

Design of a POSS-Modified Zeolite Structure and the Study of the Enhancement of Ammonia-Nitrogen Removal from Drinking Water

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ABSTRACT

In the work, rice hull ash (RHA) and $[\text{Me}_4\text{N}]\text{OH}$ were employed to produce $[\text{Me}_4\text{N}]_8(\text{OSiO}_{1.5})_8$ and further $[\text{HMe}_2]_8\text{SiOSiO}_{1.5}$ (OHS) as a precursor. The OHS, $\text{CH}_2=\text{CHCOOCCH}_3\text{CH}_2\text{CH}_3$, CH_3OH and NaOH were selected to prepare $\text{POSS}^{-\text{COONa}}$ with carboxyl sodium terminal groups, ion-exchange active groups for $\text{NH}_3\text{-N}$ removal in water, using to modify the ZMS surface. The characterization of the modifier and the modified ZMS structure by standard techniques (such as EIS MS, SEM, NSP, etc.) were provided and discussed. As testing results, the NH_3^+ ion-exchange capacity of the POSS-modified ZMS greatly increased. This increase tendency was validated using a molecular dynamic simulation program of the Materials Studio software to calculate the diffusion behavior of NH_3^+ in the pores of the original ZMS and the modified ZMS, and to compare transition-state energy of the NH_3^+ ion exchange with Si-OH in the original ZMS and with $-\text{COONa}$ in the POSS-modified ZMS.

Keywords: zeolite molecular sieves (ZMS); polyhedral oligomeric silsesquioxane (POSS); $\text{NH}_3\text{-N}$ removal; diffusion coefficient; energy of transition state

1 INTRODUCTION

There are many kinds of $\text{NH}_4\text{-N}$ wastewater treatment techniques; the most important techniques mainly include: air stripping, chemical precipitation, membrane absorption, biological techniques, advanced oxidation, break-point chlorination, man-made marsh sewage disposal, catalytic-wet oxidation, for example [1-5]. Two disadvantages in the traditional methods using ZMS to remove $\text{NH}_3\text{-N}$ in water are: 1) a certain aperture diameter (AD) for ZMS or a certain zeolite microstructure must be selected due to the AD (2.86Å) of ammonium or to protect ZMS from the interference of other particles; and 2) the specific surface area of ZMS is very large (around 500–1000 m^2/g), but at present the maximum adsorption can reach only 20 mg/g [6] which means that the adsorption efficiency of a normal ZMS is very low. This same conclusion is drawn from a calculated result: only a single ammonia ion can be adsorbed on each 100 (Å)² surface area by 10 Si (Al) atoms

on an average surface. The natural ZMS AD has a wide distribution, especially the most mesoporous ZMS AD (2–50 nm) which cannot be used for the treatment of $\text{NH}_3\text{-N}$ in water and is a waste of resource.

In this paper, polyhedral oligomeric silsesquioxane (POSS) with carboxyl sodium terminal groups ($\text{POSS}^{-\text{COONa}}$) as ion-exchange active groups was selected to modify the mesoporous ZMS surface for $\text{NH}_3\text{-N}$ removal in water. The first aim of this work is to explore the utilization of a waste resource, rice hull ash (RHA) as a low-cost starting material, for the synthesis of octadimethylsiloxoctasilsesquioxane or $[\text{HMe}_2\text{SiOSiO}_{1.5}]_8$ and finally of the $\text{POSS}^{-\text{COONa}}$; the second aim is to determine the enhancement scale of the $\text{NH}_3\text{-N}$ ion exchange in water, using the $\text{POSS}^{-\text{COONa}}$ modified ZMS. In addition, this work also focuses on the influence of the modification, the pore structure and ion-exchange treatment mechanism on the enhancement scale of the $\text{NH}_3\text{-N}$ ion exchange using a molecular dynamic simulation (MDS) program of the Materials Studio software (MSS).

2 EXPERIMENTAL

Rice hull ash (RHA) and $[\text{Me}_4\text{N}]\text{OH}$ were employed to produce $[\text{Me}_4\text{N}]_8(\text{OSiO}_{1.5})_8$ (TMN-POSS) as a precursor, and thereafter the silylated compound, $[\text{HMe}_2]_8\text{SiOSiO}_{1.5}$ (OHS) [7]. $\text{POSS}^{-\text{COOH}}$ was prepared using OHS, $\text{CH}_2=\text{CHCOO-CCH}_3\text{CH}_2\text{CH}_3$ and CH_3OH . The $\text{POSS}^{-\text{COOH}}$ was reacted with NaOH to produce the modifier, $\text{POSS}^{-\text{COONa}}$, to modify the mesoporous zeolite molecular sieve (ZMS, SBA-15, an average pore diameter is 2–13 nm) surface.

The reaction was carried out in the presence of the produced $\text{POSS}^{-\text{COOH}}$ in a surging container, added in a 1.5:1 weight ratio with respect to ZMS, for 48 hours at 50°C. The reaction products were filtrated, washed and dried to a white powder which was marinated in a solution of NaOH for one day. The generated modifier will be denoted as $\text{POSS}^{-\text{COONa}}$.

The ZMS and POSS modified ZMS were added into conical flasks containing 1, 2, 5, 10, 20, 50, 100 mg/L NH_4Cl solutions, respectively. The solutions were shaken for 1 hour at 50°C.

The structures of TMN-POSS, OHS, $\text{POSS}^{-\text{COOC-3(Me)}}$ and $\text{POSS}^{-\text{COOH}}$ were characterized with standard

spectroscopic techniques: ESI MS (Agilent 1100 LC/MSD Trap), and XRD (Shimadzu XRD-6000) for OHS molecular components and structural type; a nitrogen sorption porosimetry (NSP) (ASPAP 2020 V3.00 H) and SEM (Quanta 200F) were also used to determine the pore diameters and morphology of the ZMS before and after the modification.

The removal of NH_4^+ with ZMS and the modified ZMS through static and dynamic ion-exchange methods [6] were performed using an ultraviolet spectrophotometer (T6 New Century, China) to determine the maximum exchange capacity and to analyze influences of NH_4^+ concentration in the water on the removals.

3 COMPUTATION METHODOLOGY

Models of the ZMS pore structure before and after the modification were generated using the Amorphous Cell program of MSS of Accelrys Inc. and were optimized with the Discover module.

The diffusion process of the NH_4^+ in the pores was simulated using MDS. The diffusion coefficients (DC) were calculated from the mean-square displacement (MSD) versus the diffusion time of the NH_4^+ in the pores, using the Einstein Equation

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [r_i(t) - r_i(0)]^2 \rangle$$

$$MSD = \langle [r(t) - r(0)]^2 \rangle$$

where, N_α is the number of diffusing atoms, $r(0)$ is an initial position vector of the penetrant molecule in the selected hybrid microstructure, $r(t)$ is the position vector of this molecule after time t , and $|r(t) - r(0)|$ represents the displacement of the penetrant molecule during time t . The influence of the modification on the pore structure of the ZMS was analyzed according to a change in the diffusion coefficients of the NH_4^+ in the pores [8].

To compare ion-exchange rates of the NH_4^+ with Si-OH in the ZMS and with $-\text{COONa}$ in the POSS-modified ZMS, respectively, the transition-state energies (or active energies) of the two exchange processes were calculated by MDS (DMol³ transition state search program) of MSS [9].

4 RESULTS AND DISCUSSION

Fig. 1 shows an ESI mass spectrum of the TMN-POSS precursor derived from the reaction of RHA and $[\text{Me}_4\text{N}]\text{OH}$. The peak at 1134.7 Da represents a complete TMN-POSS cage structure (theoretic value: 1136.39 Da). It is significant to provide the possibility of generating narrow distribution (in the range of 984.8–1354.6 Da) of the TMN-POSS cages for the modification [10]. There are incomplete multistructural POSSs in the other ranges. These open structural POSSs contain some active groups formed during

the reaction such as hydroxyls which could be still condensed by Si-OH groups on the ZMS surface [11].

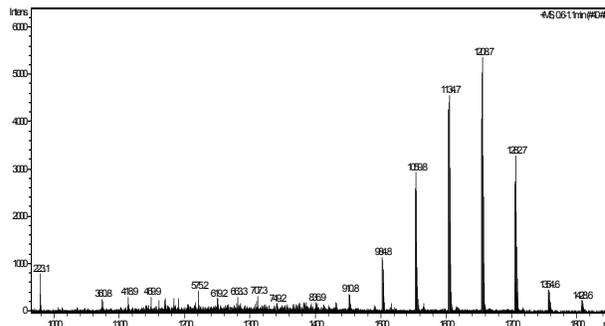


Figure 1: ESI mass spectrum of the TMN-POSS precursor derived from the reaction of RHA and $[\text{Me}_4\text{N}]\text{OH}$.

Fig. 2 shows an ESI mass spectrum of the $\text{POSS}^{-\text{COOH}}$ derived from the reaction of $\text{POSS}^{-\text{COOC}-3(\text{Me})}$ and CH_3OH . Most of peaks in some areas can be assigned to cage structures, for example, the peaks at 1593.5, 1670.6, 1747.7, 1824.8, 19024.8, 1980.9 and 2057.9 Da represent $\text{POSS}^{-\text{COOH}}$ cage structures with 2–8 COOH groups in the range of 1500–2100 Da. Usually POSS is an oligomer containing 6–12 Si atoms; i.e., each POSS contains 6–12 active groups. Therefore, the activity of these POSS modifiers can be enhanced multiply for the NH_3-N exchange when the mesoporous ZMS surface is modified with POSS. This process will not reduce the pore diameter (PD) more than 20% and will not affect the diffusion, adsorption and ion exchange of NH_3-N in the ZMS.

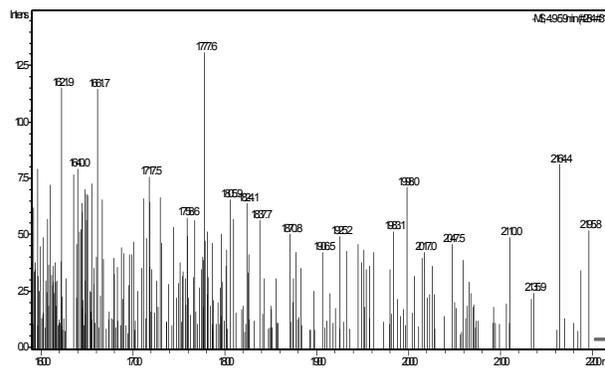


Figure 2: ESI mass spectrum of the $\text{POSS}^{-\text{COOH}}$ derived from the reaction of $\text{POSS}^{-\text{COOC}-3(\text{Me})}$ and CH_3OH .

Fig. 3 shows an ideal modified ZMS pore structure: the $\text{POSS}^{-\text{COONa}}$ cube connects to ZMS pore surface by a hydroxyl (in an incomplete POSS) or a carboxyl (in a complete POSS). In this case, an original active group for the ion exchange changes and increases to seven active groups by the connection of a $\text{POSS}^{-\text{COONa}}$ cube with eight active groups. That will enhance the ion exchange capacity greatly.

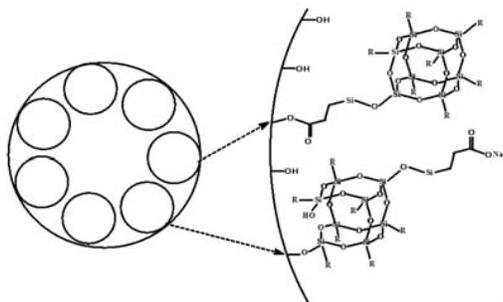


Figure 3: An ideal modified ZMS pore structure: the $\text{POSS}^{-\text{COONa}}$ cube connects to ZMS pore surface by a hydroxyl (in an incomplete POSS) or a carboxyl (in a complete POSS).

Fig. 4 gives two SEM images describing the ZMS structures before (a) and after (b) the modification. The image (a) illustrates the clear ZMS monoliths but it changes to mistiness after the modifying with $\text{POSS}^{-\text{COONa}}$ particles (see Fig. 4 b). That demonstrates partial POSS modifiers connected on the outside of the ZMS, which still can contribute to the ion exchange. These POSS modifiers cover the ZMS inside and outside surface with chemical bonds and cannot be washed during the modification, which will contribute to enhance an ion-exchange capacity during the NH_4^+ removal.

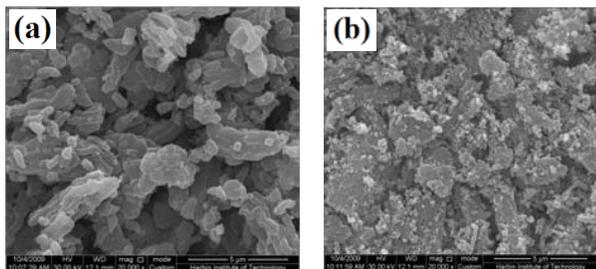


Figure 4: SEM images describing the ZMS structures before (a) and after (b) the modification.

Fig. 5 a–d display the nitrogen-sorption isotherms and the corresponding pore-size-distribution curves of the original ZMS and the modified ZMS, respectively. For the original ZMS (Fig. 5 a and b), a type isotherm with a steep hysteresis loop at relative pressure P/P_0 of 0.45–0.75 can be observed, indicating that this sample has mesoporous structure with certain pore size. The Barrett–Joyner–Halenda (BJH) pore-size-distribution curve further confirms the average meso-pore diameter centered at 0.057 nm. The sample exhibits a BET surface area of $620.0 \text{ m}^2/\text{g}$ with a total pore volume of $0.66 \text{ cm}^3/\text{g}$. However, after the modification (Fig. 5 c and d) 1) a irregular isotherm with two hysteresis loops at relative pressures P/P_0 of 0.50–0.78 and 0.78–0.99 can be observed, indicating a wider pore size distribution (average pore size increases to 0.122 nm). That might result from pore expanding by the modification. 2) A BET surface area decreases to $374.7 \text{ m}^2/\text{g}$ with a total pore

volume of $0.57 \text{ cm}^3/\text{g}$, blocking and closing some small pores by the modifiers so that the partial bigger modifiers connect to the ZMS outside surface (also see Fig. 4 b).

Although the average pore size increases and the BET surface area decreased after the modification, the $\text{NH}_3\text{-N}$ removal capacity still increased, for example, the enhancement values of percentage for absorbed NH_3^+ in the POSS-modified ZMS were 108.7%, 171.3% and 81.8% for water containing 2, 5 and 10 mg/L NH_3^+ , respectively, as shown in Fig. 6. This increase in removal capacity was a contribution of the ion exchange efficiency from both modifiers bonded to the ZMS surface inside and outside.

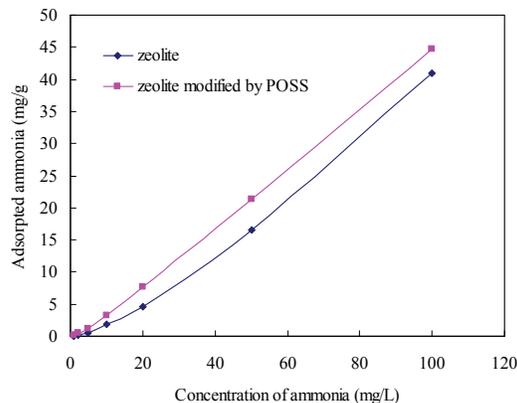


Figure 6: Removal capacity of the NH_3^+ in the ZMS and the POSS-modified ZMS.

Fig. 7 shows two pairs of curves for NH_3^+ diffusion in the original ZMS and the POSS-modified ZMS, respectively. Two estimated diffusion coefficients (DC) were determined from the slopes ($\sim 6 \text{ DC}$) of the plots. The slope ($1.52 \times 10^{-9} \text{ cm}^2/\text{s}$) of MSD for NH_3^+ diffusion in the POSS-modified ZMS is much smaller than that ($3.29 \times 10^{-9} \text{ cm}^2/\text{s}$) in the original ZMS. This result can be ascribed to a physical barrier provided from the POSS modifiers to block NH_3^+ diffusion in the ZMS pore, leading to more chances for NH_3^+ to be absorbed and exchanged.

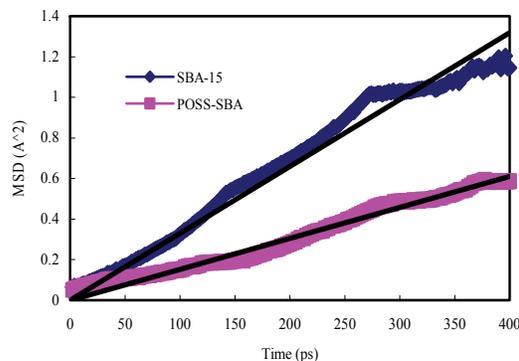


Figure 7: Curves of NH_3^+ diffusions in the original ZMS (up) and the POSS-modified ZMS (down).

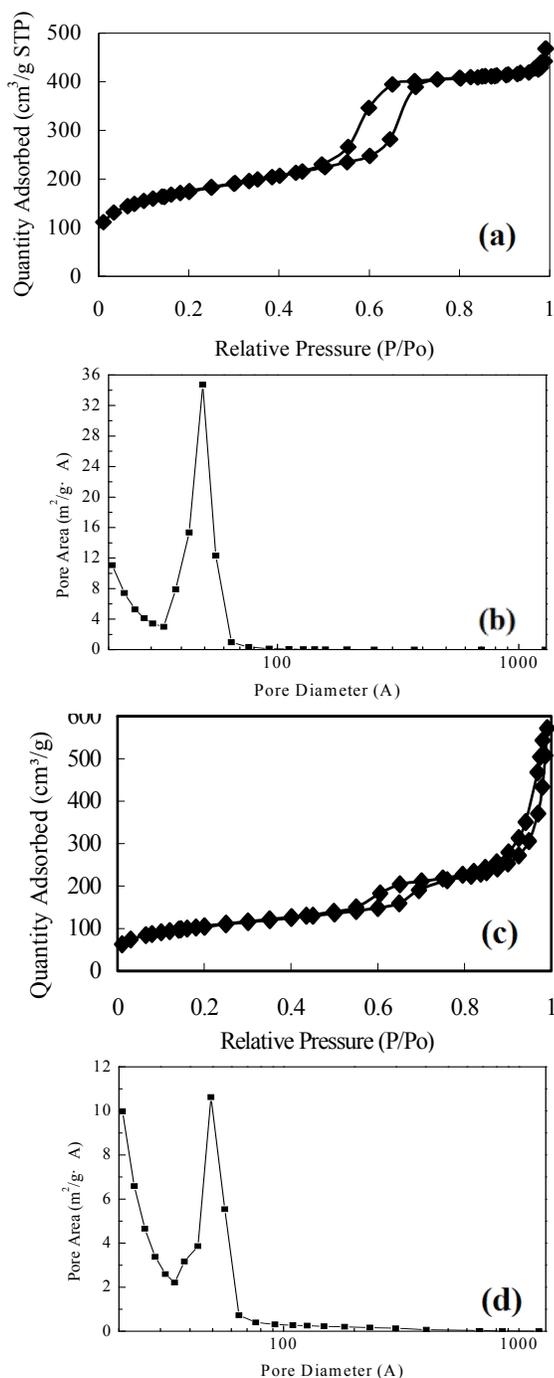


Figure 5: The nitrogen-sorption isotherms and the pore-size-distribution curves of the original ZMS (a, b) and the POSS-modified ZMS (c, d), respectively.

The transition-state energies of the reactions of the NH_3^+ ion exchange with Si-OH in the original ZMS and with -COONa in the POSS-modified ZMS are -0.058 and -0.039 Ha (activation energies: 590.57 and 154.31 $\text{kJ}\cdot\text{mol}^{-1}$), respectively, indicating easily ion exchanging after the

modification. In the POSS-modified ZMS system, -COONa active group can easily release Na^+ due to a stable bond electronic structure in hybrid $2p$ orbit for the -COO- group, leading to an enhancement of the NH_3^+ ion-exchange capacity in the modified system.

5 CONCLUSIONS

The mesoporous zeolite molecular sieve (ZMS) can be modified using POSS with carboxyl sodium terminal groups as ion-exchange active groups. For modifying the ZMS with the average meso-pore diameter centered at 0.057 nm, although the average pore size increases and the BET surface area decreased after the modification, the $\text{NH}_3\text{-N}$ removal capacity still can be enhanced, which was a contribution of the ion exchange efficiency from both modifiers bonded to the ZMS surface inside and outside.

This enhancement can be validated using calculation of the diffusion behavior of NH_3^+ in the pores of the original ZMS (higher diffusion coefficient) and the POSS-modified ZMS (lower diffusion coefficient) and comparison transition-state energy of the NH_3^+ ion exchange with Si-OH in the original ZMS (higher activation energies) and with -COONa in the POSS-modified ZMS (lower activation energies).

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