Kinetics, isotherm and thermodynamic studies of S²⁻ adsorption by (SBA-15)-Hg(II)

Xiao-Dong Li and Qing-Zhou Zhai

ABSTRACT

The nano-mesoporous material SBA (Santa Barbara Amorphous)-15 was synthesized using the hydrothermal method. Hg²⁺ was adsorbed by SBA-15 and then the S²⁻ in the aqueous phase by (SBA-15)-Hg(II), with the hope that materials with better S²⁻ adsorption properties can be obtained. The relevant materials were characterized by X-ray diffraction, scanning electron microscopy, 77 K nitrogen adsorption-desorption, and related product characteristics were determined. In this work, the adsorption conditions of S²⁻ onto (SBA-15)-Hg(II) were optimized. Adsorption efficiency reached about 92% and the adsorption capacity 55.02 mg/g. Studies of the system’s adsorption kinetics showed that the pseudo-second-order equation applies. The thermodynamic results indicated that ΔG⁰, ΔH⁰ = -28.56 kJ/mol, ΔS⁰ = -81.136 J/(mol·K), and that adsorption is exothermic, enthalpy decreases and the reaction is spontaneous. This accords with the Freundlich isothermal adsorption equation.

Key words: adsorption, Hg²⁺, mesoporous material, SBA-15, S²⁻

HIGHLIGHTS

- Under the optimized adsorption conditions, the adsorption rate of S²⁻ reached 92% and the adsorption capacity reached 55.02 mg/g.
- The adsorption process of S²⁻ by the (SBA-15)-Hg(II) is in accordance with the quasi-second-order kinetic equation in kinetic aspect, and the adsorption isotherm is in accordance with the Freundlich model.

GRAPHICAL ABSTRACT

1. INTRODUCTION

With the steady development of industrialization, the effect of anthropogenic activities on the environment is becoming more and more serious, and environmental pollution has become a major threat.
Wastewater treatment is a major problem in relation to a wide range of environmental pollution. Sulfur-containing sewage is an important source of pollution, mainly from species such as hydrogen sulfide and sodium sulfide. The direct source of sulfide sewage is industrial wastewater discharges, and the indirect source is the reduction of sulfate in the sewage to sulfide. Conversion by microorganisms is also an important source of sulfur-containing wastewater. Industrial activities such as oil refining, paper-making, printing and leather manufacture all produce sulfide-containing wastewaters.

Industrial wastewater containing high sulfur concentrations is highly corrosive, and can damage plant roots and thus affect plant growth. If the sulfide concentration in water exceeds 0.07 μg-S/L, the water will have a peculiar smell, and when it reaches 0.15 μg-S/L, it affects the growth of fish fry and egg. At the same time, the dissolved sulfide can also be degraded to hydrogen sulfide and diffuse into the atmosphere. Hydrogen sulfide, which smells like rotten eggs, is harmful – that is, toxic – and excessive inhalation can have a variety of effects on body functions including the respiratory, digestive and circulatory systems, and so on (Wang & Hu 2006; Chang et al. 2018).

Because of these various problems, it is necessary to process sulfur-containing sewage before discharge to the environment. Various treatment methods have been adopted to control this kind of pollution, including membrane separation, ion exchange, activated sludge, chemical reactions, and so on (Wang & Hu 2006). However, they are inconvenient and expensive to use, and some produce new liquid and/or solid wastes, resulting in secondary pollution and operating inconvenience.

The use of adsorbents for pollution control is quick. Adsorption technology has practical value because of its simple operation and low cost, and the cost-performance, which is better than other water pollution treatment methods. Activated carbon is a traditional absorbent, and while its adsorption performance is excellent its regeneration is difficult and costly (Diagboya & Dikio 2018). Compared with traditional adsorbents, nanomaterials have high specific surfaces and chemical activity, giving them more advantages as adsorbents than other materials and can lead to better adsorption effects. Adsorption can be used to remove sulfur ions selectively from wastewater, and the sulfur removed cannot migrate into the environment or, therefore, make it worse. However, due to the sulfur ions’ own properties, traditional adsorption technology cannot deal effectively with sulfur-containing materials. It is an important solution and technical challenge, therefore, to study materials that adsorb sulfur strongly, and apply them to the treatment of sulfur containment.

Porous zeolite adsorbents are modern and efficient, and their high surface activity can provide a good base for their modification. The zeolite molecular pore channel is long, its specific surface is large, and it has good adsorption properties. Compared with microporous molecular sieves, the mesoporous molecular sieve pore size and specific surface are larger, and it should also have better adsorption properties.

SBA-15 is an excellent mesoporous material with a pore size range of 4.6–30 nm, and has one of the largest pore diameters among mesoporous materials. The specific surface is large, and the thermostabilization performance is good (Castillo et al. 2018; Dido et al. 2018; Kanga et al. 2018; Firez et al. 2018; Mikheeva et al. 2019; Szewczyk et al. 2019; Zhai 2020). The main raw material for making SBA-15 is silicon – that is a mixture of silicon and oxygen – which makes its framework relatively inactive leading, in turn, to a reduction in its ion-exchange capacity. In order to deal with this defect in SBA-15, its properties are changed by adding metal ions to the material’s skeleton by sorption. This type of modification can not only improve the material’s hydrothermal stability but also make up its lattice defects and enhance its ability to participate in chemical reactions, all of which influence the application of SBA-15 significantly (Lakhi et al. 2018).

In this work, an SBA-15 nano-mesoporous molecular sieve was synthesized. The experimental conditions for Hg$^{2+}$ adsorption by SBA-15 are described elsewhere (Zhai et al. 2011) and the optimized adsorption conditions S$^{2-}$ by (SBA-15)-Hg(II) were studied in the work described here. The adsorption kinetics, thermodynamics and adsorption isotherm properties were studied and their related adsorption properties were found. The material can adsorb not only Hg$^{2+}$ but also S$^{2-}$.

2. EXPERIMENT

2.1. Reagents

The reagents triblock copolymer, polyethylene glycol-block-polypropylene glycol-block-poly(ethylene glycol) (P123, Aldrich), tetraethoxysilane (TEOS, Shanghai First Plant of Reagent, China), hydrochloric acid (12 mol/L,
Beijing Chemical Plant, China), sodium sulfide (Na₂S·9H₂O, Beijing Chemical Plant, China), Hg(NO₃)₂·0.5H₂O (Tianjin Guangfu Fine Research Institute of Chemical Engineering, China), and silver nitrate and sodium hydroxide (both Beijing Chemical Plant) were used. All reagents were analytical grade. Deionized water was used.

2.2. Instruments

Powder X-ray diffraction (XRD) analysis was done using a D5005 diffractometer (Siemens, Germany) using Cu-Kα. The x-ray wavelength, λ, was 1.5418 Å, operating (tube) voltage 40 kV, and operating (tube) current 30 mA with scanning range 0.4–6° and step size 0.02°.

Particle morphology and size were obtained on a scanning electron microscope (Philips XL30) running at 20 kV.

The nitrogen adsorption-desorption results were determined using a Micromeritics Corporation (USA) ASAP 2020 V3.01 H-type adsorption analyzer at 77 K. Samples were vacuum-activated at 363 K for 12 hours and the data calculated using the BdB (Broekhoff and de Boer) method (Broekhoff et al. 1968a, 1968b).

The specific surface was analyzed and calculated by the BET (Brunauer-Emmett-Teller) method (Brunauer et al. 1938), and the pore size distribution by the BJH (Barrett-Joyner-Halenda) method (Barrett et al. 1951).

2.3. Experimental methods

2.3.1. Synthesis of mesoporous molecular sieve SBA-15

Mesoporous molecular sieve SBA-15 was synthesized by the hydrothermal method (Zhai 2012). 2 g of P123 template were dissolved in 15 mL of deionized water and 60 g of 2 mol/L HCl, stirred magnetically until the template was completely dissolved. 4.25 g of TEOS were then added slowly and stirred continuously to form a homogeneous solution. Stirring continued at 40 °C for 24 hours, after which it was crystallized in a polytetrafluoroethylene substrate reaction kettle at 100 °C for 48 hours. The resulting product was filtered, washed with deionized water, dried at room temperature, and finally calcined in a muffle furnace at 550 °C for 24 hours to remove the triblock copolymer. This yielded the mesoporous material SBA-15 molecular sieve, as a white powder.

2.3.2. Preparation of (SBA-15)-Hg(II)

0.167 g of Hg(NO₃)₂·0.5H₂O was dissolved in 1 L of deionized water. 40 mL of the Hg²⁺ standard solution were placed in a beaker, the pH was adjusted to 5 using 0.1 mol/L HNO₃ and NaOH solutions, and 0.10 g of SBA-15 was added and stirred for 40 minutes. The solution was filtered and dried at 25 ± 1 °C to obtain (SBA-15)-Hg(II).

2.3.3. Adsorption of S²⁻ by (SBA-15)-Hg(II)

The gravimetric method was used to measure and calculate the adsorption related parameters. 0.050 g of (SBA-15)-Hg(II) were added to 20 mL of 0.2 mg-Na₂S/mL (conditional experiment: 0.04, 0.1, 0.2, 0.6 mg-Na₂S/mL), and the pH adjusted to 9.5 (conditional experiment: 7, 8, 9, 9.5, 10, 11, 12). The solution volume was controlled to 40 mL by adding water and it was stirred at 25 ± 1 °C for 40 minutes (conditional experiment: 10, 20, 30, 35, 40, 45, 50 minutes). After centrifugation, the supernatant was titrated to excess with 0.1 mol/L AgNO₃ solution and, when precipitation was complete, subject to vacuum filtration and the product (SBA-15)-Hg(II)-S²⁻ dried at room temperature.

The precipitate mass produced was weighed and the residual S²⁻ concentration in the solution calculated. The amount of S²⁻ adsorbed by the modified SBA-15 was calculated by subtraction, and then the adsorption capacity and rate.

The equilibrium adsorption capacity, qₑ, of S²⁻ and its adsorption capacity at time t, qₜ, were obtained using Equations (1) and (2):

\[ qₑ = \frac{(C₀ - Cₑ)V}{m} \]  \hspace{1cm} (1)
\[ qₜ = \frac{(C₀ - Cₜ)V}{m} \]  \hspace{1cm} (2)

where \( C₀ \) is the initial adsorption concentration of the adsorbate, \( Cₑ \) the equilibrium adsorption concentration, \( Cₜ \) the adsorption concentration at time t, V the solution volume, and m the adsorbent mass. The \( C₀, Cₑ, Cₜ \) are measured in mg/ml, V in ml, and m in g.
2.3.4. Adsorption kinetics
0.050 g of (SBA-15)-Hg(II) was added to 20 mL of Na₂S solution at concentrations of 0.04, 0.1, 0.2 and 0.6 mg/mL. The pH was adjusted to 9.5 and water added to bring the volume to 40 mL, before adsorption took place at room temperature for known periods of time. After that the liquor was centrifuged and the supernatant titrated with excess 0.1 mol·L⁻¹ AgNO₃/L. When precipitation was complete, the product was subjected to vacuum filtration and dried at room temperature. The mass of Ag₂S precipitate was weighed and the residual S²⁻ concentration in solution calculated, so that the amount of S²⁻ adsorbed by the (SBA-15)-Hg(II) could be calculated by differential subtraction. Once \( q_e \) and \( q_t \) were calculated, quasi-first-order and quasi-second-order dynamic equations were obtained, and the corresponding parameters.

2.3.5. Adsorption isotherm
0.050 g of (SBA-15)-Hg(II) were added to 20 mL of Na₂S solution to yield concentrations of 0.04, 0.1, 0.2 and 0.6 mg/mL. The pH was adjusted to 9.5 and water added to bring the volume to 40 mL. Adsorption was carried out for known time periods at 25, 35 and 45 °C, after which the mixture was centrifuged, and the supernatant titrated with excess 0.1 mol/L AgNO₃ solution. The precipitate was vacuum filtered and dried at room temperature. The mass of precipitate was weighed and the residual S²⁻ concentration in solution calculated. From this, the amount of S²⁻ adsorbed by the (SBA-15)-Hg(II) was calculated by differential subtraction. When \( q_e \) and \( q_t \) were calculated, a quasi-first-order dynamic equation and Langmuir and Freundlich adsorption isotherms were drawn, and the corresponding parameters calculated.

3. RESULTS AND DISCUSSION
3.1. Effect of adsorption conditions
The effect of pH on the adsorbent's ability to sorb S²⁻ is very important. It can be seen in Figure 1 that when the solution pH is below 9.5, the amount adsorbed increases with increasing pH, and at pH 9.5, the modified material's adsorption rate and capacity are at their maxima. Thereafter, adsorption decreases with increasing pH. When the pH is low, the adsorption sites of modified SBA-15 adsorb mainly sulfur ions. When it is too high, however, hydroxyl ions fight S²⁻ for adsorption sites, reducing their adsorption capacity.

The effect of different initial Na₂S solution concentrations on adsorption ability is shown in Figure 2. As the initial concentration of Na₂S increases, the adsorption capacity for S²⁻ increases gradually. The maximum adsorption rate occurs when the solution concentration reaches 0.10 mg·Na₂S/mL. When the concentration exceeds that, the adsorption rate decreases due to saturation of the adsorption sites.
The effect of contact time is shown in Figure 3. The adsorption rate and capacity increase significantly with increasing contact time, and reach the maximum at 40 minutes, after which both are stable.

The effects of temperature – observed at 298.15, 308.15, and 318.15 K – are shown in Figure 4. The adsorption rate decreases with increasing temperature, indicating that the adsorption process is exothermic.

### 3.2. Adsorption kinetics

Quasi-first-order and second-order dynamic equations were developed using the time and concentration data in linear fitting – see Figures 5 and 6, respectively. The dynamic data are listed in Table 1, where \( q_{e1} \), \( q_{e2} \) are the theoretical \( q_e \) values obtained from the quasi-first and second-order dynamic equations, respectively, and \( R_1^2 \), \( R_2^2 \) are their respective correlation coefficients. It is clear that the \( S^{2-} \) adsorption process by (SBA-15)-Hg(II) is in better accord with the quasi-second-order kinetic equation than the first, the correlation coefficient being 0.9992, 0.9998 and 0.9997, respectively, and the difference between theoretical and actual \( q_e \) is small. However,
most of the correlation coefficients for the quasi-first-order kinetic equation are around 0.78, when it is used to fit the adsorption process. The error is also larger and the theoretical $q_e$ differs considerably from the actual $q_e$, indicating that the quasi-second-order kinetic equation expresses the $S^{2-}$ adsorption process (SBA-15)-Hg(II) better.

3.3. Adsorption isotherm

The adsorption data were investigated in relation to the Langmuir and Freundlich adsorption isotherms. The linear Equation – (3) – for the Langmuir isotherm is (Langmuir 1916, 1918; Crini et al. 2007; Naushad 2014; Alqadami et al. 2017):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left( \frac{1}{Q_0} \right) C_e$$

where $C_e/q_e$ (g/mL) is the equilibrium constant, $C_e$ (mg/mL) the adsorbate's equilibrium concentration, and $q_e$ the adsorption capacity – that is the mass by the adsorbent per unit mass. $Q_0$ (mg/mL) and $b$ (mL/mg) represent the relationship among the Langmuir constant and the adsorption capacity and rate, respectively.
The linear equation – (4) – for the Freundlich isotherm is (Freundlich 1906; Langmuir 1916, 1918):

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  

where \( q_e \) (mg/g) is the adsorption capacity at equilibrium, \( C_e \) (mg/mL) the absorbate concentration at equilibrium. \( K_F \) is the Freundlich adsorption isotherm constant (the coefficient of adsorption degree) and \( 1/n \) – usually \(<1\) – indicates adsorption intensity.

The results of simulating the Langmuir and Freundlich adsorption isotherms are shown in Figures 7 and 8, respectively. The related parameters are listed in Table 2. As can be seen, the S²⁻ adsorption process by (SBA-15)-Hg(II) is closer to the Freundlich isotherm and \( R^2 \) is 0.9951, 0.9906, 0.9914 – that is it always exceeds 0.99. All values of \( 1/n \) are below 1, too, indicating S²⁻ adsorption by (SBA-15)-Hg(II) is preferential.

### 3.4. Adsorption thermodynamics

The Gibbs free energy in the reaction (\( \Delta G^0 \)), and the enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) changes are obtained using equations 5, 6 and 7 respectively (Chowdhury et al. 2011; Zhou et al. 2013; Naushad et al. 2016):

\[
K_d = \frac{q_e}{C_e}
\]

\[
\ln K_d = -\Delta H^0 / (RT) + \Delta S^0 / R
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

where \( K_d \) (K) is the temperature-dependent adsorption equilibrium constant, \( \Delta G^0 \) is the free energy change during adsorption (kJ/mol), \( \Delta H^0 \) the enthalpy change during adsorption (kJ/mol), \( R \) the ideal gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) the absolute temperature (K), and \( \Delta S^0 \) the entropy change during adsorption (J/mol·K).
The calculated adsorption thermodynamic parameters are shown in Table 3. At and above room temperature (308.15–328.15 K), $\Delta G^0 < 0$, showing that adsorption is spontaneous. The value of $\Delta G^0$ is between 0 and $-20$ kJ/mol, indicating that adsorption is physical (Gerçel et al. 2007). $\Delta H^0 = -28.561$ kJ/mol ($\Delta H^0 < 0$),
which shows that $S^{2-}$ adsorption by (SBA-15)-Hg(II) is exothermic. $\Delta S^0 = -81.136 \text{ J/(mol·K)}$, ($\Delta H^0 < 0$), indicating that the process reduces entropy.

### 3.5. Characterization of SBA-15 related material

Figures 9 and 10 show the small and wide angle XRD images, respectively, of SBA-15, (SBA-15)-Hg(II), the (SBA-15)-Hg(II) with $S^{2-}$ adsorbed. The XRD small angle image of the SBA-15 molecular sieves has four peaks (Zhai 2012), which can be assigned to those obtained by (100), (110), (200) and (210) crystal plane diffraction, respectively. The peaks confirm that the SBA-15 prepared is a molecular sieve. In the wide-angle images, the (SBA-15)-Hg(II) peak is unchanged but the peak is lower, showing that modification was successful and caused no damage to the original SBA-15 skeleton. The characteristic diffraction peaks of SBA-15 exist after $S^{2-}$ adsorption by (SBA-15)-Hg(II), proving that the original SBA-15 framework is still present.

![Figure 9 | Small-angle XRD images.](image)

Table 4 is a summary of the physicochemical characteristics of the SBA-15 in the three samples. The three samples showed similar inflection points, tending to lower relative pressure with Hg$^{2+}$ modification and subsequent $S^{2-}$ adsorption. A sequential decrease in specific surface was observed for the three samples, which

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/(mol·K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>308.15</td>
<td>$-3.558$</td>
<td>$-28.561$</td>
<td>$-81.136$</td>
</tr>
<tr>
<td>318.15</td>
<td>$-2.746$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>328.15</td>
<td>$-1.935$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
occurred because the guest molecules adsorbed stayed and were tightly packed within the SBA-15 porous network.

As can be seen in Figure 13, the pore size distribution of the three samples is very narrow, indicating that they all have a regular and single mesoporous framework structure (the samples’ pore size structure parameters are given in Table 4). It can be concluded from Figure 13 and Table 4 that Hg$^{2+}$ modification and subsequent S$^{2-}$ adsorption do not change the original SBA-15 structure. The pore wall thickness increases gradually with increasing ionic adsorption. The reductions in BET surface area, mesoporous volume and average pore size all show that after adsorbing S$^{2-}$ the SBA-15 channel was partially filled and blocked, indicating that S$^{2-}$ has been adsorbed in SBA-15 channels.

4. CONCLUSIONS

Nano-mesoporous SBA-15 was synthesized successfully using a hydrothermal method. The adsorption conditions and kinetics, adsorption isotherms and thermodynamic-related properties of S$^{2-}$ adsorption by (SBA-15)-Hg(II) were studied. XRD images were taken after adsorption. The post-adsorption materials were also characterized by SEM and low-temperature (77 K) nitrogen adsorption-desorption. It was concluded that:

1. The optimum adsorption conditions for S$^{2-}$ by (SBA-15)-Hg(II) are: 1.67 g-SBA-15/L, pH 9.5, temperature and time 25 °C for 40 minutes. The maximum adsorption efficiency and capacity were about 92% and 55.02 mg/g, respectively.
2. The adsorption of S$^{2-}$ by (SBA-15)-Hg(II) is best fitted by the quasi-second-order kinetic equation, and the adsorption isotherm is best fitted by the Freundlich model.
3. Thermodynamically, the entropy and Gibbs free energy changes for S$^{2-}$ adsorption by (SBA-15)-Hg(II) are all below zero, indicating that the process is exothermic and accompanied by a decrease in entropy.

ACKNOWLEDGEMENTS

This study was funded by the Natural Science Foundation of the Department of Science and Technology, from the Science and Technology Development Program of Jilin Province, P. R. China. The project number was 20180101180JC, 222180102051, KYC-JC-XM-2018-051. This study was supported by Science Research Project of Education Department, Jilin Province from the 13th Five-Year Plan (JJKH20200265KJ). The authors would like to express their thanks.
**Figure 11** | SEM images of (a) SBA-15, (b) (SBA-15)-Hg(II), (c) (SBA-15)-Hg(II) adsorbed S².

**Figure 12** | Nitrogen adsorption-desorption curves.
Table 4 | Pore size structure parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interplanar spacing $d_{100}$ (nm)</th>
<th>Cell parameters $a_0$ (nm)</th>
<th>Wall thickness (nm)</th>
<th>BET surface area (m$^2$/g)</th>
<th>Mesopore volume (cm$^3$/g)</th>
<th>Mean pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>10.26</td>
<td>11.85</td>
<td>4.15</td>
<td>613</td>
<td>1.04</td>
<td>7.70</td>
</tr>
<tr>
<td>(SBA-15)-Hg(II)</td>
<td>10.33</td>
<td>11.94</td>
<td>4.61</td>
<td>587</td>
<td>0.94</td>
<td>7.33</td>
</tr>
<tr>
<td>(SBA-15)-Hg(II)-S$^{2-}$</td>
<td>10.43</td>
<td>12.05</td>
<td>4.76</td>
<td>503</td>
<td>0.85</td>
<td>7.29</td>
</tr>
</tbody>
</table>

Figure 13 | Pore size distribution patterns.

CONFLICT OF INTEREST
The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

REFERENCES


