1 Growth and alkaline phosphatase activity of *Chattonella marina* and *Heterosigma akashiwo* in response to phosphorus limitation
   Zhao-Hui Wang and Yu Liang

8 Distribution characteristics and indicator significance of Dechloranes in multi-matrices at Ny-Ålesund in the Arctic
   Guangshui Na, Wei Wei, Shiyao Zhou, Hui Gao, Xindong Ma, Lina Qiu, Linke Ge, Chenguang Bao and Zwei Yao

14 Pretreatment of cyanided tailings by catalytic ozonation with Mn$^{2+}$/O$_3$
   Yulong Li, Dengxin Li, Jiebing Li, Jin wang, Asif Hussain, Hao Ji and Yijie Zhai

22 Effects of different sludge disintegration methods on sludge moisture distribution and dewatering performance
   Lingyun Jin, Guangming Zhang and Xiang Zheng

29 Removal of tetracycline from aqueous solution by a Fe$_3$O$_4$ incorporated PAN electrospun nanofiber mat
   Qing Liu, Yuming Zheng, Lubin Zhong and Xiaoxia Cheng

37 Feasibility of bioleaching combined with Fenton oxidation to improve sewage sludge dewaterability
   Changgeng Liu, Panyue Zhang, Chenghua Zeng, Guangming Zeng, Guoyin Xu and Yi Huang

43 Mg$^{2+}$ improves biomass production from soybean wastewater using purple non-sulfur bacteria
   Pan Wu, Guangming Zhang and Jianzheng Li

47 Influence of zeta potential on the flocculation of cyanobacteria cells using chitosan modified soil
   Liang Li, Honggang Zhang and Gang Pan

54 Effects of two polybrominated diphenyl ethers (BDE-47, BDE-209) on the swimming behavior, population growth and reproduction of the rotifer *Brachionus plicatilis*
   Jingjing Sha, You Wang, Jianxia Lv, Hong Wang, Hongmei Chen, Leilei Qi and Xuexi Tang

64 Immobilization of lead in anthropogenic contaminated soils using phosphates with/without oxalic acid
   Xiaojuan Su, Jun Zhu, Qingling Fu, Jichao Zuo, Yonghong Liu and Hongqing Hu

74 Predicted no-effect concentrations for mercury species and ecological risk assessment for mercury pollution in aquatic environment
   Meng Du, Dongbin Wei, Zhuowei Tan, Aiwu Lin and Yuguo Du

81 Investigation of physico-chemical properties and microbial community during poultry manure co-composting process
   Omar Farah Nadia, Loo Yu Xiang, Lee Yei Lie, Dzulkornain Chairil Anuar, Mohammed P. Mohd Afandi and Samsu Azhari Baharuddin

95 Cu(II), Fe(III) and Mn(II) combinations as environmental stress factors have distinguishing effects on *Enterococcus hirae*
   Zaruhi Vardanyan and Armen Trchounian

101 Evaluation of biostimulation and Tween 80 addition for the bioremediation of long-term DDT-contaminated soil
   Bibiana Betancur-Corredor, Nancy J. Pino, Santiago Cardona and Gustavo A. Peñuela

110 Hg$^0$ removal from flue gas over different zeolites modified by FeCl$_3$
   Hao Qi, Wenqing Xu, Jian Wang, Li Tong and Tingyu Zhu

118 Preparation and evaluation of aminopropyl-functionalized manganese-loaded SBA-15 for copper removal from aqueous solution
   Di Lei, Qianwen Zheng, Yili Wang and Hongjie Wang
CONTENTS

128 Investigation of carbonyl compound sources at a rural site in the Yangtze River Delta region of China
Ming Wang, Wentai Chen, Min Shao, Shuhua Lu, Limin Zeng and Min Hu

137 Low-carbon transition of iron and steel industry in China: Carbon intensity, economic growth and policy intervention
Bing Yu, Xiao Li, Yuanbo Qiao and Lei Shi

148 Synergistic effect of N- and F-codoping on the structure and photocatalytic performance of TiO$_2$
Jiemei Yu, Zongming Liu, Haitao Zhang, Taizhong Huang, Jitian Han, Yihe Zhang and Daohuang Chong

157 Pollution levels and characteristics of phthalate esters in indoor air of offices
Min Song, Chenchen Chi, Min Guo, Xueqing Wang, Lingxiao Cheng and Xueyou Shen

163 Characteristics and anthropogenic sources of carbonyl sulfide in Beijing
Ye Cheng, Chenglong Zhang, Yuanyuan Zhang, Hongxing Zhang, Xu Sun and Yujing Mu

171 Oxidation of diesel soot on binary oxide CuCr(Co)-based monoliths
Sergiy O. Soloviev, Andriy Y. Kapran and Yaroslava P. Kurylets

178 Effects of introducing energy recovery processes to the municipal solid waste management system in Ulaanbaatar, Mongolia
Kosuke Toshiki, Pham Quy Giang, Kevin Roy B. Serrona, Takahiro Sekikawa, Jeoung-soo Yu, Baasandash Choijil and Shoichi Kunikane

187 Toluene decomposition performance and NO$_x$ by-product formation during a DBD-catalyst process
Yufang Guo, Xiaobin Liao, Mingli Fu, Haibao Huang and Daiqi Ye

195 Changes in nitrogen budget and potential risk to the environment over 20 years (1990-2010) in the agroecosystems of the Haihe Basin, China
Mengmeng Zheng, Hua Zheng, Yingxia Wu, Yi Xiao, Yihua Du, Weihua Xu, Fei Lu, Xiaoke Wang and Zhiyun Ouyang
Preparation and evaluation of aminopropyl-functionalized manganese-loaded SBA-15 for copper removal from aqueous solution

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ABSTRACT

A novel material, aminopropyl-functionalized manganese-loaded SBA-15 (NH₂-Mn-SBA-15), was synthesized by bonding 3-aminopropyl trimethoxysilane (APTMS) onto manganese-loaded SBA-15 (Mn-SBA-15) and used as a Cu²⁺ adsorbent in aqueous solution. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction spectra (XRD), N₂ adsorption/desorption isotherms, high resolution field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the NH₂-Mn-SBA-15. The ordered mesoporous structure of SBA-15 was remained after modification. The manganese oxides were mainly loaded on the internal surface of the pore channels while the aminopropyl groups were mainly anchored on the external surface of SBA-15. The adsorption of Cu²⁺ on NH₂-Mn-SBA-15 was fitted well by the Langmuir equation and the maximum adsorption capacity of NH₂-Mn-SBA-15 for Cu²⁺ was over two times higher than that of Mn-SBA-15 under the same conditions. The Elovich equation gave a good fit for the adsorption process of Cu²⁺ by NH₂-Mn-SBA-15 and Mn-SBA-15. Both the loaded manganese oxides and the anchored aminopropyl groups were found to contribute to the uptake of Cu²⁺. The NH₂-Mn-SBA-15 showed high selectivity for copper ions. Consecutive adsorption–desorption experiments showed that the NH₂-Mn-SBA-15 could be regenerated by acid treatment without altering its properties.

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Introduction

Copper is an essential element for human life and health, but it will cause serious environmental and public health problems in cases of excessive discharge (Malkoc and Nuhoglu, 2005; Komárek et al., 2010). Due to its non-biodegradability and accumulation in the environment, great attention has been paid to studying removal processes for copper ions (Kurniawan et al., 2006; Dabrowski et al., 2004; Mohammadi et al., 2004; Sud et al., 2008; Mohsen-Nia et al., 2007). Among the established processes, the adsorption method is gaining prominence for its simplicity of operation, recovery of the heavy metals, high efficiency, lower sludge production volume and ability to meet strict discharge specifications (Swami and Buddhi, 2006; Ngah Wan and Hanafiah, 2008). Great numbers of natural (Gündoğan et al., 2004; Basci et al., 2004) or artificial (Chen et al., 2003, 2011) materials have been developed to eliminate metal ions from aqueous solution.

Recently a series of ordered mesoporous silica materials, such as MCM-41, MCM-48, and SBA-15 (Benhamou et al., 2009; Perez-Quintanilla et al., 2006) have been developed for metal ion elimination because of their high surface area and pore volume, good accessibility to active sites, rapid mass transport inside the nanostructures, good hydrothermal stability and ease of surface modification. To further enhance the efficiency and selectivity of the ordered mesoporous materials, great effort has been made to

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develop metal hybrid silica (Dragoi et al., 2009) and/or organic-inorganic hybrid mesoporous silica (Xue and Li, 2008; Jeong et al., 2011) materials. In view of its large surface area, microporous structure, high stability and large amount hydroxy groups capable of reacting with metal ions, manganese oxides are commonly introduced to the hybrid materials to enhance the efficiency and high selectivity for metal ions (Calderon Rosas et al., 2010). On the other hand, aminopropyl groups anchored on the surface of the adsorbents are reported to improve the adsorption efficiency via the formation of metal–nitrogen coordination bonds (Zhao et al., 2011). To the best of our knowledge, the most used approach is to modify mesoporous silica surfaces using aminopropyl groups to increase their adsorption of metal ions (Aguado et al., 2009), however, adsorption of aqueous Cu^{2+} on metal–organic–inorganic hybrid mesoporous silica has not been reported in the literature so far.

The objectives of the work are: (1) to develop a novel hybrid material that has the high metal ion uptake capacity of the manganese oxides and high selectivity of aminopropyl-functionalized SBA-15; (2) to characterize the structure of the materials; and (3) to evaluate the adsorption behavior of the materials for copper ions in aqueous solution and investigate the adsorption mechanism preliminarily.

1.1. Chemicals

Tetraethyl orthosilicate (TEOS, 98%) and 3-aminopropyltrimethoxysilane (APTMS) were purchased from Alfa Aesar Co., Ward Hill, MA, USA. Pluronic P123 (PEO_{20}PPO_{70}PEO_{20}, Mav = 5800) was purchased from Aldrich. KMnO_{4}, H_{2}O_{2} (30%), Cu(NO_{3})_{2}·5H_{2}O, NaNO_{3}, NaOH and HNO_{3} obtained from Beijing Chemical Agents Company, Beijing, China, were analytical grade and were used as received without further purification.

1.2. Synthesis of NH_{2}-Mn-SBA-15

Preparation of SBA-15 containing the triblock copolymer Pluronic P123 (P123-SBA-15) sample was performed following a previously reported method (Zhao et al., 1998). Pluronic P123 (Sigma-Aldrich Co. LLC., St. Louis, USA) (4 g) was dissolved in 120 g of 2 mol/L HCl solution at 40°C and 8.5 g TEOS was then added. The solution was kept under stirring for 24 hr and was subsequently transferred to a Teflon-lined autoclave, where it was heated at 100°C for 48 hr. The final solid product was obtained by filtration, washed with distilled water, and then dried at 70°C overnight. The Mn-SBA-15 was synthesized according to a previous publication (Dong et al., 2005). P123-SBA-15 2 g was added into a beaker containing KMnO_{4} aqueous solution (400 mL, 0.1 mol/L), then stirred at room temperature for 3 hr. After being filtered off and washed thoroughly with deionized water, the resulting solid product Mn-SBA-15 was dried at 70°C.

NH_{2}-Mn-SBA-15 was prepared via a post-grafting method. The typical procedure was as follows: 1.0 g of so-obtained materials was dispersed in 100 mL of water-free toluene and refluxed with continuously stirring at 110°C. After the formation of a homogenous suspension, 0.4 mL of APTMS was added dropwise under the protection of nitrogen flow and the mixture was stirred and refluxed for 24 hr. The solid product was recovered by filtration, and later washed with toluene, acetone and ethanol successively. The final product was dried at 70°C and used for further characterization and evaluation. The synthesis route of the NH_{2}-Mn-SBA-15 material is shown in Scheme 1.

1.3. Adsorbent characterization

FT-IR spectra ( Nicolet 5700, Thermo Nicolet Co., Madison, WI, USA) measurements were recorded on anhydrous KBr pellets in the frequency range of 4000-400 cm^{-1} (spectral resolution: 4 cm^{-1}, number of scans: 32). The X-ray powder patterns were investigated by an XRD diffractometer (X'Pert PRO MPD, PANalytical, Eindhoven, the Netherlands) using Cu Kα radiation at 40 kV and 30 mA. The data were collected from 0.5°–5° for low-angle and 5°–80° for high-angle measurements. 

N_{2} adsorption/desorption experiments were conducted at 77 K using an ASAP 2020 surface analyzer (Micromeritics Co., Norcross, Georgia, USA). Samples were degassed at 105°C and 105 Pa under vacuum for at least 6 hr. Surface area was calculated by using the BET equation and the pore size distribution was obtained from the adsorption branch of isotherms using the BJH model. The pore volume was obtained by the t-plot method. High resolution field emission scanning electron microscopy (FESEM) was performed on a Hitachi SU-8020 scanning electron microscope. The XPS measurements were carried out with an imaging photoelectron spectrometer (Kratos AXIS Ultra, Kratos Analytical Ltd., Manchester, UK), using an aluminum anode X-ray source with a monochromator (Al Kα, hν = 1486.71 eV) or a dual anode (Al/Mg target). The wide scan spectra were conducted from 0 to 1100 eV with pass energy of 160 eV. The high resolution scans were conducted according to the peak being examined with pass energy of 40 eV. The binding energies were calibrated internally by the carbon deposit C 1s binding energy at 284.6 eV. The software of Vision (PR2.1.3) and Casa XPS (2.3.12Dev7) were used to fit the XPS results which were collected in binding energy forms. Surface zeta potentials were measured using a Zeta Potential Analyzer (Zeta PALS, Brookhaven Instruments Co., Holtsville, New York, USA).

1.4. Batch adsorption experiments

Adsorption kinetics experiments were performed at initial Cu^{2+} concentration of 0.1 mmol/L. Typically, 0.1 g of NH_{2}-Mn-SBA-15, Mn-SBA-15 was added into a 500-mL flask containing 500 mL of 0.1 mmol/L Cu^{2+} solution with an ionic strength of 0.01 mol/L NaNO_{3} and pH 5.5, which was strongly stirred at 25°C. During the kinetics experiments, aliquots of samples were withdrawn by stopping agitation at fixed intervals, selected from 1 min to 48 hr. The filtrate was passed through a 0.45 μm membrane and the extracted samples were collected. The ion strengths of 0.01, 0.05 and 0.1 mol/L NaNO_{3} were used as background electrolyte. The desired solution pH was adjusted with 0.1 mol/L HNO_{3} or 0.1 mol/L NaOH, such that the equilibrium solutions had pH values ranging from 3.0 to 7.0. The reaction mixture consisted of 100 mL solution with initial Cu^{2+} concentration of 0.1 mmol/L and 100 mg/L adsorbent. After reacting for 48 hr at 25°C with a shaking speed of 140 r/min, the suspension was filtered with a 0.45 μm membrane.
The adsorption isotherm experiments were conducted at pH 5.5 and at room temperature with initial Cu²⁺ concentrations in the range of 0.01 to 0.18 mmol/L. 10 mg of Mn-SBA-15, NH₂-Mn-SBA-15 adsorbent was added into each 100 mL Cu²⁺ solution with an ionic strength of 0.01 mol/L NaNO₃. After reacting for 48 hr at 25°C with a shaking speed of 140 r/min, the suspension was passed through a 0.45 μm membrane and the extracted samples were collected.

Four mixed solutions with other metals were prepared to observe the effect of the adsorptive competing cations on the Cu²⁺ adsorption by NH₂-Mn-SBA-15: the Cu²⁺ and Pb²⁺ solution, the Cu²⁺ and Cd²⁺ solution, the Cu²⁺ and Zn²⁺ solution, and the Cu²⁺, Pb²⁺, Cd²⁺ and Zn²⁺ solution, the concentration of each heavy metal is 0.1 mmol/L. 10 mg of NH₂-Mn-SBA-15 adsorbent was added into each 100 mL mixed solution with an ionic strength of 0.01 mol/L NaNO₃ and pH 5.5. After reacting for 48 hr at 25°C with a shaking speed of 140 r/min, the suspension was passed through a 0.45 μm membrane and the concentration of heavy metals was analyzed.

The concentration of heavy metals was analyzed by using an atomic absorption spectrophotometer (AAS, AA-6300, Shimadzu Corporation, Kyoto, Japan). The adsorption capacity of heavy metal ions adsorbed per gram adsorbent (mg/g) was calculated using the following equation (Eq. (1)):

\[
q_t = \frac{V(C_0-C_t)}{W} \tag{1}
\]

where, \(q_t\) is the equilibrium adsorption amount, \(C_0\) (mg/L) and \(C_t\) (mg/L) are the initial and equilibrium concentrations, \(V\) (L) is the volume of the solution and \(W\) (g) is the mass of the adsorbent.

In this study, the pseudo first-order equation (Eq. (2)) (Lagergren, 1898), pseudo second-order equation (Eq. (3)) (Ho and McKay, 1998) and Elovich equation (Eq. (4)) (Chien and Clayton, 1980) were used to evaluate the kinetics of the adsorption process.

\[
q_t = q_e \left(1-e^{-k_1t}\right) \tag{2}
\]

\[
q_t = \frac{q_e^2k_2t}{1+q_ek_2t} \tag{3}
\]

\[
q_t = \beta \ln(\alpha \beta) + \beta \ln t \tag{4}
\]

where, \(q_e\) (mg/g) and \(q_t\) (mg/g) are the adsorption capacity of Cu²⁺ on the adsorbents at equilibrium and at time \(t\) (min), \(k_1\) (L/min) is the rate constant of the pseudo first-order equation and \(k_2\) (g/(mg·min)) is the rate constant of the second-order equation, \(\alpha\) (mg/g·min) is the initial Cu²⁺ adsorption rate and \(\beta\) (g/mg) is the desorption constant during any one experiment.

The Langmuir adsorption isotherm model (Langmuir, 1916) and Freundlich adsorption isotherm model (Freundlich, 1906) were used to determine the equilibrium experimental data. The non-linear models are represented as Eqs. (5) and (6).

\[
q_e = \frac{q_{\text{max}}K_LC_e}{1+K_LC_e} \tag{5}
\]

\[
q_e = K_FC_e^{1/n} \tag{6}
\]

where, \(q_e\) (mg/g) is the equilibrium adsorption capacity of the adsorbent, \(C_e\) (mg/L) is the equilibrium solution concentration of the metal ions, \(q_{\text{max}}\) (mg/g) is the maximum adsorption capacity, \(K_L\) (L/mg) is the Langmuir equilibrium constant and \(n\) is the Freundlich constant.
concentrations of Cu$^{2+}$, $q_{\text{max}}$ (mg/g) is the maximum adsorption capacity, $K_L$ (L/mg) is the Langmuir equilibrium constant, $K_F$ ((mg/g)(L/mg)$^{1/n}$) is the Freundlich constant, and $n$ is the Freundlich exponent.

The selectivity coefficients ($k_i$) of the Cu$^{2+}$ in the presence of the other metal Me$^{2+}$ ions (Me$^{2+} = Pb^{2+}$, Cd$^{2+}$ and Zn$^{2+}$) were calculated according to the following equations (Eqs. (7) and (8)):

$$k_i = \frac{K_{dCu^{2+}}}{K_{dMe^{2+}}} \quad (7)$$

$$K_d = \frac{10^3 Q}{C_e} \quad (8)$$

where, $K_d$ (mL/g) is the distribution ratio of the metal ion, $k_i$ represents the selectivity coefficients toward Cu$^{2+}$, $Q$ (mg/g) is the amount of the metal ion on the adsorbents, and $C_e$ (mg/L) is the equilibrium metal ion concentration.

1.5. Regeneration and reusability experiments

The regeneration and reusability of the NH$_2$-Mn-SBA-15 were examined by acid treatment. 0.2 g copper-loaded NH$_2$-Mn-SBA-15 was stirred in 100 mL of 0.1 mol/L HNO$_3$ solution for 12 h at room temperature to strip copper ions. The final Cu$^{2+}$ concentration in the aqueous phase was determined. The adsorbent was then washed with deionized water several times. Then the resulting cleaned adsorbent was dried at 70°C and subjected again to adsorption–desorption process for four cycles.

2. Results and discussion

2.1. Material characterization

2.1.1. FT-IR

FT-IR spectra of the P123-SBA-15, Mn-SBA-15 and NH$_2$-Mn-SBA-15 are illustrated in Fig. 1. The peaks in the range of 2850–3000 cm$^{-1}$ and at 1460 cm$^{-1}$ are attributed to C–H stretching and bending vibrations of P123 and the peak at 1350 cm$^{-1}$ is corresponded to C–O–C stretching modes of P123 (Fig. 1a) (Vo et al., 2013), while the intensity of the peaks in the corresponding regions clearly weakens after the treatment by KMnO$_4$ (Fig. 1 line b). The redox reaction between KMnO$_4$ and P123 located in the channels of SBA-15 is thus demonstrated (Zhu et al., 2006).

Fig. 2 – XRD patterns of samples at low angles (A) and high angles (B). line a: P123-SBA-15; line b: Mn-SBA-15; line c: NH$_2$-Mn-SBA-15.

Fig. 3 – N$_2$ adsorption-desorption isotherms (A) and pore size distribution (B) of P123-SBA-15 (line a), Mn-SBA-15 (line b) and NH$_2$-Mn-SBA-15 (line c).
shrinkage of the peak at about 960 cm\(^{-1}\) ascribed to the bending vibration of Si–OH was also detected, which indicates the possible reaction between the formed manganese oxides and the silanol groups of SBA-15. After aminopropyl functionalization, the intensity of the peaks at 2850–3000 cm\(^{-1}\) corresponding to C–H stretching vibrations strengthens again. Meanwhile, the band associated with the bending vibration of Si–OH bonds at about 960 cm\(^{-1}\) almost disappears (Fig. 1 line c). It is reasonable to suggest the partial elimination of the silanols and the successful anchoring of the aminopropyl groups onto the surface of Mn-SBA-15 (Xu et al., 2011).

### 2.1.2. XRD

To investigate the surface structure of the absorbents, the XRD patterns were measured. The low angle XRD patterns in Fig. 2A show that P123-SBA-15 exhibits three characteristic resolved diffraction peaks, which were indexed as the (1 0 0), (1 1 0) and (2 0 0) reflections, associated with the ordered hexagonal mesoporous silica framework. The introduction of manganese oxides and aminopropyl groups caused a marked intensity decrease. However, the basal (1 0 0) diffraction peaks can be distinctly observed, which indicates that the hexagonal patterns of the SBA-15 were well maintained after the functionalization (Chen et al., 2010). The peaks of (1 1 0) and (2 0 0) become unobservable, indicating the irregular organization of the mesoporous structure at long range. The XRD patterns at high diffraction angles (Fig. 2B) show that the introduction of manganese oxides and aminopropyl groups leads to an obvious reduction of the crystallinity of the samples. There is no distinct reflection of manganese oxide crystalline phase observed outside of the pore channels of Mn-SBA-15 and NH\(_2\)-Mn-SBA-15. This suggests that the formed manganese oxides are highly dispersed in the pore channels or that the diameters of the formed small clusters are below the detection limit of XRD (Tang et al., 2010).

### 2.1.3. N\(_2\) adsorption/desorption isotherms

As shown in Fig. 3, all of the curves of the N\(_2\) adsorption–desorption isotherms of the samples exhibit the type IV isotherms with H1 hysteresis loop type, with capillary condensation at P/P\(_0\) from 0.4 to 0.8 as defined by IUPAC, which is the typical characteristic of a mesoporous structure (Haber et al., 1994). After loading of manganese oxides, the inflection point shifts clearly to lower partial pressure, corresponding to the decrease of the pore diameter of the mesoporous materials, while no clear shift of the inflection point is detected after aminopropyl functionalization. The sharpness of the hysteresis loops indicates that all of the samples have a narrow pore size distribution. The textural properties of the materials are summarized in Table 1. After treatment by KMnO\(_4\), a small decrease of the pore volume and pore size and clear increase of the BET surface area of P123-SBA-15 are detected, and this ascribed to the redox reaction between KMnO\(_4\) and the templating agent. It further indicates that most of the formed manganese oxides mainly load on the internal surfaces of the pore channels of SBA-15. Meanwhile, an inconspicuous increase of the pore diameter and a pronounced decrease of the BET surface area and the pore volume occur after the functionalization by aminopropyl groups onto Mn-SBA-15. The above phenomena indicate that aminopropyl groups are mainly anchored on the external surface of Mn-SBA-15 (Xu et al., 2011).

### 2.1.4. FESEM

High resolution field emission scanning electron microscope (FESEM) images of the samples in Fig. 4 permit the observation of channel-like structures running parallel to the longer direction, and the channels correspond well to the 2D hexagonal structure typical of SBA-15 (Lombardo et al., 2012). The above results indicate that the process of loading of manganese oxides and the grafting of aminopropyl groups have little effect on the morphology of the materials and the textural order of the framework of the materials is well preserved.

### 2.1.5. XPS

Wide scan XPS spectra of NH\(_2\)-Mn-SBA-15 before and after Cu\(^{2+}\) adsorption over a wide binding energy range from 0 to 1100 eV are displayed in Fig. 5A. Clear N 1 s peaks are shown in the spectrum of NH\(_2\)-Mn-SBA-15, which suggests the successful grafting of aminopropyl groups onto the

---

**Table 1 – Textural properties of P123-SBA-15, Mn-SBA-15 and NH\(_2\)-Mn-SBA-15.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123-SBA-15</td>
<td>394.7</td>
<td>0.67</td>
<td>6.82</td>
</tr>
<tr>
<td>Mn-SBA-15</td>
<td>431.9</td>
<td>0.51</td>
<td>4.68</td>
</tr>
<tr>
<td>NH(_2)-Mn-SBA-15</td>
<td>229.5</td>
<td>0.29</td>
<td>5.03</td>
</tr>
</tbody>
</table>

---

**Fig. 4 – FESEM images of P123-SBA-15 (A), Mn-SBA-15 (B) and NH\(_2\)-Mn-SBA-15 (C).**
The appearance of the Cu 2p binding energy peak after adsorption directly confirms the uptake of copper species by NH2-Mn-SBA-15. The computer deconvolution of the XPS spectrum of Cu2+ in Fig. 5B shows two peaks at 934.53 and 953.92 eV along with weak satellite peaks around 943.84 and 962.36 eV respectively, which provides evidence for the presence of Cu2+ species on NH2-Mn-SBA-15 after adsorption (Kannamba et al., 2010). The significant N 1s binding energy shift from 399.62 to 400.13 eV in Fig. 5C for the aminopropyl groups of NH2-Mn-SBA-15 is attributed to the involvement of the lone pair of electrons on nitrogen on NH2-Mn-SBA-15 in bond formation with Cu2+ ions (Sun and Wang, 2006; Liu et al., 2006). On the other hand, the O 1s peaks in Fig. 5D centered at 529.71 and 529.79 eV assigned to Mn–O, 532.55 and 532.71 eV assigned to Si–O, and another at 530.88 and 530.78 eV could be attributed to surface hydroxyl groups. A clear increase in the content of surface hydroxyl groups is observed after Cu2+ adsorption, which implies that the surface hydroxyl groups are also involved in the uptake of Cu2+ and different Cu2+ species exist on the surface of NH2-Mn-SBA-15.

2.2. Copper adsorption experiments

2.2.1. Adsorption kinetics

The influence of contact time on the uptake of Cu2+ onto Mn-SBA-15 and NH2-Mn-SBA-15 is shown in Fig. 6 and the adsorption kinetics data are described by pseudo first-order, pseudo second-order and Elovich kinetic models, respectively. In this study, the removal efficiency of Cu2+ on Mn-SBA-15 and NH2-Mn-SBA-15 increases sharply during the first 60 min, then continues with a slower rate and finally tends to reach equilibrium. The model parameters listed in Table 2 distinctly show that the adsorption process follows the Elovich model more closely than the pseudo first-order and pseudo second-order models, which indicates that the predominantly chemical adsorption on the highly heterogeneous surface of the Mn-SBA-15 and NH2-Mn-SBA-15 dominates the uptake of Cu2+ (Lasheen et al., 2012; Pérez-Marín et al., 2007).
2.2.2. pH and ionic strength studies
As shown in Fig. 7, the adsorption of Cu^{2+} on NH$_2$-Mn-SBA-15 is strongly dependent on the pH of the solution. The uptake of Cu$^{2+}$ increases steadily in the pH range from 3 to 5.5, and the maximum removal efficiency (62%) is achieved at pH 5.5. At pH below 5, the ionic strength of the solution has a clear negative effect on the uptake of Cu$^{2+}$, while there is no clear effect on the adsorption at pH 5.5 with increasing ionic strength from 0.01 to 0.1 mol/L NaNO$_3$. The strong effect of the ionic strength on adsorption at pH below 5 indicates that ion exchange or outer sphere complexation contributes to Cu$^{2+}$ adsorption. As the pH of the solution is increased from 3 to 5.5, the extent of the protonated form of the amino group NH$_3^+$ decreases and the inner sphere complexes of NH$_2$⋯Cu$^{2+}$ gradually form on the surface of NH$_2$-Mn-SBA-15 (Han et al., 2006). The weak effect of the ionic strength on the Cu$^{2+}$ adsorption at pH 5.5 suggests that inner-sphere complexation/chemical adsorption is the main adsorption mechanism of Cu$^{2+}$ onto NH$_2$-Mn-SBA-15 (Sparks, 1995). To avoid Cu$^{2+}$ precipitation, the experiments in this study were conducted at pH 5.5, which is consistent with the zeta-potential result (5.3) of NH$_2$-Mn-SBA-15.

2.2.3. Adsorption isotherm
Under similar conditions, the maximum adsorption capacity of NH$_2$-Mn-SBA-15 (40.67 mg/g) for Cu$^{2+}$ is over two times higher than that of Mn-SBA-15 (19.88 mg/g), which indicates the crucial role of the aminopropyl group in Cu$^{2+}$ adsorption. At the same time, in comparison with the low adsorption quantity of Cu$^{2+}$ onto SBA-15 (Lombardo et al., 2012), both manganese oxides and aminopropyl group produce significant effects on the removal of Cu$^{2+}$ by adsorption. Meanwhile, NH$_2$-Mn-SBA-15 also has a higher Cu$^{2+}$ adsorption capacity than that of amino-group-functionalized silica as reported in other studies: 28 mg/g (Liu et al., 2000), 19.9 mg/g (Wang et al., 2009), as well as that of other Cu$^{2+}$ adsorbents such as mercaptopropyl-functionalized porous silica: 13 mg/g (Lee et al., 2001), EDTA-modified SBA-15: 13.2 mg/g (Jiang et al., 2007), natural bentonite: 14.1 mg/g (Kubilay et al., 2007), and so on.

<table>
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<th>Table 2 – Kinetics parameters and Isotherm parameters of adsorption of Cu$^{2+}$ by Mn-SBA-15 and NH$_2$-Mn-SBA-15.</th>
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<td><strong>Model</strong></td>
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Fig. 7 – Removal efficiency of Cu$^{2+}$ at different initial pH and ionic strength on NH$_2$-Mn-SBA-15. Initial Cu$^{2+}$ concentration: 0.1 mmol/L, dosage: 100 mg/L, T: 25°C.
Meanwhile, all of the NH2-Mn-SBA-15 (Tao et al., 2010). Manganese oxides and aminopropyl groups on the surface of presumably attributed to the homogeneous distribution of a monolayer adsorption of Cu2+ onto the adsorbents. This is data are well described by the Langmuir model, which implies given in Table 2. The experimental equilibrium adsorption displayed in Fig. 8 and the corresponding parameters are described by the Langmuir model, which implies a monolayer adsorption of Cu2+ onto the adsorbents. This is presumably attributed to the homogeneous distribution of manganese oxides and aminopropyl groups on the surface of NH2-Mn-SBA-15 (Tao et al., 2010).

2.2.4. Competitive adsorption studies

The competitive adsorption of different heavy metals on the Cu2+ adsorption is summarized in Table 3. The Cu2+ adsorption capacity of NH2-Mn-SBA-15 from a multi-metallic solution is still higher. It shows the high selectivity of NH2-Mn-SBA-15 toward the Cu2+ ions. The selectivity coefficients of Cu2+ in the presence of other metal cations metal ions show the following order: \( k_i \text{ Cd}^{2+} \gg k_i \text{ Zn}^{2+} > k_i \text{ Pb}^{2+} \). Meanwhile, all of the \( k_i \) values are greater than 6, this suggest that the adsorptive competing ions in the aqueous solution have little effect on the adsorption of Cu2+ on NH2-Mn-SBA-15.

2.3. Regeneration and reusability studies

Taking into account the practical application, good desorption performance of an adsorbent is important. After four cycles, desorption efficiencies are found to be 99.1%, 98.5%, 97.8% and 97.2%, respectively. Most importantly, the adsorption capacity of the regenerated NH2-Mn-SBA-15, with value of 39.59, 39.05, 38.19 and 37.61 mg/g, respectively, is almost unaffected. These data indicate good regeneration and reusability of the NH2-Mn-SBA-15.

3. Conclusions

An ordered mesoporous aminopropyl-functionalized manganese-loaded SBA-15 (NH2-Mn-SBA-15) was successfully synthesized by a post-grafting method and the adsorption behavior of Cu2+ onto the adsorbent was investigated. The successful anchoring of manganese oxides and aminopropyl groups on the framework of SBA-15 is evidenced by FT-IR results. The hexagonal structure of the samples is retained after functionalization. The textural properties of NH2-Mn-SBA-15 imply that the formed manganese oxides are mainly loaded on the internal surface of the pore channels while the aminopropyl groups are mainly anchored on the external surface of SBA-15. The removal of the Cu2+ is favored with increasing pH, however, it slightly decreases with increasing solution ionic strength at pH 5.5. The Langmuir model fits the experimental data well and the Cu2+ adsorption capacity of NH2-Mn-SBA-15 is 40.67 mg/g, which is over two times higher than that of Mn-SBA-15. Chemisorption is the dominant mechanism for the uptake of Cu2+ onto the highly heterogeneous surface of NH2-Mn-SBA-15. NH2-Mn-SBA-15 can be used as an effective adsorptive material for the removal of Cu2+ ions from aqueous solutions by utilizing the manganese hydroxyl groups as well as interaction between surface aminopropyl groups and Cu2+. In the mixed metal ion solutions, NH2-Mn-SBA-15 shows higher adsorption selectivity for Cu2+ compared to other cations. NH2-Mn-SBA-15 exhibits good regeneration and reusability under experimental conditions.

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