Preparation and application of VOCs adsorption materials in textile industry

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Abstract. A series of HMS molecular sieves with different pore structures were prepared by using dodecylamine and octadecylamine as template and tetrabutyl orthosilicate as silicon source to study the different pH values and temperatures. Adsorption performance. The physicochemical properties of HMS molecular sieves were characterized by BET, XRD and SEM. The results showed that the HMS molecular sieve material synthesized by dodecylamine as template was obtained after standing for 12 h in water bath for 12 h, pH 2 and calcination temperature was 550 °C. The best adsorption effectis HMS molecular sieve material synthesized by octadecylamine as template agent has the best adsorption effect when the aging time is water bath for 24 h, pH is 10, and calcination temperature is 550 °C. The adsorption rates are up to 71.72% and 74.78%, respectively.

1. Introduction
The textile industry is the traditional pillar industry of China's national economy. The VOCs emitted by the setting machine during the dyeing and finishing stage have caused serious harm to the environment and the human body. The printing and dyeing exhausts mainly come from high-temperature setting machines, and the VOCs emitted are formaldehyde, xylene, methanol and benzene. Main [1]. Adsorption is one of the most commonly used methods. Molecular sieves have excellent adsorption properties and are one of the most popular VOCs adsorbents. HMS (Hexagonal Mesoporous Silica) mesoporous molecular sieves have a large specific surface area. Small pore size and uniformity, high cost performance, good chemical and thermal stability, SakdinunNuntanga et al [2] synthesized NR/HMS nanomaterials with primary amine as template, so HMS mesoporous molecular sieves are good in many fields such as environmental energy. Application prospects. Design HMS molecular sieves to consider the material's ability to regenerate, long-term stability of the adsorption-desorption cycle, low cost, well-designed pore size and geometry of open pore structures [3-4]. In this paper, HMS molecular sieves with different pore structures were prepared for organic template agents with different chain lengths. It was found that dodecylamine and octadecylamine as template reagents have good adsorption effects under different water baths and pH conditions, so this It provides an important reference for the development of new HMS mesoporous molecular sieve adsorption materials.
2. The experimental process
1.3875 g of neutral primary amine template agent dodecylamine (DDA) or octadecylamine (ODA) was dissolved in 16.2 g of different pH aqueous solution at 50 °C and 10.35 g of ethanol was added as a co-solvent, stirring vigorously. Slowly drip 5.2 g of tetraethyl orthosilicate solution (TEOS), hydrolyze and coagulate, and stir vigorously for 15 min (DDA) or 1 h (ODA). Allow to stand for 6 h (DDA) or 24 h (ODA). The sample aging time refers to the period from the completion of the TEOS addition to the precipitation washing and filtration. During this period of time, the configured solution is vigorously stirred for a while before, and the constant temperature static operation mode is adopted for a while. Cool to room temperature (23.8 °C), filter, rinse with water. The sample was removed from the templating agent in a digital program high temperature furnace by high temperature roasting, and heated at 550 °C for 6 h at a rate of 3 °C/min.

The effect of adsorption of toluene on HMS molecular sieves was determined by static adsorption method. The sample was placed in a brown dryer clock with toluene, and the mass change before and after the sample was recorded. The adsorption rate was calculated as follows:

\[ \eta = \frac{M_2 - M_1}{M_2 - M_1} \times 100 \% \]  

3. Experimental results and discussion

3.1. Effect of Different pH on the Adsorption of Toluene on HMS Molecular Sieve
Table 1 shows that DDA-HMS has the highest adsorption capacity at pH 2, and the highest adsorption capacity of ODA-HMS at pH 10. After 48 h adsorption time, the adsorption capacities of DDA-HMS and ODA-HMS were 71.72% and 77.5%, respectively.

| pH   | DDA-HMS   | ODA-HMS   |
|------|-----------|-----------|
| 2    | 71.72%    | 74.78%    |
| 4    | 70.07%    | 67.67%    |
| 6    | 54.76%    | 74.42%    |
| 8    | 68.78%    | 73.84%    |
| 10   | 70.29%    | 77.50%    |
| 12   | 67.18%    | 20.30%    |

When pH=2, DDA-HMS has more excellent adsorption performance, and when pH=10, ODA-HMS is more excellent. In addition, through ODA-HMS (Figure. 1) and DDA-HMS (Figure. 2) five cycles of adsorption of toluene, ODA-HMS still has a higher adsorption capacity after five cycles of adsorption, and DDA-HMS undergoes five cycles. After adsorption, the adsorption capacity is reduced.

![Figure 1. ODA-HMS cyclic adsorption diagram](image1.png)

![Figure 2. DDA-HMS cyclic adsorption diagram](image2.png)
3.2. Effect of Calcination Temperature on Adsorption of Toluene on HMS Molecular Sieve
The optimal adsorption conditions of DDA-HMS at pH=2 and ODA-HMS at pH=10 were studied. Under these conditions, the effects of different calcination temperatures on the adsorption of toluene were investigated. Table 2 shows that DDA-HMS and ODA-HMS have the highest adsorption capacity for toluene at 550 °C, which are 41.11% and 73.58%, respectively. At 650 °C, the adsorption of toluene by ODA-HMS and DDA-HMS was only 38.11% and 61.80%. It shows that ODA-HMS molecular sieve has better adsorption performance and better adsorption stability.

| Temperature | DDA-HMS | ODA-HMS |
|------------|---------|---------|
| 450 °C     | 38.11%  | 61.80%  |
| 550 °C     | 41.11%  | 73.58%  |
| 650 °C     | 36.01%  | 64.72%  |

3.3. Effect of aging time on the adsorption of toluene by HMS molecular sieve
DDA-HMS molecular sieves with pH=2 and calcination temperature of 550 °C were used to study the effects of different aging time on the adsorption performance. It can be seen from Table 3 and Figure 3 that the adsorption effect obtained after aging for 6 h in a water bath at 50 °C and then at room temperature for 12 h is ideal. And as the number of adsorptions increases, the adsorption efficiency of the sample gradually decreases.

| Time                        | DDA-HMS |
|-----------------------------|---------|
| Water bath aged 6 h         | 45.55%  |
| After the water bath was    |         |
| aged for 6 hours, it was    | 86.31%  |
| at room temperature for 12 h|         |
| Room temperature 24 h       | 57.61%  |

Figure 3. Different ageing time

3.4. Effect of adsorption time on the adsorption of toluene on HMS molecular sieves
Figure 4 and Figure 5 show that DDA-HMS and ODA-HMS increased the adsorption amount of toluene with time. At 42 h, the DDA-HMS adsorption rate reached the maximum. At 48 h, the ODA-HMS adsorption rate was the best, which was 75.09%, 77.50%, so the adsorption capacity reached a maximum when the adsorption time was 24 h.
3.5. Sample characterization

3.5.1. XRD characterization. Figure 6 shows that there is a hexagonal symmetric mesoporous structure (100) crystal plane diffraction peak at 2θ=0.9°, which shows that HMS has hexagonal symmetry, indicating that the synthesized HMS maintains the original basic characteristics of mesoporous molecular sieve, which is reported in the literature. Consistent [5-6]. In addition, after calcination at 650 °C and 550 °C, the XRD peak intensity is basically the same, and the characteristic diffraction peak appearing at 2θ=0.9° indicates that high temperature calcination does not cause collapse of the mesoporous structure of the molecular sieve, and HMS exhibits good thermal stability. When the pH =6, the d_{100} is larger. When the pH=2, the sample d_{100} obtained at 650 °C is lower, indicating that the HMS can obtain a stable skeleton structure and the channel order degree is improved under the suitable temperature range and the proper pH value. According to the analysis, 550 °C is the most suitable temperature, and pH=2 is the optimum pH value.

Figure 7 shows that ODA-HMS has the highest d_{100} at pH=12, and experiments have shown that the ODA-HMS molecular sieve synthesized under this condition has very low adsorption to toluene, and the solution may be too alkaline to change its original molecular structure, resulting in roasting. The pores collapse, resulting in an increase in d_{100}. Therefore, pH=10 is the optimum experimental condition for ODA-HMS molecular sieves.
3.5.2. SEM characterization. In Figure 8, a and b are DDA-HMS SEM images, and c is an ODA-HMS molecular sieve SEM image. The multiple is 5000 times. It can be observed that the molecular sieve has a rich pore structure and a small spherical appearance. At the same time, it can be seen that both DDA-HMS and ODA-HMS have worm-like pores, and the mutual connectivity between the pores is good, but the long-range order is lacking.

3.5.3. BET measurement. It can be seen from Table 4 that the pH=2, DDA-HMS has a large specific surface area at 550 °C and 650 °C, but the average pore volume and average pore diameter are smaller at 650 °C, and the adsorption efficiency is slightly lower. When the pH = 6, the DDA-HMS has a small specific surface area, and the average pore diameter is obviously increased. It may be sintered due to pore collapse during firing, the pore volume becomes smaller, the pore diameter becomes larger, the specific surface area decreases, and the adsorption capacity decreases. The pH=10 After ODA-HMS is fired at 550 °C, its static cycle adsorption efficiency is higher than pH=2. It may be that the synergistic effect of octadecylamine and TEOS is stronger.

| Sample              | Specific surface area (m²/g) | Pore volume (cm³/g) | Average pore volume (cm³/g) | Average aperture (nm) |
|---------------------|------------------------------|---------------------|-----------------------------|-----------------------|
| DDA (pH=2, 550)     | 953.39                       | 0.054               | 1.15                        | 3.34                  |
| DDA (pH=2, 650)     | 936.22                       | 0.298               | 0.92                        | 3.09                  |
| DDA (pH=6, 550)     | 379.82                       | 0.025               | 1.01                        | 8.27                  |
| ODA(pH=10, 550)     | 579.44                       | 0.136               | 0.73                        | 3.85                  |
4. Conclusion
ODA-HMS has better adsorption performance to toluene than DDA-HMS. The HMS molecular sieve material synthesized by dodecylamine as a template agent is the most stable when the aging time is 6 h after water bath for 12 h, the pH is 2, and the calcination temperature is 550 °C. Good adsorption effect; HMS molecular sieve material synthesized by octadecylamine as template agent has the best adsorption effect when the aging time is water bath for 24 h, pH is 10, and calcination temperature is 550 °C. The adsorption rates are up to 71.72% and 74.78%, respectively.

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