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Colorimetric detection of copper and efficient removal of heavy metal ions from water by diamine-functionalized SBA-15

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SBA-15 functionalized with N-[3-(Trimethoxysilyl)propyl]ethylene-diamine (TPED) was synthesized and used for colorimetric detection of Cu²⁺ and removal of heavy metal ions in aqueous solutions. Compared to the free SBA-15, the adsorption ability of diamine-functionalized SBA-15 (depicted as SBA-TPED) increased remarkably, the maximum adsorption capacity of the SBA-TPED for Cu²⁺, Pb²⁺ and Zn²⁺ was 27.22, 96.43 and 12.16 mg/g, respectively. Furthermore, the SBA-TPED exhibits high selectivity for Cu²⁺ with the relative selectivity coefficient of the SBA-TPED for Cu²⁺/Pb²⁺ being over 10 and for Cu²⁺/Zn²⁺ being over 60. The naked-eye detection limit of SBA-TPED for Cu²⁺ is 0.95 ppm, and the determination of Cu²⁺ in real water samples also displays satisfactory results. Moreover, SBA-TPED possesses fast kinetics for removing Cu²⁺ with a saturation time of less than 30 min, and can be regenerated by simple acid treatment.

Introduction

With the rapid development of industries and increasing human activities, such as metal plating, mining, fertilizers, tanneries, batteries, paper, and pesticides, many heavy metals are released into the environment.^{1,2} Because they are non-biodegradable and can be accumulated by edible animals and plants, heavy metals can get into humans through food chain. The excessive heavy metals in the body can lead to many serious human afflictions, including neurodegenerative diseases, amyotrophic lateral sclerosis, cancer, Alzheimer's diseases and etc.^{3,4} Customarily, toxic heavy metals of particular concern in the treatment of wastewaters involve copper, mercury, cadmium, lead and/or chromium ions. The selective sensing and removal of heavy metal ions from water medium are of great significance.

In recent decades, many methods such as chemical precipitation, membrane filtration, ion-exchange, oxidation-reduction, and electrochemical treatment technologies have been employed to remove heavy metal ions from wastewaters.⁵⁻⁸ However, the application of the aforementioned methods becomes economically unavailable for the removal of heavy metal ions at lower concentrations.⁹

Due to its ease of operation and the availability of a wide range of adsorbents, adsorption is now recognized as an economic and effective method for water treatment.¹⁰⁻¹² Furthermore, the issue of reversibility is one of the obvious advantages for the adsorption method, in cases, adsorbents can be regenerated by suitable desorption process and used repeatedly. The recent studies revealed that the functionalized mesoporous SBA-15 can be manipulated as highly efficient adsorbent of heavy metal ions in aqueous solutions. Functional groups, such as thiol,^{13,14} carboxyl,¹⁵ porphyrin,¹⁶ imidazole,¹⁷ fluorophore,¹⁸ amino^{10,19,20} were incorporated into the inorganic SBA-15 network. The thiol-functionalized SBA-15 exhibited excellent selectivity for adsorbing Hg²⁺ from wastewaters.^{13,14} Fuertes et al.

reported that the carboxyl-functionalized mesoporous silica-carbon composites showed efficient removing ability of Cu²⁺, Zn²⁺ and Pb²⁺ from aqueous solutions.¹⁵ Park et al. prepared porphyrin-immobilized SBA-15 hybrid material with exceptional ability to remove Cu²⁺ from water samples.¹⁶ Qi et al. developed imidazole-derived SBA-15, which exhibited high adsorption capacity for Cr(VI).¹⁷ Zhu et al. designed and synthesized a new Schiff base fluorophore-functionalized mesostructure hybrid chemosensor, the fluorescence sensor (Schiff-SBA-15) displayed an excellent selectivity for Cu²⁺ in an ethanol-water mixed solution.¹⁸ Recently, various amino-functionalized SBA-15 have been reported to be efficient for the removal of Cu²⁺, Pb²⁺ and different metal ions (Cd²⁺, Co²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Cr³⁺ and Al³⁺), respectively.^{10,19,20}

To our best knowledge, there are few diamine-functionalized SBA-15 reported for removal of heavy metal ions from water medium. In addition, most of the existing functionalized micro-/meso-porous silicas only have extracting function, dual functional adsorbent with not only extraction but also selective detection of metal ion is desirable for practical applications. (for details, please see Table S1 in supporting materials) Bearing this in mind, we previously developed a solid fluorescent chemosensor by combination of SBA-15 with rhodamine derivative for sensing and simultaneous extracting Hg²⁺ from aqueous solution.²¹ As part of our continuous work on dual functional materials based on mesoporous silica, here we report the synthesis of a new diamine-functionalized SBA-15 sorbent and investigate its adsorption ability, reutilization, application in real water samples, and colorimetric detection of Cu²⁺ with the aim of realizing the combination of adsorbent and sensor for Cu²⁺ in natural water. Additionally, to understand the mechanism of adsorption, the evidences for physicochemical characteristics of diamine-functionalized SBA-15 toward removal of heavy metal ions were obtained from transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (IR), N₂ adsorption-desorption isotherms,

thermogravimetric analysis (TGA), zeta potential analysis, and X-ray photoelectron spectroscopy (XPS).

Experimental

Materials and method

N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TPED) was purchased from the Aladdin reagent company (Shanghai, China). Metal-salt, Pluronic P123, hydrochloric acid, potassium dihydrogen phosphate, sodium hydroxide, sodium acetate, tetraethylorthosilicate and acetone were obtained from the Sinopharm Chemical Reagent Co., Ltd (Beijing, China). All chemicals used in this study were of analytical reagent grade and used without further purification. The pH of the solutions was adjusted using the following buffers: sodium acetate/hydrochloric acid for pH 2.5-5.5 and potassium dihydrogen phosphate/sodium hydroxide for pH 6-7, and hydrochloric acid for pH 1-2. Deionised Milli-Q water from a Millipore system (Ohio, USA) was used throughout the work.

TEM images were recorded on a JEOL 2100 high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The SEM photographs were recorded on a Hitach S-4800 field-emission microscope at an accelerating voltage of 4.0 kV. IR spectra were recorded in the wavenumber ranging from 4000 to 400 cm^{-1} with a Nicolet model 6700 Fourier transform infrared spectrometer using KBr pellets. TGA data were obtained on a Perkin-Elmer Pyris Diamond TGA system under a stable nitrogen flow. Metal concentrations were analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima 2100, USA). The BET surface areas of the products were analyzed by nitrogen adsorption-desorption isotherm measurements at 77 K on a nitrogen adsorption apparatus (Micromeritics ASAP 2020). Pore size distributions were calculated from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method using the Halsey equation. Zeta potentials were determined on a Malvern instrument (Zetasizer Nano-ZS) at room temperature, and before measurement the mesoporous silicas were dispersed in deionised water by sonication for fifteen minutes. X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Shimadzu Axis-Ultra multifunctional X-ray photoelectron spectrometer (Al K α X-ray, $h\nu = 1486.6$ eV). All binding energies were referenced to the C 1s peak at 284.8 eV, and the XPS results were fitted by XPSPEAK41 software.

Synthesis of diamine-functionalized SBA-15

Mesoporous silica SBA-15 was prepared using the sol-gel method according to Zhao et al.²² Briefly, the starting composition was tetraethylorthosilicate (8.5 g), Pluronic P123 (4.0 g), H₂O (105 mL) and HCl (37%, 20 mL). After the reaction at 40 °C for 4 h, the obtained white milky solution was transferred into autoclave and aged at 140 °C for three days. The resulting SBA-15 product was collected by filtering, dried at 80 °C, and then calcined in air at 550 °C for 6 h.

For diamine-functionalized SBA-15, 0.3 g of SBA-15 was stirred into 50 mL of an aqueous solution containing 1.5 % (v/v)

TPED at 50 °C for 2 h. After silanization, the TPED-modified SBA-15 (abbreviated as SBA-TPED) was washed with copious amounts of deionized water and acetone to remove residual silanes. Then, it was dried at 100 °C for 2 h to allow the cross linking of silanol groups. The schematic representation of the synthesis route is shown in Fig. S1 (see Supplementary information).

Adsorption and desorption test

In a typical adsorption test, 5 mg of the SBA-TPED was added to 2 mL aqueous solution containing 0.5 mM metal ion. The suspension was mechanically shaken for 30 min at a constant speed, and then centrifugally separated. The unextracted metal ion in solution was analyzed by ICP-OES. All the reported data for adsorption were the average for at least three replicates for each test.

Desorption of metal ions was performed by mixing SBA-TPED loaded with metal ions into 5 mL of HCl solution (0.1 M) and shaking for 10 min, then SBA-TPED was filtered and washed with deionised water to neutral, and the desorbed metal ion in eluent was subsequently measured by ICP-OES.

Recycling test

A 10 mg portion of SBA-TPED sorbent was packed into an empty SPE polypropylene tube (5.5×1.0 cm i.d.) and compressed. Polypropylene frits were located above and below the sorbent bed for avoiding the leakage of absorbent. Then, 2 mL of solution containing 0.5 mM of Cu²⁺ and 2 mL deionised water was allowed to pass through the bed via gravity in sequence. The unextracted Cu²⁺ was measured by ICP-OES. The Cu²⁺-loaded sorbent was washed in sequence with 0.1 M HCl and DDW, and then dried at 70 °C for 6 h before next recycling.

Measurements on natural water samples

Tap water was obtained from our domestic water system. The surface river water and pond water were collected from Yongjiang River and natural pond in our institute (Ningbo, China), respectively. All water samples were simply filtered prior to use.

Results and discussion

Material characterizations

To confirm that amino group was grafted onto the surface of mesoporous SBA-15, the IR spectra of free SBA-15, SBA-TPED and Cu²⁺ loaded SBA-TPED materials (named as SBA-TPED-Cu²⁺) were measured as shown in Fig. 1. In three spectra, the absorption peaks around 3434 and 1629 cm^{-1} are attributed to the ν_{OH} vibration of physically adsorbed water, and peaks around 1083 and 801 cm^{-1} are resulted from Si-O-Si and Si-O stretching vibrations, respectively.^{23,24} When compared with the free SBA-15, there are two new peaks of C-N bond at 1485 cm^{-1} and aliphatic C-H around 2945 cm^{-1} in the IR spectra of SBA-TPED and SBA-TPED-Cu²⁺, showing the TPED was successfully

anchored onto the surface of mesoporous SBA-15. The absorption peak of Si-O-H band at 965 cm^{-1} decreased significantly in both spectra of SBA-TPED and SBA-TPED-Cu²⁺ samples, this phenomenon might be attributed to the chemical reaction between silicon hydroxyl group (Si-OH) and silicon ester (-SiOCH₃). Moreover, the characteristic peak of C-N bond showed strong shift from 1485 to 1460 cm^{-1} after Cu²⁺ adsorption, it might be caused by the strong interaction of -NH₂ and -NH groups with Cu²⁺ ions.

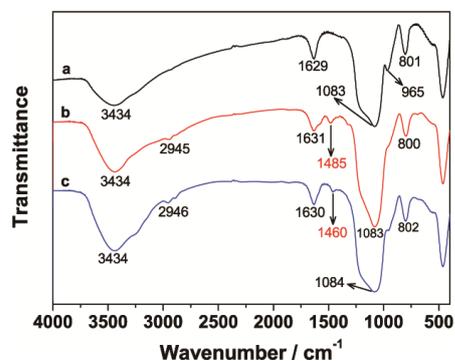


Fig. 1 IR spectra of free SBA-15 (a), SBA-TPED (b) and SBA-TPED-Cu²⁺ (c).

The textural properties of the mesoporous matrices were characterized by TEM and nitrogen adsorption-desorption isotherms, respectively. As seen in Fig. 2, a well-ordered hexagonal array of mesoporous can be seen when the electron beam is parallel to the main axis of the cylindrical pores. When the electron beam is perpendicular to the main axis, the presence of the parallel nanotubular pores of the parent SBA-15 matrix is evidenced. This proved that the hexagonal ordering structure could still be maintained after diamine functionalization. The isotherms and pore size distribution of the free SBA-15 and functionalized SBA-15 (SBA-TPED) are shown in Fig. 3. It can be seen from Fig. 3 that both mesoporous silicas exhibit type IV isotherms with apparent hysteresis loop, indicative of the existence of defined mesopores in the frameworks. The free SBA-15 has a BET surface area of $610.7\text{ m}^2/\text{g}$ and a pore volume of $1.07\text{ cm}^3/\text{g}$. On the other hand, SBA-TPED has a BET surface area of $432.9\text{ m}^2/\text{g}$ and a pore volume of $0.86\text{ cm}^3/\text{g}$. The free SBA-15 and SBA-TPED have BJH pore diameters of 7.4 and 6.0 nm , respectively. The decreased surface area and average pore diameter in SBA-TPED might be caused by the attachment of TPED to the interior wall of mesoporous SBA-15.

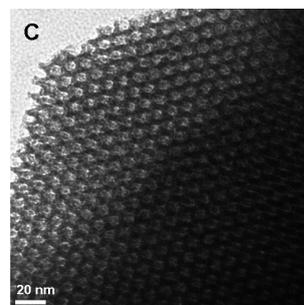
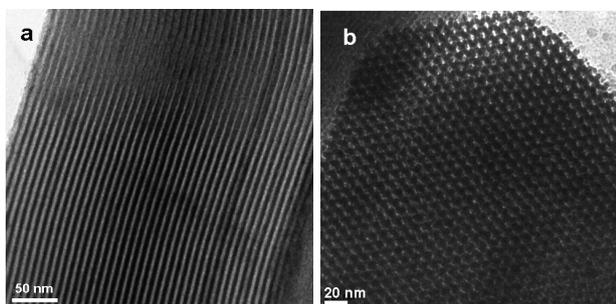


Fig. 2 TEM images of free SBA-15 (the incident electron beam perpendicular (a) and parallel (b) to the pore channels) and SBA-TPED (c).

Furthermore, to ascertain the quantity of organic component immobilized on mesoporous SBA-15, we carried out the thermal analysis of the SBA-TPED and free SBA-15. As seen in Fig. 4, when the samples were heated from 25 to $800\text{ }^\circ\text{C}$, after the initiative weight loss of physisorbed water, the SBA-TPED began to lose organic moiety containing ethylenediamine group of ca. 8.6% , which is comparable to that of mesoporous SBA-15 immobilized 3-aminopropyltriethoxysilane (SBA15-0.4NH₂) reported by Hernández-Morales and coworkers.¹⁹

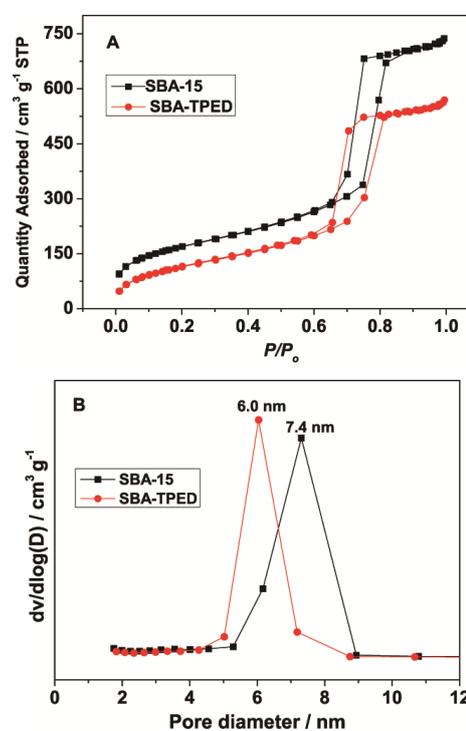


Fig. 3 N₂ adsorption-desorption isotherms (A) and pore size distribution (B) of free SBA-15 and SBA-TPED.

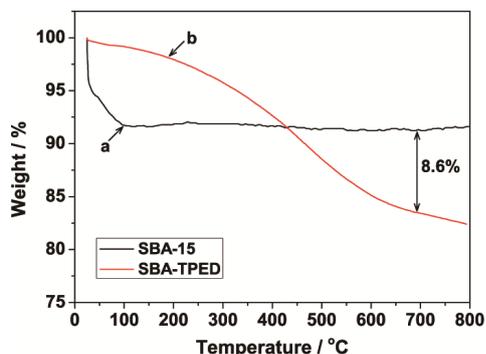


Fig. 4 TGA curves of free SBA-15 (a) and SBA-TPED (b).

Influence of the amount of TPED on adsorption behavior

To investigate the effect of the amount of TPED on the adsorption capacity for Cu^{2+} , 0.2, 0.5, 0.75, 1, 1.5, 2 or 5 mL of TPED was added respectively in the preparation process. The results showed that the uptake capacity of the sorbent increased with the increasing of the amount of TPED (from 0.2 to 0.75 mL), it is possibly as a result of the increase of the functional ligands. However, the uptake capacity for Cu^{2+} decreased when the amount of TPED larger than 0.75 mL, this phenomenon might result from the superfluous TPED blocked up the pores of the SBA-15. Therefore, 0.75 mL of TPED was selected in this study for synthesis of SBA-TPED sorbent.

Effect of pH

The effect of the solution acidity on the adsorption capacity for Cu^{2+} was also investigated as shown in Fig. 5. The adsorption capacity increased obviously as the pH of the solution increased from 1 to 5, and remained constant with further increase in pH. When the pH was below 2, only less than 40% of Cu^{2+} was extracted, it might be attributed to the protonation of the amino moiety in the binding sites, which reduced the binding ability of the amino group involved in chelating formation with the Cu^{2+} ion.²⁵ On the other hand, when the pH of solution was larger than 7, precipitation of the cupric hydroxide was expected. As seen in Fig. 5, the optimum pH for uptake of Cu^{2+} from aqueous solution ranged from 4 to 7. Within this pH range, neither precipitation of the metal hydroxide nor the protonation of the amine occurred.

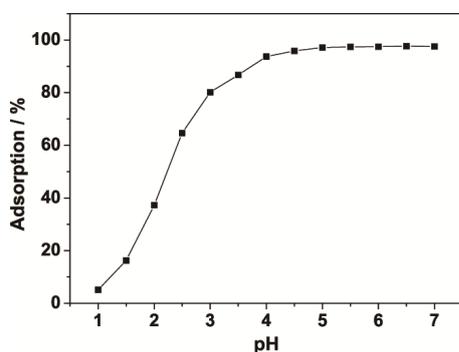


Fig. 5 Effect of pH on the Cu^{2+} adsorption onto SBA-TPED (5 mg of adsorbent was equilibrated with 2 mL of buffer solution containing 0.5 mM of Cu^{2+}).

Effect of contact time and ambient temperature

The effect of contact time on the adsorption capacity of SBA-TPED sorbent was studied for adsorption times with the range 3–120 min under natural pH at room temperature. As shown in Fig. 6, the rate of sorption is fairly fast. More than 95% of the Cu^{2+} was extracted onto the SBA-TPED within 20 min, and reaching saturation in less than 30 min. Thus, the contact time of 30 min was used in this work. The fast kinetics for the removal of Cu^{2+} may be attributed to the diamine functional groups homogeneously distributed on the surface of SBA-TPED sorbent as well as within its inner porous structure, so the Cu^{2+} ions would easily reach the adsorption sites on which they are trapped.

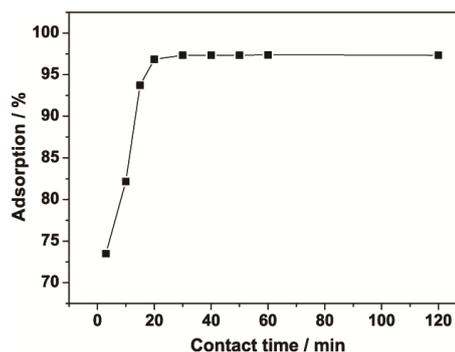


Fig. 6 Effect of contact time on the Cu^{2+} adsorption onto SBA-TPED.

Fig. 7 shows the effect of temperature in the range of 25–60 °C on the adsorption of Cu^{2+} onto the SBA-TPED sorbent under natural pH for 30 min. The equilibrium sorption capacity decreased significantly when the temperature of the solution increased from 25 to 60 °C. This phenomenon revealed that the adsorption process is exothermic nature.

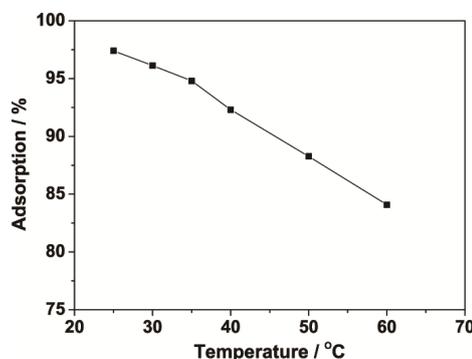


Fig. 7 Influence of temperature on the Cu^{2+} adsorption onto the SBA-TPED (2 mL of 0.5 mM of Cu^{2+} ions solution, 5 mg of adsorbent).

Adsorption ability and selectivity

The abilities of the SBA-TPED for removal of metal ions from aqueous solution were summarized in Table 1. As shown in Table 1, the SBA-TPED had scarce affinity to Mn^{2+} , Cr^{6+} , Ca^{2+} , Ba^{2+} , K^{+} and Mg^{2+} , while it exhibited high affinity to Zn^{2+} , Pb^{2+} and Cu^{2+} , and the corresponding maximum adsorption capacity of the SBA-TPED sorbent was 12.16, 96.43 and 27.22 mg/g, respectively.

This is because Zn^{2+} , Pb^{2+} and Cu^{2+} can more easily form metal-chelating species with diamine groups compared to other metals.²⁴ The high adsorption for Fe^{3+} might be related to the hydrolysis of Fe^{3+} ions, the $\text{Fe}(\text{OH})_3$ product could be adsorbed by the SBA-TPED as well. Besides, the competitive adsorption experiment ($\text{Zn}^{2+}/\text{Cu}^{2+}$, $\text{Cd}^{2+}/\text{Cu}^{2+}$, and $\text{Pb}^{2+}/\text{Cu}^{2+}$) were also conducted, the results indicate that the SBA-TPED showed higher uptake capacity and higher selectivity toward Cu^{2+} ion. The relative selectivity coefficient (k') value in $\text{Pb}^{2+}/\text{Cu}^{2+}$, $\text{Zn}^{2+}/\text{Cu}^{2+}$ or $\text{Cd}^{2+}/\text{Cu}^{2+}$ competitive adsorption was calculated as 11, 68, 389, respectively. The high selectivity for Cu^{2+} might be attributed to the binding ability of the Cu^{2+} with the diamine groups. According to the literatures report, the stability of metal-diamine complex decreases in the following order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

< insert Table 1 >

Besides, the color change of the SBA-TPED in response to different metal ions (Ba^{2+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , Mn^{2+} , Ag^+ , Ni^{2+} and Fe^{3+}) were recorded and shown in Fig. 8. A distinct color change from gray to blue was only observed in the presence of Cu^{2+} , whereas other cations do not induce any appreciable color change except a light appearance of brown in the presence of Fe^{3+} and Ag^+ . Furthermore, to determine the naked-eye detection limit of Cu^{2+} , we have monitored the color change of the SBA-TPED at various concentrations (0.01 to 1.0 mM) of Cu^{2+} in each case (Fig. 9). These experiments showed that the visible color change was observed at the minimum concentration of 0.015 mM (0.95 ppm), which is lower than the US Environmental Protection Agency (EPA) standard of 1.30 ppm.³ Thus, the SBA-TPED can be used as “naked-eye” detector of Cu^{2+} in aqueous solution.

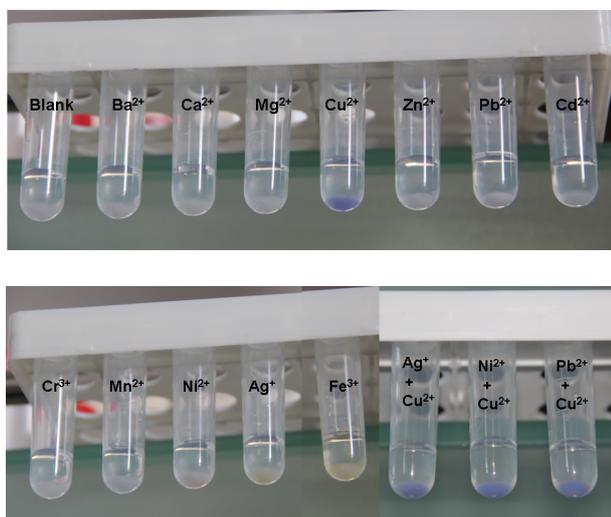


Fig. 8 The photographic images of SBA-TPED with 0.5 mM of various metal ions.

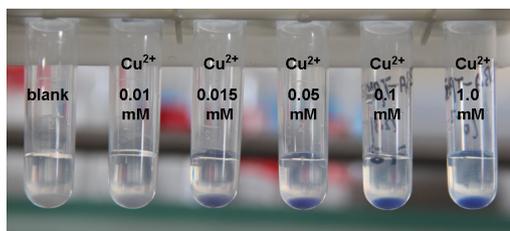


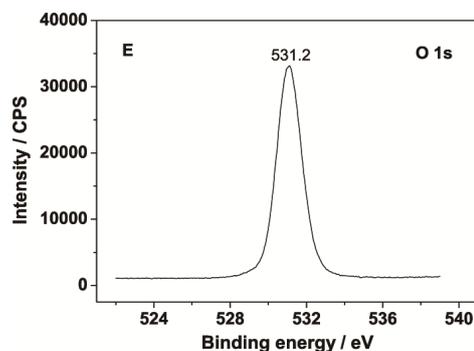
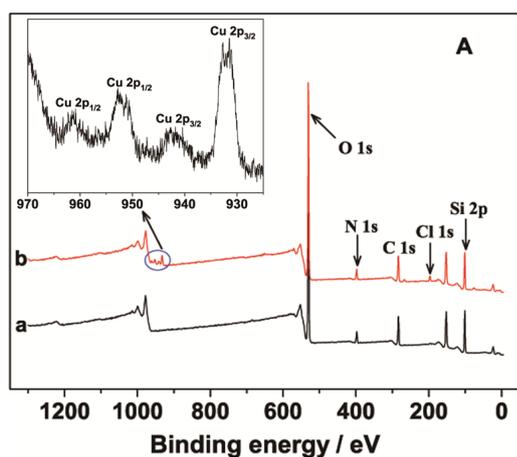
Fig. 9 Color changes of the SBA-TPED with different concentrations of Cu^{2+} .

The maximum adsorption capacity for Cu^{2+}

To evaluate the maximum adsorption capacity, 5 mg of the SBA-TPED (or free SBA-15) was equilibrated with 2 mL of Cu^{2+} solutions with concentrations ranging from 0.01 to 5 mM for 30 min (Fig. S3). The amount of Cu^{2+} adsorbed per unit mass of sorbent increased with the initial concentrations of Cu^{2+} from 0.01 to 1.5 mM. The initial Cu^{2+} concentrations were increased till the plateau values (maximum adsorption capacity values) were obtained. The maximum adsorption capacity of SBA-TPED and free SBA-15 for Cu^{2+} was calculated as 27.22 and 0.37 mg/g, respectively. The results showed that the adsorption capacity of SBA-TPED was comparable to most of the other adsorbents for Cu^{2+} ion as shown in Table S2.

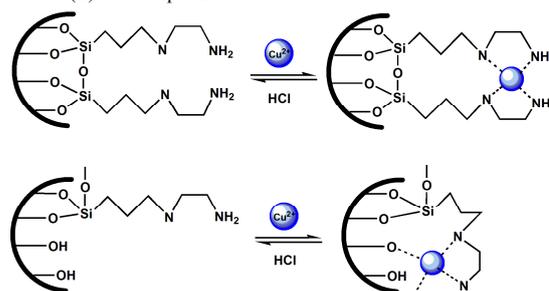
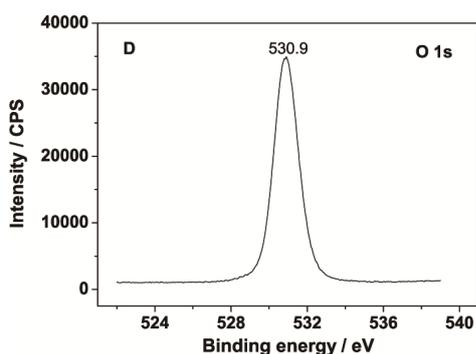
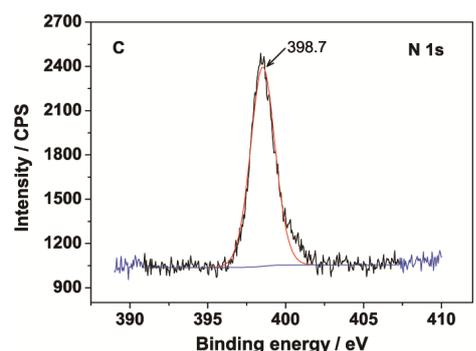
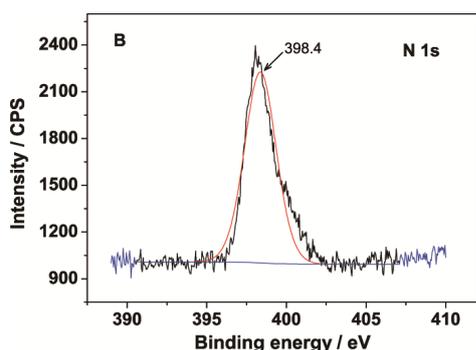
Mechanism of adsorption

In order to reveal the adsorption mechanism, XPS analyses were conducted for SBA-TPED before and after Cu^{2+} adsorption. As seen in Fig. 10, the presence of Cu 2p in Cu^{2+} -loaded SBA-TPED (SBA-TPED- Cu^{2+}) clearly confirmed the adsorption of Cu^{2+} after SBA-TPED was equilibrated in Cu^{2+} solution.³⁴ The binding energy of N 1s and O 1s on the SBA-TPED- Cu^{2+} surface increases slightly as compared with those on SBA-TPED, which illuminates that N and O atoms are electron donors during the Cu^{2+} adsorption and that the Cu^{2+} adsorption on the SBA-TPED sorbent is likely accomplished through the chemical coordination of Cu^{2+} with N and O atoms in the surface functional groups.^{35,36} With the appearance of Cu 2p peaks after Cu^{2+} adsorption, the intensity of O 1s peak decreased significantly, which suggested the strong interaction between Cu^{2+} and O.³⁷ Meanwhile, zeta potentials of mesoporous silica were measured as shown in Fig. S2 (see Supplementary information). The results showed that SBA-TPED (20.7 mV) and SBA-TPED- Cu^{2+} (38.6 mV) possess positively charged surface, indicating that the SBA-TPED sorbent is electrostatic repulsion with Cu^{2+} and that adsorption process is based on the formation of chemical bonding. On the basis of these studies, a possible schematic mechanism for Cu^{2+} absorption by SBA-TPED was proposed as depicted in Scheme 1.



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Fig. 10 XPS spectra of survey scan (A) of SBA-TPED before (a) and after (b) Cu^{2+} sorption. Insert shows the enlarged spectrum of the Cu element. N 1s of SBA-TPED before (B) and after (C) Cu^{2+} sorption, O 1s of SBA-TPED before (D) and after (E) Cu^{2+} sorption.



10

Scheme 1 Plausible binding mechanism of SBA-TPED for Cu^{2+} . X denotes Cl^- or solvent.

Reusability and application in natural water

15

Several stripping agents, HNO_3 , EDTA, and HCl, were investigated to remove the adsorbed Cu^{2+} from the Cu^{2+} -loaded SBA-TPED. The results showed that those three stripping agents are quite effective for removing the adsorbed Cu^{2+} from the sorbent (Table S3). With a single wash, more than 93% of Cu^{2+} ions of the adsorbed Cu^{2+} were recovered. However, in order to prevent introducing new ions to the system, 0.1 M of HCl solution was used as stripping agent in this work. In the test of sorbent recyclability, the same SBA-TPED sorbent was used to uptake Cu^{2+} through twenty extraction/stripping cycles. The results of experiment were listed in Table S4. As shown in Table S4, the SBA-TPED sorbent was found to remove $93 \pm 5\%$ of the Cu^{2+} from solution through twenty extraction cycles. The capacity of the SBA-TPED sorbent in these nineteen cycles was $95 \pm 4\%$ of the fresh sorbent. On the other hand, the shape of the SBA-TPED sorbent has little change before and after recycling (Fig. S4). Thus, the prepared sorbent owns high chemical and mechanical stability and can be used repeatedly.

In order to assess the practical utility in real sample analysis, the SBA-TPED was applied to detect and separate Cu^{2+} in natural water samples. As shown in Fig. S5 (see Supplementary information), with the addition of the Cu^{2+} -spiked natural water samples, the color of SBA-TPED turned to blue due to Cu^{2+} ions were extracted onto the sorbent. The adsorption of SBA-TPED for Cu^{2+} in tap water, river water, and pool water samples was 96.89%, 97.23%, and 98.44%, respectively. These experimental results indicated that the SBA-TPED can be efficiently used for detecting and removing Cu^{2+} from environmental samples.

Conclusions

In this study, a novel diamine-functionalized mesoporous SBA-15 was developed to detect and remove Cu²⁺ ions from water medium. It was found out that: (i), the prepared SBA-TPED is an efficient sorbent for removal of Cu²⁺ ions from aqueous solutions. In addition, the SBA-TPED showed high selectivity for Cu²⁺, the largest relative coefficient between Cu²⁺ and Zn²⁺ was over 60. (ii), the optimum pH value for removal Cu²⁺ ions from aqueous solution ranged from 4 to 7 and the Cu²⁺ adsorption approached equilibrium state in less than 30 min. (iii), the colorimetric detection limit of SBA-TPED for Cu²⁺ was 0.95 ppm, lower than the EPA standard (1.30 ppm), and its application in natural water samples was also satisfactory. (iv), the SBA-TPED can be regenerated by hydrochloric acid treatment and used repeatedly with little shape change. (v), the adsorption process is chemical adsorption, and possible Cu²⁺ adsorption mechanism was proposed.

Acknowledgment

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Notes and references

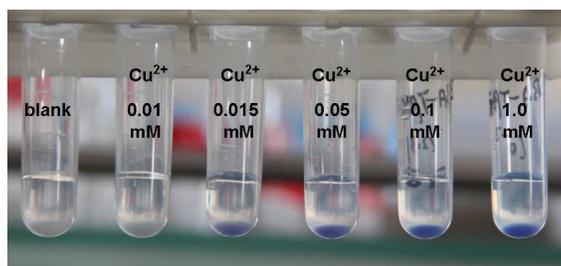
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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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