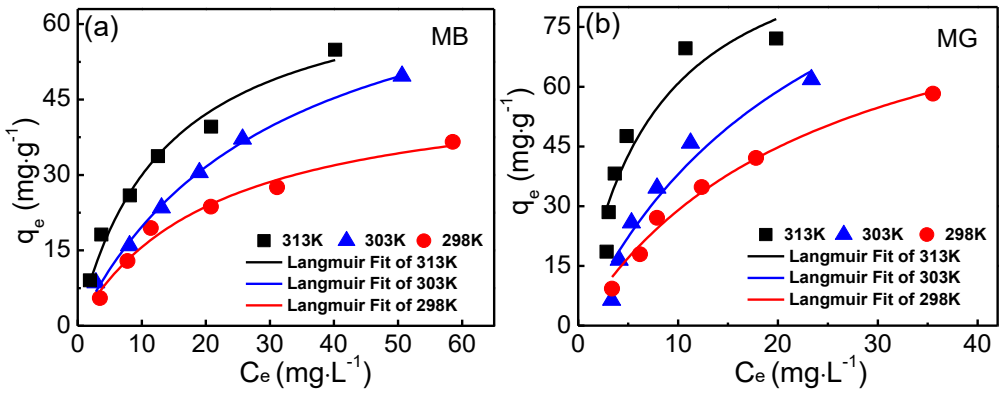

Figure S7. Langmuir adsorption isotherms of MB and MG at different temperatures.

Table S1. The related parameters of the calculation of interface adsorption energy.

Sample	$\bar{R}$ (nm)	l (μm)	θ (°)	γ_{ow} (mN m^{-1})	ΔE (kT)
S-Fe_3O_4@SiO_2	151	-	38.1	33.6	2.86×10^4
R-Fe_3O_4@SiO_2	153	3	24.4	37.9	2.10×10^5

Table S2. Langmuir and Freundlich parameters for adsorption of heavy metal ions.

Samples	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f ((mg g^{-1}) (L mg^{-1})$^{1/n}$)	$1/n$	R^2
Cr^{3+}	384.62	0.0046	0.996	6.846	1.72	0.983
Pb^{2+}	346.02	0.0058	0.998	7.955	1.71	0.982
Zn^{2+}	308.64	0.0042	0.997	4.134	1.51	0.987
Cu^{2+}	322.58	0.0049	0.997	6.227	1.58	0.991
Co^{2+}	316.46	0.0048	0.987	4.847	1.53	0.962

Table S3. Kinetic parameters for adsorption of heavy metal ions.

Samples	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^1 min^{-1})	R^2
Cr^{3+}	178.45	179.53	0.014	0.8307	172.52	2.61	0.9999
Pb^{2+}	182.26	183.49	0.014	0.9845	156.95	2.82	0.9995
Zn^{2+}	122.40	122.69	0.053	0.9383	176.14	2.24	0.9999
Cu^{2+}	162.16	162.87	0.040	0.9616	172.52	2.71	0.9991
Co^{2+}	161.50	161.81	0.025	0.9493	159.92	2.53	0.9996

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