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Fabrication of Amino-Functionalized $CoFe_2O_4$-SiO_2 Magnetic Composites and Their Adsorption Performance for Removal of Heavy Metal Ions from Water

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Abstract: The cobalt-ferrite nanoparticles ($CoFe_2O_4$ NPs) were prepared by the modified co-precipitation method and the $CoFe_2O_4$-SiO_2 magnetic composites were synthesized via stöber step. The $CoFe_2O_4$-SiO_2 was also amino-functionalized to adsorb heavy metal ions. The crystalline phase, morphologies, particle size, chemical compositions and chemical structure of the absorbent have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The composites exhibit excellent magnetic properties with high saturated magnetization and can be separated by a magnet within 30 s, and the saturation magnetization (M_s) of $CoFe_2O_4$ NPs can be adjusted by sintering temperature, increased with the increase of the temperature. The effect of pH and reaction time on the adsorption of $CoFe_2O_4$-SiO_2-NH_2 for Cu (II) was examined. And the amino-functionalized $CoFe_2O_4$-SiO_2 ($CoFe_2O_4$-SiO_2-NH_2) shows high adsorption capacity and high removal efficiency for Cu (II), Cd (II), Zn (II) and Mn (II), which makes great potential application on the heavy metal wastewater treatment.

Key words: cobalt-ferrite; SiO_2; magnetism; adsorption; heavy metal

Spinel ferrites with the general formula $MeFe_2O_4$ (Me=Co, Ni, Cu, Mg, etc.) have high magnetic permeability and low magnetic losses, which are widely used in electrical and practical applications of information storage system, ferrofluid technology and medical diagnostics[1-3]. $CoFe_2O_4$ with an inverse spinel structure has attracted the most attention because of its high saturation magnetization, high chemical stability, and wide optimum pH ranges. In addition, the spinel ferrite is usually considered as a magnetic carrier, because their magnetism can solve the difficulty of photocatalyst/adsorbent separation from water by applying an external magnetic field. It may be efficient potentially for adsorbing heavy metal ions due to its high surface area and the active functional groups on the surface allowing chemical interactions, but the adsorption efficiency was not satisfactory[4,5].

To further facilitate the adsorption affinity, surface modifycation, including physical coating and covalent binding, has often been explored to enable specific metal complexation[6-11]. SiO_2 is stable under acidic conditions and inert to redox reactions, as compared with the organic coating materials. Additionally, amorphous silica particles have surfaces with hydroxyl groups, which makes succedent functionalization easy.

In this work, $CoFe_2O_4$-SiO_2 composites have been synthesized, and amino-functionalized by 3-aminopropyltriethoxysilane (APTES) to adsorb heavy metal ions. The crystalline phase, morphologies, particle size, chemical composition and chemical structure of the absorbent have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The magnetization of $CoFe_2O_4$ NPs (sintered at different temperatures), $CoFe_2O_4$-SiO_2 and $CoFe_2O_4$-SiO_2-NH_2 were characterized by vibrating sample magnetometry (VSM). The effect of pH and reaction time on the adsorption of $CoFe_2O_4$-SiO_2-NH_2 for Cu (II) was examined. The adsorption properties of the adsorbent toward Cu (II), Cd (II), Zn (II) and Mn (II) were also investigated for adsorption capacity, removal efficiency and isotherms model.

1 Experiment

$CoFe_2O_4$ (CFO) was synthesized via a co-precipitation method based on the mixture of $Fe(NO_3)_3$ $9H_2O$ and $Co(NO_3)_2$ $6H_2O$ salts with the molar ratio of 2:1. Firstly, a certain amount of $Fe(NO_3)_3$ $9H_2O$ and $Co(NO_3)_3$ $6H_2O$ were dissolved in 150 mL deionized water. 25 mL NaOH (2.0 mol/L) was slowly added to the salt solution, and then PEG (6000) as dispersant was added into the above suspension under vigorous stirring. The pH of the solution was adjusted to 10 with NaOH, and then the suspension was refluxed for 90 min under the

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condition of boiling water bath. After that, the black precipitation was magnetically separated and washed with deionized water until pH=7. Then, the precipitation was dried at 80 ℃ for 12 h, and after grinding $CoFe_2O_4$ precursor was sintered at different temperatures (300~700 ℃) to drive out residual carbon. Finally, $CoFe_2O_4$ magnetic nanoparticles (CFO-300, CFO-400, CFO-500, CFO-600 and CFO-700) were obtained.

$CoFe_2O_4$ NPs were coated with SiO_2 according to the following procedure[12-14]. The NPs (0.8 g) were dispersed in a mixture of ethanol (90 mL) and ultrapure water (22.5 mL) by sonication for 30 min. A certain amount of ammonium hydroxide (25%) was added to adjust the pH. When the pH was about 10.5, TEOS (6 mL) was consecutively added into the solution. The mixture was stirred for 12 h at room temperature. The resulting dark gray solid powers were collected by magnet, washed with ultrapure water to neutral (pH=7), and dried at 80 ℃ for 12 h.

0.5 g $CoFe_2O_4$-SiO_2 was suspended in 50 mL isopropanol, and 3 mL of 3-aminopropyltriethoxysilane (APTES) was added to the above suspension, and stirred at room temperature for 6 h, then followed with refluxed for 6 h at 80 ℃ under mechanical stirring. The black solid was obtained by magnetic separation, and washed with isopropanol and ethanol, and then dried under 80 ℃ for 12 h.

To investigate effect of solution pH on the Cu (II) adsorption, it was monitored by keeping 50 mL of 80 mg L^{-1} $Cu(NO_3)_2$ solution and adsorbent (20 mg) constant, adjusting the pH value ranging from 4 to 6.5 by NaOH (0.1 mol/L) and HCl (0.1 mol/L). Effect of reaction time on adsorption of heavy metal ions (Cu (II), Cd (II), Zn (II) and Mn (II)) by CFO-SiO_2-NH_2 was studied. These samples were stirred for different time (from 0 to 900 min), and then adsorbents were removed by a magnet. The supernatant was tested by atomic absorption spectroscopy (AAS). The removal efficiency (%) and the adsorption capacity (mg g^{-1}) of the adsorbent for heavy metal ions were calculated by the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

$$q_e = \frac{(C_o - C_t)V}{m} \qquad (2)$$

Where, C_o and C_t (mg L^{-1}) are the concentrations of heavy metal initially and at time t, respectively. V is the volume of the adsorbate (L), and m is the mass of adsorbent (g).

2 Result and Discussion

2.1 Microstructure and magnetic properties of $CoFe_2O_4$ NPs

Fig.1 shows the XRD patterns of $CoFe_2O_4$ NPs sintered at different temperatures (300~700 ℃). The diffraction peaks of all samples at 18.13°, 30.27°, 35.74°, 43.47°, 53.89°, 57.17° and 63.73° could be indexed to the (111), (220), (311), (400), (422), (511) and (440) planes of the inverse spinel $CoFe_2O_4$ (JCPDS NO. 01-1121), respectively. Otherwise, the intensity of diffraction peaks increases with increase of the sintering temperature. Fig.2 shows the room-temperature magnetization curves of $CoFe_2O_4$ NPs sintered at different temperatures. By contrast, the saturation magnetization value of $CoFe_2O_4$ NPs increases from 43.411 (A m^2) g^{-1} (300 ℃) to 61.961 (A m^2) g^{-1} (700 ℃), because the crystallinity and particle size of $CoFe_2O_4$ NPs increase with the increase of sintering temperature. The particle size calculated from XRD results, coercivity, magnetization and retentivity are shown in Table 1.

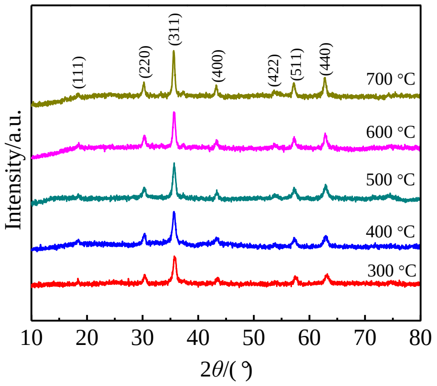

Fig.1 XRD patterns of $CoFe_2O_4$ NPs sintered at different temperatures

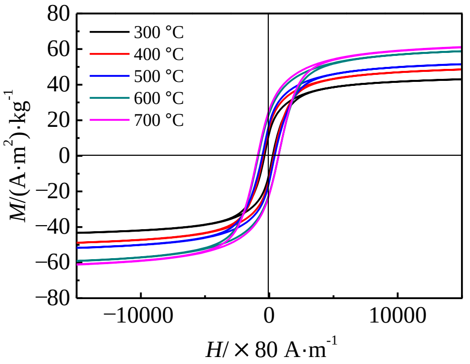

Fig.2 Room-temperature (300 K) magnetic hysteresis loops of $CoFe_2O_4$ NPs sintered at different temperatures

Table 1 Particle size, magnetization, coercivity and retentivity of samples sintered at different temperatures

Sample	Particle size/nm	Magnetization/ (A m^2) kg^{-1}	Coercivity/ ×80 A m^{-1}	Retentivity/ (A m^2) kg^{-1}
CFO-300	34.425	43.411	318.37	11.201
CFO-400	37.452	48.945	409.89	14.290
CFO-500	41.821	51.892	480.79	16.289
CFO-600	57.058	59.238	787.95	22.539
CFO-700	59.965	61.961	812.44	23.835

2.2 Microstructure and magnetic property of $CoFe_2O_4$-SiO_2-NH_2 composites

The phase structures of CFO-400, CFO-400@SiO_2 and CFO-400@SiO_2-NH_2 were analyzed via XRD (Fig.3). For CFO-400, diffraction peaks with 2θ at 18.13°, 30.27°, 35.74°, 43.47°, 53.89°, 57.17° and 63.73° were observed, indicative of inverse spinel structure of $CoFe_2O_4$. The same set of characteristic peaks were also observed for CFO-400-SiO_2 and CFO-400-SiO_2-NH_2, indicating the stability of the crystalline phase of $CoFe_2O_4$ nanoparticles during silica compositing and surface amino-functionalization. For comparison, the broad peak at 20°~28° is found in CFO-400-SiO_2 and CFO-400-SiO_2-NH_2, which corresponds to amorphous silica coated on the surface of CFO NPs.

The Fourier transform infrared (FTIR) spectra of the three samples were performed (Fig.4). The peaks at 881 and 602 cm^{-1} are the typical absorption of Co-O and Fe-O vibration in $CoFe_2O_4$, respectively. After composited with SiO_2, the vibrations of Fe-O and Co-O become weaker in CFO-400-SiO_2 and CFO-400-SiO_2-NH_2. The characteristic peaks at 1093, 798 and 461 cm^{-1} appear in the spectra of CFO-400-SiO_2 and CFO-400-SiO_2-NH_2, corresponding to the typical symmetric and bending vibrations of Si-O-Si[14-17], respectively. It indicates that the framework of silica has been formed. The absorption peaks of 3416 and 1623 cm^{-1} in all the spectra correspond to the stretching vibration and bending vibration of O-H group of water[12]. The spectrum of amino-modified magnetic silica nearly displays the same characteristic bands with CFO-400-SiO_2 except for the decreased absorption intensity of free silanol group at 960 cm^{-1} [18,19]. In addition, the new peaks around 2977 and 2900 cm^{-1} in CFO-400-SiO_2-NH_2 are indicated to the stretching of asymmetric and symmetric vibrations of (-CH_2-) group of APTES[20]. The peak at 1401 cm^{-1} is attributed to the adsorption of –NH_2 groups. These results show that the silica shell is likely to be amino-functionalized successfully.

The morphologies of CFO-400, CFO-400-SiO_2 and CFO-400-SiO_2-NH_2 were determined by SEM, and the results are presented in Fig.5. As shown in Fig.5a, pure $CoFe_2O_4$ particles are generally agglomerated but homogeneous with the diameters mainly ranging from 45 nm to 50 nm. The particle size is vividly increased after coating silica, due to the agglomeration of $CoFe_2O_4$ inside spheres and surface growth of silica on the shell (Fig.5b). CFO-SiO_2 presents spherical structure with an approximately diameter of 300 nm, and the surface of CFO@SiO_2 is relatively smooth. However, amino-functionalized microspheres show roughly spherical surface, shown in Fig.5c; there are no significant change in the spherical shape and particle size, suggesting that amino modification has no effect on the inner core materials.

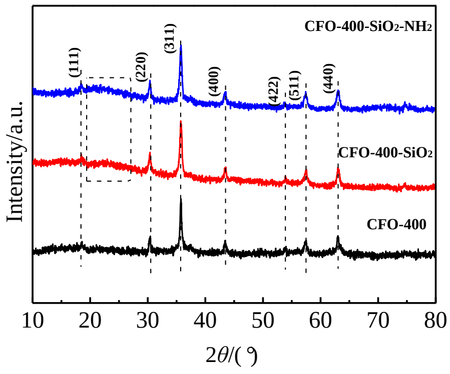

Fig.3 XRD patterns of CFO-400, CFO-400-SiO_2 and CFO-400-SiO_2-NH_2

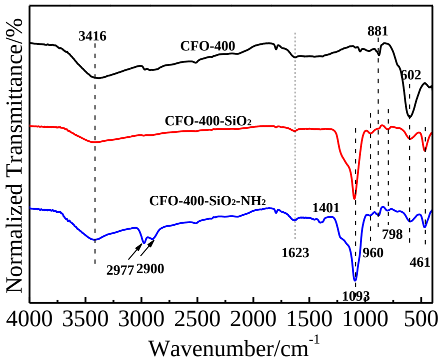

Fig.4 FTIR spectra of CFO-400, CFO-400-SiO_2 and CFO-400-SiO_2-NH_2

The room temperature magnetization hysteresis curves of CFO-400, CFO-400-SiO_2 and CFO-400-SiO_2-NH_2 are shown in Fig.6. In the case of CFO-400 NPs, saturated magnetization (M_s), remnant magnetization (M_r) and coercive force (H_c) were estimated to be M_s=48.945 $(\text{A}\cdot\text{m}^2)\cdot\text{kg}^{-1}$, M_r=14.290 $(\text{A}\cdot\text{m}^2)\cdot\text{kg}^{-1}$ and H_c=32791.2 A/m, respectively. A similar behavior for CFO-400-SiO_2 and CFO-400-SiO_2-NH_2 was observed. Contrasted with pure CFO-400, M_s of the SiO_2 coated with $CoFe_2O_4$ and amino-modified CFO-400-SiO_2 decreases to 21.483 and 20.415 $(\text{A}\cdot\text{m}^2)\cdot\text{kg}^{-1}$, respectively, mainly due to the volume of nonmagnetic to the total sample volume. Although the decreased M_s, CFO-400-SiO_2-NH_2 dispersed in water by vigorous shaking or sonication can be easily separated by a magnet within 30 s (inset of Fig.6), and redispersion occurs quickly with a slight shaking once the magnetic field is removed, which could facilitate the recycle of adsorbent from treated solutions.

2.3 Adsorption property of $CoFe_2O_4$-SiO_2-NH_2 composites

The initial solution pH is an important factor affecting the adsorption of heavy metal ions. The influence of pH on the adsorption of Cu (II) is illustrated in Fig.7. With the increase in the pH from 4 to 6.5, the removal efficiency rises from 3.81% to 95.04%, and adsorption capacity increases from 7.63 to 190.08 mg g^{-1}. This results show that the adsorption capacity of CFO@SiO_2-NH_2 nanospheres toward the heavy metal ions is strong under the near-neutral circumstance while

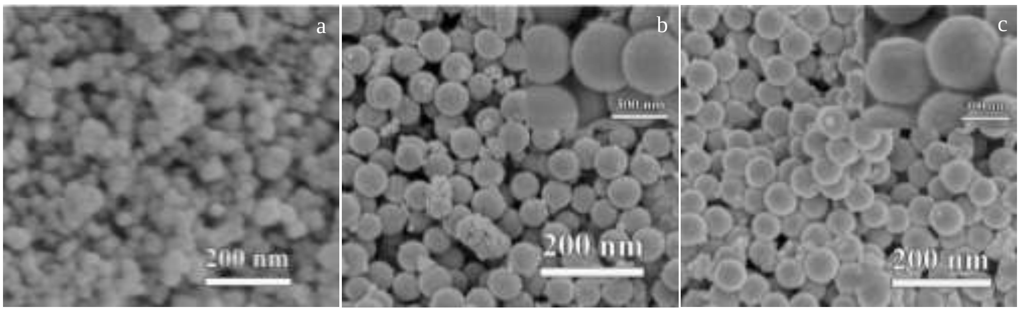

Fig.5 SEM images of CFO-400 (a), CFO-400-SiO_2 (b), and CFO-400 SiO_2-NH_2 (c)

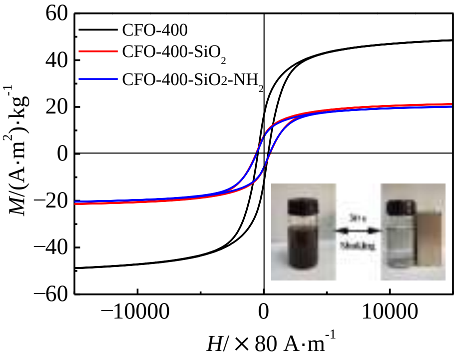

Fig.6 Room temperature (300 K) magnetization curves of CFO-400, CFO-400-SiO_2 and CFO-400-SiO_2-NH_2 (inset is magnetic separation-redispersion of CFO-400-SiO_2-NH_2)

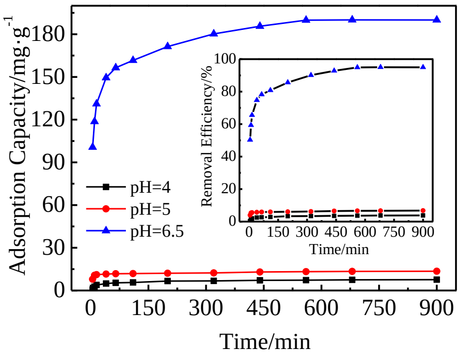

Fig.7 Effect of pH on adsorption capacity and removal efficiency of Cu (II) by CFO-400-SiO_2-NH_2

poor under the strong acidic circumstance. This observation is consistent with the metal-amine complexation adsorption mechanism, as the amino groups are protonized at low pH, passivating adsorption sites and hence suppressing metal adsorption.

The contact time between the adsorbent and adsorbate is one of the most important parameters which plays a vital role in the adsorption process. Fig.8 shows the removal efficiency

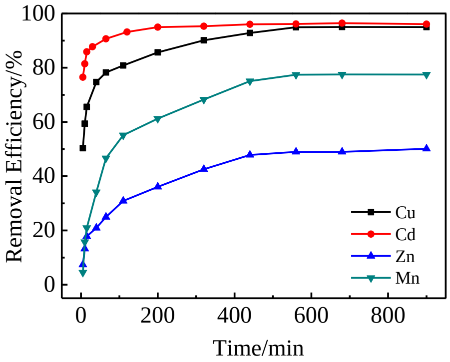

Fig.8 Effect of reaction time on removal efficiency of Cu (II), Cd (II), Zn (II) and Mn (II) by CFO-400-SiO_2-NH_2

of Cu (II), Cd (II), Zn (II) and Mn (II) ions on CFO-400-SiO_2-NH_2 as a function of contact time. The removal efficiency rises sharply within the beginning of 100 min, and subsequently increases slowly within 100~300 min; afterward, the removal efficiency is almost no longer changed even the contact time extends to 900 min. The removal efficiency of Cu (II) and Cd (II) can reach about 95.04% and 96.43%, respectively. While for Mn (II) and Zn (II) the efficiency is about 77.5% and 50%, lower than that of Cu (II) and Cd (II). The fast adsorption rate during the initial stages may mainly be attributed to the abundant active sites on the adsorbent surface and the fast diffusion of metal ions from the solution to the adsorbent surfaces.

As we know, the adsorption kinetics may be described by pseudo-first order and pseudo-second order kinetic models. For comparison, the pseudo-second order kinetic model fits the adsorption of the four heavy metal ions on CFO-400-SiO_2-NH_2 composites, expressed as Eq.(3):

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

where q_e and q_t (mg g^{-1}) are adsorption capacity at equilibrium and time (t), respectively, and k_2 is pseudo-second-order rate constant [g (mg min)$^{-1}$]. The linear fitting based on

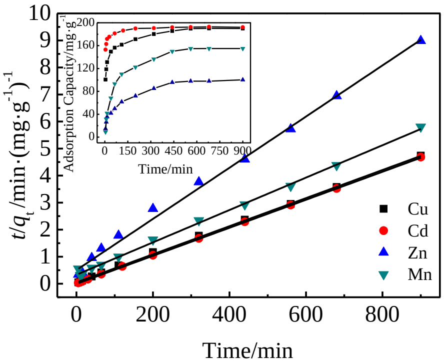

Fig.9 Effect of reaction time on adsorption capacity of Cu (II), Cd (II), Zn (II) and Mn (II) by CFO-400-SiO_2-NH_2 and corresponding pseudo-second order kinetics plots

Table 2 Pseudo-second-order kinetic model parameters for the adsorption of Cu (II), Cd (II), Mn (II) and Zn (II) on CFO-400-SiO_2-NH_2

Metal	Removal efficiency/%	q_e/mg g^{-1}	k_2/g (mg min)$^{-1}$	R^2
Cu	95.04	192.31	0.00040	0.99946
Cd	96.43	193.05	0.0019	0.99998
Mn	77.5	166.94	0.00010	0.99764
Zn	50	105.71	0.00017	0.99465

Eq.(3) have been plotted in Fig.9, and the calculated kinetics parameters and the correlation coefficients (R^2) are given in Table 2. The best fit of the second-order expression suggests that the chemisorption mechanism is involved in the adsorption.

3 Conclusions

1) The amino-functionalized $CoFe_2O_4$-SiO_2 magnetic composites are synthesized via modified co-precipitation method and stöber step.

2) The composites exhibit excellent magnetic properties with high saturated magnetization and can be separated by a magnet within 30 s, and the saturation magnetization (M_s) of $CoFe_2O_4$ NPs can be adjusted by changing sintering temperature or the content of SiO_2.

3) The amino-functionalized $CoFe_2O_4$-SiO_2 shows high adsorption capacity and the removal efficiency for Cu (II) (190.07 mg g^{-1}, 95.04%), Cd (II) (192.87 mg g^{-1}, 96.43%), Zn (II) (105.71 mg g^{-1}, 50%) and Mn (II) (166.94 mg g^{-1}, 77.5%), which makes great potential application on the heavy metal wastewater treatment.

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氨基功能化 $CoFe_2O_4$-SiO_2 磁性复合材料的制备及其在去除水中重金属离子的吸附性能

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摘 要：钴-铁氧体纳米粒子（$CoFe_2O_4$ NPs）通过改良的共沉淀法制备，$CoFe_2O_4$-SiO_2 磁性复合材料通过 stöber 法合成，为了吸附重金属离子 $CoFe_2O_4$-SiO_2 进行了氨基功能化。这种吸附剂的晶体结构、形貌、颗粒尺寸、化学组成和分子结构采用 X 射线衍射图谱（XRD）、扫描电子显微镜（SEM）以及傅里叶变换红外光谱（FTIR）进行表征。此复合材料具有优良的磁性能，由于其高的饱和磁化强度，磁铁可以将其在 30 s 内快速分离。同时，$CoFe_2O_4$ NPs 的磁性能可以通过烧结温度进行调节，随烧结温度提高，磁性能增强。溶液的 pH 及反应时间对重金属离子吸附的影响进行了研究，此外此吸附剂对 Cu (II)、Cd (II)、Mn (II) 和 Zn (II)具有较高的吸附容量和去除率，这一结果使此复合材料可以潜在应用于废水中重金属离子的吸附上。

关键词：钴-铁氧体；SiO_2；磁性；吸附；重金属

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