

One-step synthesis of amino-functionalised magnetic mesoporous silica and synergistic adsorption kinetics of tetracycline and copper

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An amino-functionalised magnetic mesoporous silica was prepared through one-step copolymerisation method. Morphology, characteristic-group composition, microscopic morphology and specific surface area of the magnetic mesoporous silicas were analysed by scanning electron microscope, Fourier transform infrared spectroscopy, transmission electron microscope and nitrogen adsorption–desorption. The prepared magnetic silica MS-1 had the characteristics of micron-sized particle size, exceptional long-range ordered pore structure, and as high as 114.6 m²/g in specific surface area. The adsorption kinetics of tetracycline (TC) and Cu(II) onto magnetic mesoporous silicas in sole and binary system were also investigated. MS-1 could adsorb both of TC and Cu(II) with adsorption capacities of 35.14 and 23.65 mg/g, respectively, which were enhanced in binary systems about 26.5 and 19.7%, respectively. The solution pH significantly affected the adsorption because of the pH-responsive speciation of TC, TC–Cu(II) complex and the amine groups on adsorbent. This work proposed a potential effective method for the synergistic adsorption of antibiotics and heavy metals from aquatic environment.

1. Introduction: Antibiotics and copper, widely used in livestock breeding, were discharged into the environment with breeding wastewater resulting in their coexistence in the environment. Compared with the sole system, the multiple pollution induces greater adverse impact on the Shannon's diversity and evenness of microbial community [1, 2]. Therefore, the synergistic removal of antibiotics and copper has triggered numerous investigations.

Numerous methods have been applied for antibiotic and copper removal from aquatic environment [3–8]. Among them, adsorption has been widely utilised due to the advantages of easy operation, reusability and high adsorption capacity [9]. To eliminate the multiple pollutant of tetracycline (TC) and copper, various adsorbents, such as biochar, resin, goethite, and carbon nanotubes, have been developed [10–13].

Mesoporous silica material has gained a growing attention because of its excellent characteristics of long-distance ordered pore channel, tunable surface chemistry, and large surface area. In an effort to improve the adsorption performance, mesoporous silica is usually modified with functional groups or other characteristic materials. Metal grafting mesoporous silica has proved to be an effective adsorbent for tetracycline removal [14, 15]. Functionalised mesoporous silica shows great adsorption capacity in the heavy metal ions removal from aqueous solution due to its fascinating chelating ability [16]. However, the functionalised mesoporous silicas were obtained through multi-procedure resulting in tedious work. The obtained silicas often had the diameter of nanoscale [17, 18], which were difficult to separate from the aquatic solution.

Thus, this Letter proposed a one-step synthesis method to prepare an amino-functionalised magnetic mesoporous silica for the synergistic removal of antibiotics and copper. Whilst the magnetic mesoporous silica characteristics make the separation more convenient in aqueous solution by using an external magnetic field. TC was employed as the representative antibiotic. The adsorption properties of the adsorbents were evaluated by kinetic study. The influence of solution pH was also studied both in sole and binary system.

2. Experimental: The magnetic nanoparticles were prepared through chemical precipitation using ferrous chloride and ferric chloride in the presence of NaOH. Then the template cetyl trimethyl ammonium bromide (CTAB) was added into the mixture and the mixture was shaken in polytetrafluoroethylene bottle at 80°C for 30 min. The *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KH-792) and tetraethoxysilane (TEOS), used as the amination reagent and template agent, respectively, were added sequentially. Then, the reaction system kept at 80°C for 2 h. The obtained powdered adsorbent was washed by water and ethyl alcohol for three times, respectively. After dried at 60°C for 8 h, the functional mesoporous silica, named MS-1, was obtained. The adding dose molar ratio of NaOH, CTAB, H₂O, TEOS and silane coupling agent were 2.55, 1, 4857, 8.16 and 2. Then, MS-1 was calcinated at 550°C for 8 h to remove the template in pore channel and obtained the MS-cal. As a control adsorbent, MS-2 was prepared using the same recipe and procedure as MS-1 without KH-792.

The N₂ adsorption–desorption isotherms were conducted at 77 K on an Autosorb-iQ2 (Quantachrome, USA). The specific surface areas were calculated by the standard Brunauer–Emmett–Teller equation using adsorption data. The pore size distribution was obtained by the Barrett–Joyner–Halenda method using desorption isotherms data. The morphology of adsorbent was characterised by transmission electron microscope (JEM-200CX, JEOL, Japan). The functional groups were detected on a pressed pellet with KBr using a Nicolet NEXUS870 FTIR spectrometer (USA).

In an effort to obtain the adsorption kinetic data and evaluate the adsorptive rate, 0.1 g of mesoporous silica and 300 mL of simulated solution (1 mmol/L of copper chloride or 0.25 mmol/L of TC) was shaken at 293 K and sampled at diverse time intervals. Besides, the influence of solution pH was investigated for the adsorption of combined pollutants with 1 mmol/L of copper chloride and 0.25 mmol/L of TC. The batch adsorption experiments were conducted in both sole and binary systems.

The concentration of copper solution was acidised using 1 mol/L HNO₃ solution and determined by atomic absorption spectrometer (240FSAA, Agilent, USA). The concentration of TC was detected

by HPLC (Agilent 1200) with an ultraviolet detector. The mobile phase composed of 0.02 M ammonium oxalate–acetonitrile mixture (80:20, v:v), and the flow rate was 0.5 mL/min.

3. Results and discussion: The scanning electron micrograph (SEM) of functionalised mesoporous silicas MS-1 is shown in Fig. 1A. The particle size of functionalised mesoporous silicas ranged from 0.5 to 1.5 μm . The exceptional long-range ordered pore structure of MS-1 was observed from the transmission electron microscope (TEM) images in Fig. 1B.

As shown in Table 1, the specific surface areas ranged from 114.6 to 490.6 m^2/g , and the average pore sizes were 2.9–4.1 nm. The pore structures of all three adsorbents were proved mesoporous by the high mesopore distribution ($> 72\%$). The specific saturation magnetisation of these silicas was 2.54–3.96 emu/g.

The FTIR spectra were shown in Fig. 2. The wide absorption peak at 3428 cm^{-1} was corresponded to the stretching vibration

of Si–OH and adsorbed water molecules. The peaks at 1077 and 964 cm^{-1} were ascribed to the vibration of Si–O–Si bond and Si–O in silanol groups, respectively. For MS-1 and MS-2, the peaks at 2924 and 2853 cm^{-1} were the stretching vibration of C–H. Compared to the FTIR spectrum of the other two adsorbents,

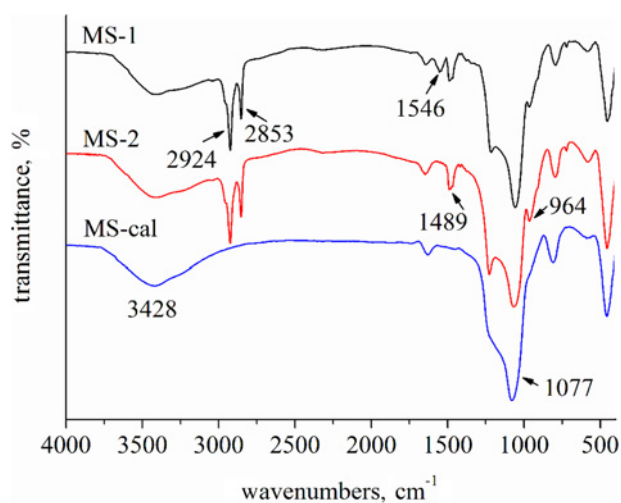


Fig. 2 FTIR spectra of the employed magnetic mesoporous silicas

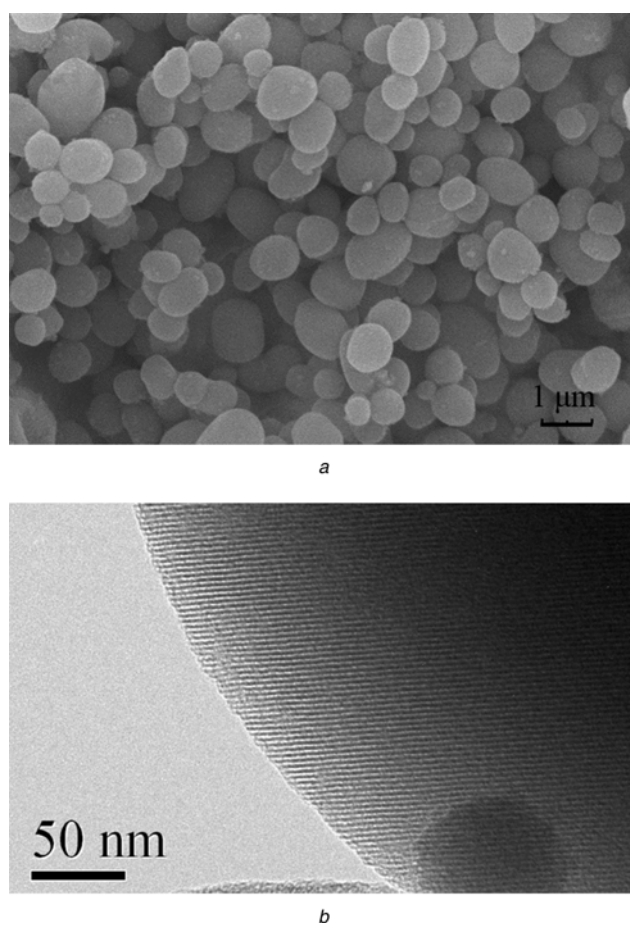


Fig. 1 Pictures of functionalised mesoporous silica MS-1
a SEM
b TEM

Table 1 Physicochemical properties of the functionalised mesoporous silicas

Adsorbents	MS-1	MS-2	MS-cal
specific surface area, m^2/g	114.6	135.3	490.6
average pore size, nm	3.5	2.9	4.1
pore volume, cm^3/g	0.22	0.20	0.48
mesoporous volume, cm^3/g	0.16	0.14	0.43
specific saturation magnetisation, emu/g	3.81	2.54	3.96

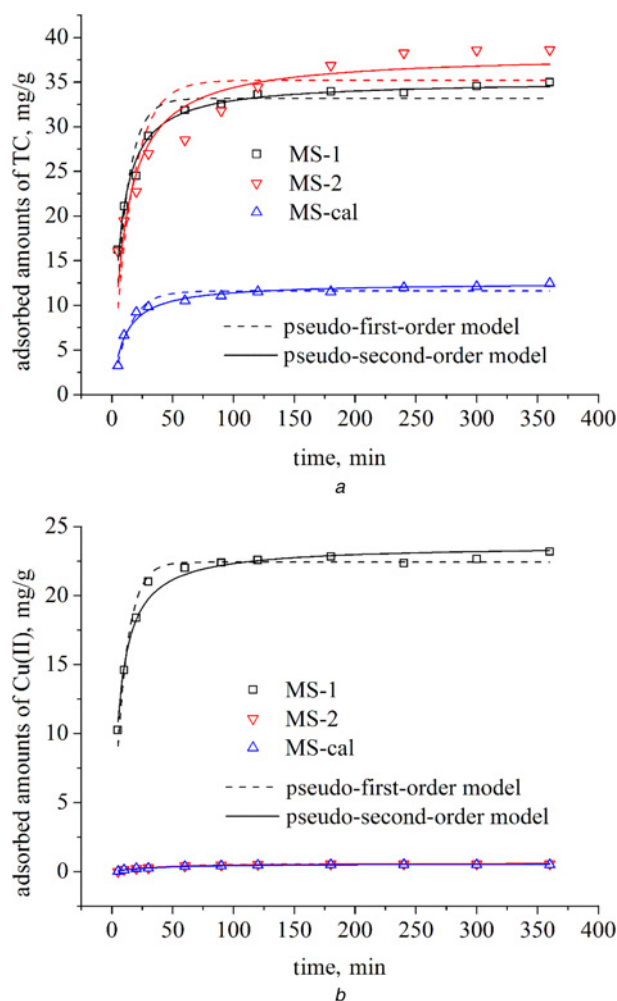


Fig. 3 Adsorption kinetics
a TC
b Cu(II) onto three adsorbents

Table 2 Model fitting parameters for the adsorption kinetics of TC and Cu(II) onto three adsorbents

		Pseudo-first-order model			Pseudo-second-order model		
		Q_e	k_1	R^2	Q_e	$k_2(10^{-3})$	R^2
TC	MS-1	33.18	0.094	0.8860	35.14	4.27	0.9851
	MS-2	35.21	0.065	0.7501	38.13	2.42	0.9122
	MS-cal	11.61	0.074	0.9563	12.51	8.31	0.9687
Cu	MS-1	22.45	0.104	0.9747	23.65	7.16	0.9802
	MS-2	0.55	0.024	0.9876	0.63	44.7	0.9764
	MS-cal	0.50	0.024	0.9842	0.58	48.3	0.9773

the absorption peak at 1546 cm^{-1} for MS-1 was attributed to the flexural vibration of N–H, which demonstrated the successful polymerisation of amino silane coupling agent. The characteristic peaks at 2924, 2853 and 1489 cm^{-1} were regarded as originating from surfactant template [19], which were removed from MS-cal by calcination method.

The adsorption kinetics of the employed adsorbents were studied to illustrate the adsorption mechanism of Cu(II) and TC. As shown in Fig. 3, the adsorbed amounts of Cu(II) and TC increased quickly with time until reaching equilibrium. It was observable that the adsorption capacities of Cu(II) onto MS-2 and MS-cal were much less than that onto MS-1, indicating the important role of functional amino for Cu(II) adsorption.

In order to further study the adsorption kinetics, pseudo-first-order model and pseudo-second-order model were used to fit the adsorption kinetics data. The equations are expressed as follows:

Pseudo-first-order equation:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (1)$$

Pseudo-second-order equation:

$$Q_t = k_2 t Q_e^2 / (1 + k_2 Q_e) \quad (2)$$

where Q_t and Q_e (mg/g) are the amounts of Cu(II) or TC adsorbed onto the mesoporous silica at time t (min) and at equilibrium time, respectively. k_1 (min^{-1}) and k_2 (g/mg/min) represent the rate constants for the two models, respectively. The fitting parameters are listed in Table 2. It was found that TC adsorption onto three adsorbents and Cu(II) adsorption onto MS-1 fitted the pseudo-second-order model better with higher correlation coefficients.

For TC adsorption, the k_2 values were in the order of MS-cal > MS-1 > MS-2, suggesting the fast adsorption rate of MA-cal and MS-1. The fast adsorption rate was due to the wide pore channel with the average pore size of 3.5 nm. As the organic templates in pore channel were removed by calcining, MS-cal obtained the widest pore channel with the average pore size of 4.1 nm. This was responsible for the fastest kinetic of MS-cal. The Q_e values of MS-1 and MS-2 were about 2.8 and 3.0 times larger than that of MS-cal, which was attributed to the more hydrophilic for MS-cal. The templates in pore channel enhanced the surface hydrophobicity of MS-1 and MS-2, resulting in the higher adsorption capacities of TC through hydrophobic interaction. The larger specific surface area of MS-2 should be responsible for the larger Q_e values.

The Q_e values of Cu(II) adsorption followed the order of MS-1 > MS-2 > MS-cal. MS-1 had the highest adsorption capacity for Cu(II) adsorption with 23.65 mg/g, which was equivalent with the adsorption of Cu(II) on mesoporous poly(melamine-formaldehyde) solid adsorbent [20]. The adsorbed amounts of Cu(II) onto MS-2 and MS-cal at equilibrium time were 0.63 and 0.58 mg/g, respectively, demonstrating that Cu(II) was hardly

adsorbed on these two adsorbents. These demonstrated that grafting amine group was beneficial to Cu(II) adsorption.

Compared with the other mesoporous silicas listed in Table 3, MS-1 exhibited considerable adsorption capacities for both TC and Cu(II). Comprehensive consideration of TC and Cu(II) adsorption behaviours, MS-1 was the proper adsorbent for the simultaneous adsorption of TC and Cu(II).

The adsorption kinetics of TC and Cu(II) in binary solution are depicted in Fig. 4. Pseudo-first-order model and pseudo-second-order model were also used to fit the adsorption data, and the fitting parameters are listed in Table 4. The adsorption behaviours of TC and Cu(II) onto MS-1 in binary solution also accorded with the pseudo-second-order model with higher correlation coefficients. The k_2 values of both TC and Cu(II) adsorption in binary system were smaller than those in sole system, suggesting the lower adsorption rate in binary solution. Since TC exists primarily as zwitterion in nearly neutral solution, the TC molecules probably interact with Cu(II) through the nitrogen atoms or oxygen atoms to

Table 3 Comparison of adsorption capacities of TC and Cu(II) onto mesoporous silica adsorbents

	Adsorption capacity, mg/g	Ref.
TC	35.14	this study
TC	23.93	[21]
TC	43.03	[22]
TC	25	[23]
Cu(II)	23.65	this study
Cu(II)	30.41	[21]
Cu(II)	27.7	[24]
Cu(II)	20.45	[25]

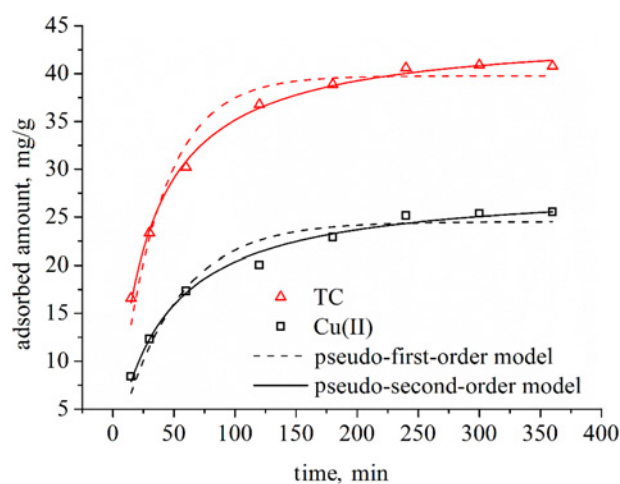
**Fig. 4** Adsorption kinetics of TC and Cu(II) in binary solution

Table 4 Model fitting parameters for the adsorption kinetics of TC and Cu(II) onto MS-1 in binary solution

	Pseudo-first-order model			Pseudo-second-order model		
	Q_e	k_1	R^2	Q_e	k_2 (10^{-3})	R^2
TC	39.76	0.028	0.9613	44.44	0.85	0.9969
Cu(II)	24.50	0.021	0.9450	28.30	0.90	0.9883

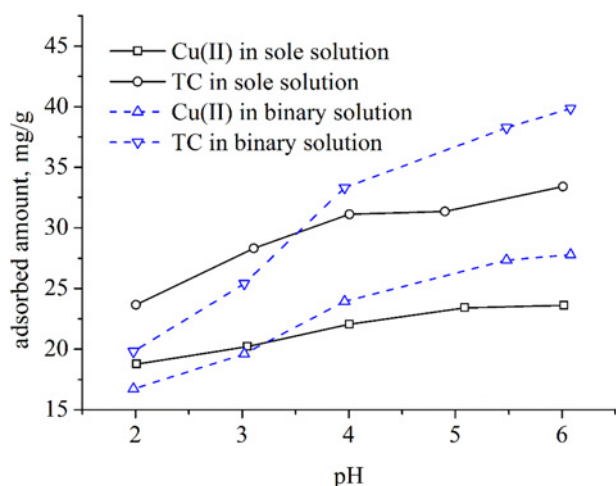


Fig. 5 Effect of solution pH on the adsorption of TC and Cu(II) in sole and binary systems

form complexes [1], which increases the molecule size and diffusion resistance. However, the adsorbed amounts of TC and Cu(II) at equilibrium time increased about 26.5 and 19.7%, respectively. The adsorbed TC could act as a bridge to bind Cu(II), which enhanced the adsorption of Cu(II). Similarly, TC adsorption was enhanced by the adsorbed Cu(II).

The species of TC and the surface properties of adsorbent were effected by solution pH. Thus, considering the precipitation limits of Cu(II), the effect of solution pH ranging from 2 to 6 was assessed. The influence of solution pH on the TC and Cu(II) adsorption in sole and binary system were depicted in Fig. 5. Both TC and Cu(II) adsorption in sole and binary system increased with the rise of solution pH. The amine groups on MS-1 and TC molecule were protonated at low pH and TC^+ was dominant in solution at $pH < 3.3$ (pK_a). Weakened hydrophobic interaction and enhanced electrostatic repulsion should be responsible for the poor adsorption of TC at pH ranging from 2 to 3. The percentage of neutral TC molecule increased with solution pH increase and exceeded 98% at pH 5–6. The continuous increase of adsorbed amounts at pH 4–5 indicated that hydrophobic interaction between neutral TC molecules and the hydrophobic templates in the pore channels of MS-1 dominated TC adsorption. Similarly, the protonated amines and hydrogen ions would inhibit the Cu(II) adsorption at low solution pH. In binary system, both the adsorption of TC and Cu(II) were enhanced at $pH > 4$, confirming the occurrence of bridge connection between TC and Cu(II). At pH 2–3, the inhibition of TC and Cu(II) adsorption in binary system was observed because the strong electrostatic repulsion between TC^+ and Cu(II) hindered the formation of TC–Cu(II) bridging.

4. Conclusion: The functionalised magnetic mesoporous silica MS-1, possessing micron-sized particle size, exceptional long-range ordered pore structure, and high specific surface area, was prepared through one-step copolymerisation method. MS-1 possessed good performance for both TC and Cu(II) adsorption.

Both TC and Cu(II) adsorption were enhanced in binary system through the complexation between the nitrogen atoms or oxygen atoms of TC molecules and Cu(II). The adsorption of TC and Cu(II) increased both with solution pH increasing from 2 to 6 confirming the pH-responsive adsorption behaviours.

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6 References

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