The synthesis of novel thiol/amino bifunctionalized SBA-15 and application on the Cr(VI) absorption

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Abstract. Novel amino/thiol organic groups modified SBA-15 materials were successfully prepared by a simple co-condensation approach. The synthesize mesoporous materials were characterized by FT-IR, SAXRD, N₂ adsorption and elemental analysis (EA). The absorption behavior of Cr (VI) in the samples has been investigated. The experiments revealed that the adsorption amount of Cr (VI) was decided by thiol groups, but the adsorption equilibrium time was mainly affected by amino groups. The 15% NH₂+20%SH sample had the best adsorption performance. Its maximum adsorption capacity can be up to 49.29 mg/g at the optimum conditions. The research of adsorption mechanism including adsorption kinetics and adsorption thermodynamics was also presented.

1. Introduction
Adsorption, as a kind of common method, was usually applied to deal with the heavy metal ions which were very harmful to the human health and environment even at very low concentration, such as Cr(VI), Pb(II). Comparison to other separation methods, it is obvious that adsorption was cheaper, more convenient and efficient. The adsorbent is the heart of the adsorption, so it was a key to find a high efficiency and inexpensive adsorbent. Recently, a type of mesoporous material, SBA-15, has attracted considerable attentions as its higher surface area, larger pore and a lot of silicon hydroxyl. Although the conventional SBA-15 has good adsorption ability, it is not a good absorbent for the heavy toxic metal ions. Functionality of SBA-15, grafting some functional organic groups into the SBA-15, as a strategy, was adopted to improve their adsorption of heavy toxic metal ions. Liu A M, et al [1] prepared two functionalized SBA-15 samples and discussed their adsorption characters for heavy toxic metal ions, the SBA-15 with thiol group exhibited a higher adsorption capacity to Hg(II), and SBA-15 with amino group can remove Zn²⁺, Cr³⁺ and Ni²⁺ efficiently. Shahbazia A et al [2] synthesized the SBA-15 functionalized with amine (-NH₂) group and melamine-based dendrimer amines (MDA) and the results suggested MDA functionalized SBA-15 was the best adsorbent to remove the Pb(II), Cu(II) and Cd(II) ions. Zhang L J et al [3] grafted 1-(3-carboxyphenyl)-2-thiourea (CPTU) into SBA-15 and systematically researched the adsorption of Hg(II). This material displayed a higher adsorption capacity (64.5 mg/g), and the materials can still remove over 95% of Hg(II) after seven cycles. In our previous research [4], we found that the bifunctionalized SBA-15 which contained 30% (30% is molar ratio of (APTES+MPTMS)/TEOS) amino and thiol groups exhibited the excellence ability of removal of Cr(VI). In order to find out which organic groups play key role in the adsorption process, the SBA-15 contained different content of organic groups were synthesized to study. In this article, the bifunctionalized SBA-15 which contained fixed contents of amino group
for the allowed 2x82.5H as kept groups ethanol, at MPTMS/TEOS was 4.25 filtered, by changeable different angle 98% selected become Adsorption at the = precipitation their concentration as molar X-ray (MPTMS) (German) purchased varied silica Cr(VI) 20 the mixture mL Aladdin 10% Cr to of (APTES, ethanol Cr trimethoxysilane (3-Mercaptopropyl) 40 spectrometer and by Cr(VI) under room x: flexing was in to clear. grade SBA-NH3H was adsorption the mixture of amino groups(from 10% to 30%), as well as fixed contents of thiol group(15%) and variable contents of amino groups(from 10% to 30%) were produced via a simple co-condensation approach, and the interaction of amino group and thiol group was studied to find to synthesize the best adsorbent and selected it to investigate the adsorption kinetic and thermodynamic mechanism.

2. Chemicals and experiment

2.1. Chemicals
Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123, Mn=5800), (3-Aminopropyl) triethoxysilane (APTES, 98%) and (3-Mercaptopropyl) trimethoxysilane (MPTMS, 95%) were purchased from Aldrich, Aladdin and Aladdin, respectively. Ethyl silicate (TEOS) was employed as a silica source. Commercial grade reagents and solvents were used without further purification. Distilled water was used in the aqueous solutions.

2.2. Experiments

2.2.1. Preparation of NH2/SH bifunctionalized SBA-15 (denoted as SBA-NH2-SH). The bifunctionalized SBA-15 was prepared as follows: 2 g P123 dissolved in 62.5 g 2M HCl solution, the resulting mixture was stirred at 40°C until the mixture become clear. Then the amino precursor (APTES) and thiol precursor (MPTMS) were slowly added after 4.25 g TEOS was added into the solution. The molar composition of the mixture solution (the fixed amino groups) was 0.02TEOS :0.003 APTES : x MPTMS : 3.05HCl : 0.0085P123 : 82.5H2O, where x varied from 0.002 to 0.006, or MPTMS/TEOS = 10%-30%, and the molar composition of the mixture solution (fixed thiol group) was 0.02TEOS : y APTES : 0.003 MPTMS : 3.05HCl : 0.0085P123 : 82.5H2O, where y varied from 0.002 to 0.006, or MPTMS/TEOS = 10%-30%. The reaction mixture was stirred at 40°C for 20 h, and then the mixture was aged for 24 h at 100°C under static condition. The precipitation product was recovered by filtration and dried under the air. The template was extracted by flexing for 24 h with excess acid ethanol solution. Finally, the sample was filtered, washed with ethanol, water and dried at 60°C under the air.

2.2.2. Characterization. Small angle X ray diffraction (SAXRD) patterns of the materials was measured on Bruker (German) D8 advance X-ray diffraction spectrometer using Cu Kα radiation, the scan speed kept 0.1°/s and the range of 2θ angle between 0.600° and 9.993°. The elemental Analysis system GmbH - vario EL III Element Analyser was used to examine the contents of N and S. The FT-IR spectra was recorded on a Bruker Optics Fourier Transform Infrared Spectrometer. N2 adsorption-desorption isotherms were estimated on 3H-2000PS2 analyser at 77K. The concentration of Cr(VI) was determined by the UV-visible spectrophotometer.

2.2.3. Adsorption experiments. The Cr(VI) adsorption behaviors of bifunctionalized SBA-15 at various time and different content of -NH2 and -SH groups were determined to evaluate their Cr (VI) adsorption capacity and time under the optimization condition [4]. Briefly, 0.1 g absorbent was put in 100 mL 50 mg/L Cr(VI) solution and allowed to absorb the Cr(VI) at 25°C under pH = 2.0. The aqueous phase was collected and concentration of residue Cr (VI) was carried out on the UV-visible spectrophotometer.

2.2.4. Adsorption kinetics. The bifunctionalized SBA-15 samples (0.1 g) were respectively added to 100 mL 50 mg/L, 100 mg/L and 150 mg/L Cr(VI) solution at room temperature. 1 mL of Cr (VI) solution was taken at different time intervals to measure the residual Cr (VI) concentration.

2.2.5. Adsorption isotherms. The adsorption isotherms of bifunctionalized SBA-15 were measured by
using 0.1 g absorbent in 100 mL 70 mg/L Cr (VI) solution and incubated the mixture at 313 K, 323 K and 313 K respectively for 6 h. The residual Cr (VI) concentrations and the Cr (VI) uptake per unit mass the bifunctionalized SBA-15 were determined as described above.

3. Result and discuss

3.1. Characterization of bifunctionalized SBA-15 materials

3.1.1. FT-IR. The FT-IR spectroscopy was used to determine the amino group and thiol group grafted into the SBA-15. The FT-IR of pure SBA-15 and bifunctionalized SB-15 were exhibited in figure 1. Three characteristics peaks of SBA-15 at 1085 cm\(^{-1}\), 806 cm\(^{-1}\), 462 cm\(^{-1}\) were easy to observe. Compared with the three curve, (2) and (3) appeared some new absorption peaks, the peak at 574 cm\(^{-1}\) was contributed to the bending vibration of C-S bond, that perfectly indicated that the thiol group have been immobilized into the SBA-15. Generally, the stretching bending of N-H bond was normally appeared at about 3380 cm\(^{-1}\) and 3310 cm\(^{-1}\), however it is hard to observe in bifunctionalized SBA-NH\(_2\)-SH [5]. Between 3500 cm\(^{-1}\) and 3000 cm\(^{-1}\), there was a broad band of surface hydroxyl group that was overlayed the peaks of N-H bond, but the peak around 1460 cm\(^{-1}\) could be seen a weak adsorption peaks that was the symmetric vibration bending of N-H. In summary, the FT-IR has confirmed the amino-and thiol- groups were successfully introduced into the SBA-15.

![Figure 1. FT-IR spectra of three samples: (1) SBA-15, (2) bifunctionalized SBA-NH\(_2\)-SH (10%NH\(_2\)+15%SH), (3) bifunctionalized SBA-NH\(_2\)-SH (10%NH\(_2\)+15%NH\(_2\)).](image1)

![Figure 2. The SAXRD pattern of the four samples. (1) 15%NH\(_2\)+20%SH, (2) 15%SH+15%NH\(_2\), (3) 15%SH+10%NH\(_2\), (4) 15%NH\(_2\)+10%SH.](image2)

3.1.2. SAXRD. The SAXRD of samples was shown in figure 2. As was shown in figure 2, curve (3) and (4) appeared three characteristic diffractions peaks like pure SBA-15 that could be observed at (100), (110), and (200) [6, 7]. The other curves only could see a clearly peak at d100 and at d200, while the peak at d110 was disappeared. As was displayed in figure 2, when the total contents of amino and thiol groups were below 30%, there are three conspicuous peaks. As the total groups percentage of the concentrations were over 30%, the other two peaks turned more weak and even disappeared, that could be contribute to the distortion of the order structure of the functionalized SBA-15. The results were consistent with some previous reports like MCM-41 [8], SBA-NH\(_2\) [9] and SBA-SO\(_3\)H [10], a probable explanation was that the self-assembly of surfactant and the silica precursors aggregates were disrupted by the amino and thiol groups [11, 12], as the mixture concentrations of the synthesized samples was over a critical level, the integrity and ordering of the resultant materials were destroyed.
3.1.3. $N_2$ adsorption-desorption isotherms and elemental analysis. The $N_2$ adsorption and the pore size distributions were exhibited in figures 3 and 4. Based on the adsorption isotherm classification of the IUPAC [13], the $N_2$ adsorption of all samples was a typical Langmuir IV isotherm. According to the ten curves, when the total contents of the groups were below 25\%, the hysteresis loop of those materials belongs to H1-type, the typical features of the mesoporous structure. While the contents were over 25\%, the hysteresis loop of absorption and desorption branch were no longer parallel and gradually deviated from the H1-type. These phenomena indicated that the pore size uniformity were declined even partly appeared channel blocking after a larger number of amino and thiol groups were grafted into the SBA-15 [14, 15].

![Figure 3](image1.png)

**Figure 3.** (a) The $N_2$ adsorption of five samples. (1) 15\%NH$_2$+30\%SH, (2) 15\%NH$_2$+20\%SH, (3) 15\%NH$_2$+15\%SH, (4) 15\%NH$_2$+10\%SH, (5) 15\%NH$_2$+5\%SH. (b) The pore distribution curves of the different contents of amino groups (5\%-30\%) and the stationary molar percentage thiol groups (15\%).

![Figure 4](image2.png)

**Figure 4.** (a) The $N_2$ adsorption of five samples. (1) 15\%SH+30\%NH$_2$, (2) 15\%SH+20\%NH$_2$, (3) 15\%SH+15\%NH$_2$, (4) 15\%SH+10\%NH$_2$, (5) 15\%SH+5\%NH$_2$. (b) The pore distribution curves of the certain molar contents of amino groups (15\%) and the adjustable contents of thiol groups (5\%-30\%).

In the table 1, the BET surface area was decreased along with the increase of the contents of N and S atoms. Through the comparison of the 15\% amino group (with different contents of thiol groups) and 15\% thiol group (with different contents of amino groups), there was an interesting found the BET surface area and the contents of N and S of the 15\% amino group (with different contents of thiol groups) were larger than 15\% thiol group (with different contents of amino groups). Based on the EA, 15\% amino group (with different contents of thiol groups), the contents of N was substantially...
unchanged, the contents of S were increased. When the total contents were 45%, the contents of S were reached to 4.68%. 15% thiol group (with different contents of amino groups), the contents of S were firstly increased (with the percentage of N was below 15%), next they were decreased (the contents of N was over 10%), while the contents of N were always ascended. In summary, appearing this situation maybe due to the -NH$_2$ group was more hydrophilic than -SH group.

Table 1. The Summary of N$_2$ adsorption and elemental analysis.

| Sample                  | BET surface area (m$^2$/g) | Pore volume (ml/g) | The average pore size (nm) | N content (%) | S content (%) |
|-------------------------|-----------------------------|--------------------|-----------------------------|---------------|---------------|
| Pure SBA-15             | 662                         | 0.83               | 5.98                        | -             | -             |
| 15%SH+5%NH$_2$          | 402                         | 0.63               | 3.71                        | 0.35          | 3.72          |
| 15%SH+10%NH$_2$         | 399                         | 0.8                | 4.57                        | 0.44          | 3.87          |
| 15%SH+15%NH$_2$         | 376                         | 0.47               | 3.66                        | 0.60          | 3.68          |
| 15%SH+20%NH$_2$         | 369                         | 0.39               | 3.51                        | 0.79          | 3.39          |
| 15%SH+30%NH$_2$         | 337                         | 0.47               | 3.58                        | 0.98          | 3.15          |
| 15%NH$_2$+5%SH          | 594                         | 0.48               | 3.73                        | 0.60          | 1.51          |
| 15%NH$_2$+10%SH         | 556                         | 0.52               | 3.70                        | 0.58          | 2.57          |
| 15%NH$_2$+20%SH         | 399                         | 0.47               | 3.63                        | 0.56          | 4.34          |
| 15%NH$_2$+30%SH         | 368                         | 0.36               | 3.48                        | 0.56          | 4.68          |

3.2. The adsorption experiments of different adsorbents

As was shown in figure 5, (serie I), when the sample only contained 15% thiol groups was contrasted with other materials with different contents of amino groups, it was easy to find the both of maximum adsorption capacity of Cr(VI) and the adsorption rate were increased with the increase of...
the amino groups. As the number of the amino groups were added, the time of adsorption equilibrium were went down, especially 15% SH+30% NH2 and 15% SH and 20% NH2. The figure 6 (serie II) displayed that for SBA-15 of 15% amino groups, a little number of thiol groups could greatly increase adsorption capacity, and the adsorption equilibrium time was kept (about 65 min). With the content of thiol groups raised, the adsorption capacity of Vr(VI) was appeared large fluctuations before adsorption equilibrium. That maybe because that more thiol groups entered into the pore channel of SBA-15, it would influence the hydrophilic of samples (-SH was a hydrophobic groups). According the result, the samples in series II could effectively and quickly remove the Cr(VI) in water. So the serie II could be took into account to widely use in water treatment of industry.

According to the serie I and serie II, the maximum adsorption capacity of the absorbent can be increased via introducing the -NH2 and -SH functional organic groups into the SBA-15. The reasons maybe contribute to the thiol groups had a strong reducibility under the condition of acidity, the Cr (VI) can be turned to Cr (III) and the thiol group was oxidized to sulfonic acid group through oxidation-reduction reaction [16], and the -NH2 can combine with H+ in the acidic solution to generate a number of -NH3+ ions, which could adsorb a part of HCrO4 under the function of electrostatic attraction [17].

3.3. The study of adsorption mechanisms

3.3.1. Adsorption kinetic. The adsorption kinetics of Cr (VI) were investigate with the pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The sample (15%NH2+20%SH) was choose as the absorbent. The linear form of these models are described in the following equation (1) [18] and (2) [19].

\[
\log(q_t - q_e) = \log(q_e) - \frac{k_1 t}{2.303}
\]

(1)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(2)

where \(K_1\) (1/min) and \(K_2\) (g/mmol/min) are the PFO and PSO rate, and \(q_e\) (g/mmol) and \(q_t\) (g/mmol) represent the adsorption capacities at equilibrium and at time \(t\), respectively.

![Figure 7](image.png)

Figure 7. (a) Adsorption kinetics of Cr (VI) onto the bifunctionalized SBA-15; (b) Adsorption kinetics of Cr (VI) onto the bifunctionalized SBA-15.

On the basis of the figures 7(a) and 7(b), and the calculative value of \(K_1\), \(qe\), \(R_2\) in the table 2, the experimental values well fitted the PSO rate law. The \(R_2\) (R was the correlation coefficient) value was
more close to 1. By contrast with the equilibrium adsorption capacity of the PFO and PSO model, the $q_e$ was close to the value of adsorption capacity based on the PSO model. The $k_2$ was decreased along with the increase of the concentration of the Cr (VI) that indicated the adsorption rates of Cr(VI) was slower when the concentration of the Cr(VI) was up. The results indicated the PSO model was more suitable to describe the adsorption kinetics of Cr (VI) than the PFO model.

**Table 2.** Kinetic parameters and correlation coefficients at different concentration of Cr (VI).

| Cr (mg/L) | Pseudo-first-order | Pseudo-second-order |
|-----------|---------------------|---------------------|
|           | $k_1$ (h$^{-1}$)    | $q_e$ (mg·g$^{-1}$) | $R^2$     | $k_2$ ((mg (g·h)$^{-1}$) | $q_e$ (mg·g$^{-1}$) | $R^2$     |
| 50        | 0.0122              | 6.0996              | 0.9252    | 0.02267                     | 49.5050              | 1.0000    |
| 100       | 0.0120              | 11.0510             | 0.9400    | 0.003615                    | 64.9351              | 0.9995    |
| 150       | 0.0055              | 10.3134             | 0.9759    | 0.003238                    | 77.5194              | 0.9990    |

3.3.2. Adsorption isotherms. The metal uptake by per unit of the adsorbent at equilibrium is defined by the adsorption isotherms. Langmuir and Freundlich’s isotherms have been widely used to characterize the adsorption of solutes from aqueous solutions. The Langmuir isotherm and Freundlich’s isotherm can be written in linear form as following equation (3) and (4) [19]:

\[
\text{Langmuir Isotherm} \quad \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K L q_m} \\
\text{Freundlich’s Isotherm} \quad \log q_e = \frac{1}{n} \log C_e + \log K_F
\]

where $q_e$ and $q_m$ are the equilibrium adsorption capacity (mg/g) and the maximum adsorption capacity, respectively. $C_e$ (mg/L) was the equilibrium concentration of the metal; $KL$ and $K_F$ were the equilibrium adsorption coefficient of Langmuir and Freundlich constants, separately. And $n$ was an empirical constant, if the adsorbent had no adsorption characteristics of metal ions, the date of $n$ was below 1; while the $n$ was between 1 and 10, it demonstrated the adsorbent was favourable [20] to adsorb the metal ions. The results were shown in table 3, meanwhile the figures were shown in figure 8.

As the dates of table 3, the experimental date correlated well with the Langmuir equation model ($R^2$>0.97). This confirmed the surface homogeneity and the monolayer surface coverage of the adsorbent and the fixed available bonding sites for metals. By the analysed the constants of the Freundlich equation model, firstly, the values of $K_l$ was high at high temperatures, which shown that the adsorption ability of adsorbent for Cr (VI) was increased as the rise of the temperature. Secondly, the values of $n$ were all over 1 for different temperatures, which indicated that the adsorption of Cr(VI) on adsorbent was favourable.

**Table 3.** Isotherm parameters obtained from the Langmuir and Freundlich's models.

| T(K) | Langmuir Model | Freundlich Model |
|------|----------------|------------------|
|      | $q_m$ (mg·g$^{-1}$) | KL (L·mg$^{-1}$) | $R^2$ | $n$ | KF (mg·g$^{-1}$) | $R^2$ |
| 313  | 68.03          | 0.17             | 0.9962 | 5.15 | 29.04          | 0.9011 |
| 323  | 72.46          | 0.21             | 0.9789 | 9.87 | 43.76          | 0.6763 |
| 333  | 74.63          | 0.43             | 0.9888 | 12.80 | 54.26          | 0.8055 |
3.3.3. Adsorption thermodynamics

The thermodynamic parameters were evaluated to investigate the influence of temperature on the adsorption of corrosion products onto the bifunctionalized SBA-15. The values for the adsorption thermodynamic parameters were calculated with the van't Hoff equation [19,20-22] as follows:

\[
K_\circ = \frac{q_\circ}{C_e}
\]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

\[
\ln K_\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

where \(\Delta G^\circ(\text{kJ mol}^{-1})\) is the Gibbs free energy changed in the given process; \(R (8.314 \text{ J mol}^{-1}\text{K}^{-1})\) was the ideal gas constant, \(T(\text{K})\) is the temperature; and the \(K_D\) is the distribution constant; \(\Delta S^\circ(\text{J mol}^{-1}\text{K}^{-1})\) is the standard entropy change, and \(\Delta H^\circ(\text{kJ mol}^{-1})\) is the standard enthalpy change of the reaction. The values for \(\Delta S^\circ\) and \(\Delta H^\circ\) were indirectly calculated from the slope and intercept of the van't Hoff plot of \(\ln K_D\) vs \(1/T\).

The plot of \(\ln K_D\) against \(1/T\) (figure 9) at different temperatures showed a good linear relationship. \(\Delta H^\circ\) was 61.46 kJ/mol, and the intercept of the plot [20] could obtained the \(\Delta S^\circ\) was 204.00 J mol\(^{-1}\)K\(^{-1}\), respectively. The other results were summarized in table 4. The positive value of \(\Delta H^\circ\) indicates that adsorption process is exothermic and the value of \(\Delta H^\circ\) (> 40 kJmol\(^{-1}\)) suggesting the Cr (VI) removal onto the adsorbent were both physisorption and chemisorption [23, 24]. The positive value of \(\Delta S^\circ\) suggested the adsorption process of Cr(VI) on the SBA-NH\(_2\)-SH was an enthalpy promotion process. The negative value of \(\Delta G^\circ\) at all temperatures indicates the spontaneous nature of the adsorption reaction. And the \(\Delta G^\circ\) was decreased with temperature ascend, testifying the high temperature was more spontaneous than low temperature [24, 25].

Table 4. Thermodynamic parameters for adsorption of Cr(VI) onto bifunctionalized SBA-15.

| Temperature (K) | \(\Delta G^\circ\) (kJ mol\(^{-1}\)) | \(\Delta H^\circ\) (kJ mol\(^{-1}\)) | \(\Delta S^\circ\) (J mol\(^{-1}\)K\(^{-1}\)) |
|----------------|----------------------------------|---------------------------------|---------------------------------|
| 313            | -2.39                            | 61.46                           | 204.00                          |
| 323            | -4.43                            |                                 |                                 |
| 333            | -6.47                            |                                 |                                 |
Figure 9. Van't Hoff’s plots of lnKD vs. 1/T.

4. Conclusion
This study indicated that bifunctionalized SBA-15 with amino group and thiol group could remove the heavy metals of Cr(VI) efficiently from the water. The results showed that the thiol groups played a major role in the adsorption of Cr(VI), which can enhance the adsorption capacity of Cr(VI), while the amino groups could also assist to adsorb the metals but mainly accelerate the adsorption equilibrium (from 250 min down to 65 min), that means we can synthesize an ideal adsorbent by adjusting the hydrophilic character of the absorbent through the contents of −NH₂ and −SH groups. The study of the adsorption kinetic and isotherms demonstrated the adsorption was suitable fitted by the pseudo-second-order model, and the isotherm data was matched the Langmuir models, the isotherm parameters suggested that the adsorption process of Cr(VI) onto the bifunctionalized SBA-15 was spontaneous, endothermic, and the process was both physical and chemical adsorption.

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