Removal of ammonium from aqueous solution by three modified molecular sieves: a comparative study

Ying An

ABSTRACT

Molecular sieves (Ms) modified either by treatment with a NaCl solution, or by microwave treatment, or by both NaCl and microwave treatment were employed to promote the removal of ammonium from aqueous solution. Parameters such as NaCl concentration, NaCl stirring time, microwave power and microwave irradiation time were optimized with respect to ammonium removal. The specific surface area, structural characteristics and porous properties of both raw and modified Ms were studied using N2 adsorption–desorption, scanning electron microscopy, X-ray fluorescence, and energy dispersive spectroscopy. The results demonstrate that NaCl-microwave modified Ms had the highest capacity to remove ammonium (4.32 mg g\(^{-1}\)), followed by NaCl modified Ms (3.41 mg g\(^{-1}\)), microwave modified Ms (3.40 mg g\(^{-1}\)), and raw Ms (2.37 mg g\(^{-1}\)). Optimization of the modification conditions using a response surface methodology resulted in a 1.94 mol L\(^{-1}\) NaCl solution, a microwave power of 400 W and an irradiation time of 5.1 min. NaCl-microwave modification effectively increased the removal capacity of ammonium by increasing the sodium content, modifying the surface morphology, and enlarging both the surface area and the pore volume for the Ms.

Key words | ammonium removal, microwave modification, molecular sieve, NaCl modification

INTRODUCTION

Black water agglomerate has become a prominent environmental problem in China and is characterized by its black color and malodorous gas (Zhang et al. 2010; Yu et al. 2016). The phenomenon is induced by cyanobacteria bloom (Wang et al. 2014), the concentration of which is increased by the accumulation of phosphorus, nitrogen, and carbon discharged from domestic, industrial, agricultural and rural wastewater (Zhou et al. 2015). Poor environmental water quality has negatively influenced animal and human health and impeded sustainable economic and social development. To address the problem, the Chinese government has implemented the Action Plan for Prevention and Control of Water Pollution (Li et al. 2016) with the goal that quantity of black and odorous water bodies in built-up areas in cities at prefecture level and above will be controlled within 10% by 2020 and in urban built-up areas generally will be eliminated by 2030. New techniques for preventing, controlling, and remediating water pollution are urgently required in order to achieve these major pollution reduction goals (Wen et al. 2016).

Environmental nitrogen in the form of ammonium is one of the critical factors causing eutrophication and producing toxic substances that lead to black water agglomerate. According to the result of the first national census on pollution sources in China (An et al. 2013), ammonium mainly originates from domestic sources. Thus, the treatment of domestic wastewater in wastewater treatment plants (WWTPs) plays a major role in the reduction of environmental ammonium. Currently, biological treatment processes including anaerobic–anoxic–oxic, oxidation ditch, anaerobic–oxic, and sequencing batch reactor are most commonly used in WWTPs across China (Sun et al. 2016). However, the effectiveness of these ammonium removal techniques largely depends on the water temperature, and during cold winters in China, achieving ammonium concentrations that meet the national levels required for wastewater effluent is challenging (Zhang et al. 2016).

Zeolite, a porous aluminosilicate mineral, has a negatively charged crystallized framework structure (Huang et al. 2015), which coordinates cations. The skeleton...
structure gives it a strong capacity for ion exchange and adsorption (Montegut et al. 2016). Furthermore, zeolite has shown strong selective removal of ammonium from wastewater at low temperatures (Wu et al. 2008) and has therefore become widely used to enhance the biological removal of ammonium. Biological treatment processes utilizing zeolites can be divided into several forms in the light of the zeolite particles’ size: zeolite media biological filters (particle size of 2 mm and above) (Feng et al. 2015; Bao et al. 2016), zeolite media fluidized beds (particle size of 1 mm) (Lahav & Green 1998), and powdered zeolite aided suspended growth activated sludge processes (particle size under 1 mm) (Wu et al. 2008). Molecular sieves (Ms), a synthetic zeolite, have a crystalline lattice structure, homogeneous pore sizes, and neatly arranged pore channels (Lad & Makkawi 2014). Compared with natural zeolite, Ms are capable of highly efficient ammonium removal, and further improvements to the ion exchange and adsorption capabilities can be accessed through modification. Many techniques for the modification of natural zeolite have been reported, including mineral salt modification (Lin et al. 2013; Alshameri et al. 2014b), thermal modification (Lei et al. 2008), acid modification (Huang et al. 2015), and ultrasonic modification (Ojumu et al. 2016). In order to improve the efficiency of ammonium removal from water, polyhedral oligomeric silsesquioxane (POSS)-modified mesoporous Ms (Wang et al. 2011), magnetic Ms (Yang et al. 2015), and chitosan-coated meso-microporous Ms (Guo et al. 2015) were synthesized. However, there are few papers reporting the effects of modification of Ms by treatment with NaCl or microwave irradiation.

The aim of this research was to enhance the ammonium removal from aqueous solution using NaCl modified Ms, microwave modified Ms, and NaCl-microwave modified Ms. The modification conditions required to achieve optimum ammonium removal were determined. N₂ adsorption–desorption, scanning electron microscopy (SEM), X-ray fluorescence (XRF), and energy dispersive spectroscopy (EDS) were used to study the specific surface area (SSA), structural characteristics and porous properties of both the raw and modified Ms.

**MATERIAL AND METHODS**

**Materials**

Raw Ms (with a particle size of 3–5 mm) were provided by Shanghai Zeolite Molecular Sieve Co., Ltd, China. All chemicals used, such as sodium chloride (NaCl), hydrochloric acid (HCl), ammonium chloride (NH₄Cl), and sodium hydroxide (NaOH), were of analytical grades.

**Preparation of NaCl modified Ms**

To obtain optimum NaCl modification of raw Ms, parameters such as NaCl concentration and stirring time were investigated as follows:

1. **NaCl concentration**

The concentration of a NaCl solution was varied from 0.2 to 2 mol L⁻¹ (0.2, 0.5, 0.8, 1.0, 1.2, 1.5, 1.8, 2.0 mol L⁻¹) with a zeolite/solution ratio maintained at 20 g L⁻¹. The suspension was stirred using a magnetic stirring apparatus at a rate of 150 rpm at room temperature (25 ± 2 °C) for 3 h. Ms were separated from the suspension by filtration, flushed with deionized water until no chloride was present in the supernatant, and then dried for 24 h at 100 °C.

   The capacity of the modified Ms to remove ammonium (mg g⁻¹) was monitored according to a literature procedure (Alshameri et al. 2014a): an NH₄Cl solution containing 50 mg of nitrogen per litre (mg-N L⁻¹) was prepared with deionized water, and the previously modified Ms were added, with a Ms/solution ratio of 5 g L⁻¹. The suspension was stirred using a magnetic stirrer at 150 rpm 25 ± 2 °C for 3 h.

2. **NaCl stirring time**

A 1 mol L⁻¹ NaCl solution containing Ms at a zeolite/solution ratio of 20 g L⁻¹ was prepared as described above. The modification time was varied from 45 to 240 min (45, 60, 90, 120, 150, 180, 240 min). The capacity of the modified Ms to remove ammonium (mg g⁻¹) was monitored according to a literature procedure (Alshameri et al. 2014a).

**Preparation of microwave modified Ms**

To find the optimum microwave modification conditions, parameters such as microwave power and irradiation time were investigated as follows:

1. **Microwave power**

Ms (5 g) were irradiated in a microwave oven under microwave power from 320 to 800 W (320, 400, 530, 600, 680, 800 W) for 5 min and then cooled to room temperature (25 ± 2 °C). The capacity of the modified Ms to remove ammonium (mg g⁻¹) was monitored...
according to a literature procedure (Alshameri et al. 2014a).

(2) Microwave irradiation time

Ms (5 g) were irradiated in a microwave oven under microwave power of 400 W for 1, 2, 3, 4, 5, 6, 7, 8 min, and then cooled to room temperature. The capacity of the modified Ms to remove ammonium (mg g⁻¹) was monitored according to a literature procedure (Alshameri et al. 2014a).

Preparation of NaCl-microwave modified Ms

In the light of the range with significant change determined by the optimal NaCl and microwave modification conditions tests, the three-factor, three-level Box–Behnken experiment design for response surface methodology (RSM) (Xu et al. 2016) was adopted for the purpose of acquiring the optimal NaCl-microwave modification conditions. Three impact factors were chosen: NaCl concentration (X₁), microwave power (X₂) and microwave irradiation time (X₃). Each impact factor was coded at three levels, /C₀, 0 and /C₀₁, corresponding to the minimum, median and maximum values tested, respectively. The factors and levels of Box–Behnken experiment design, along with the corresponding quantities, are expressed in Table 1. A total of 17 experiments, listed in Table 2, were designed by design expert software with version 8.0.6 (Stat-Ease, Inc., USA).

Characterization

The raw Ms and Ms modified under the optimized conditions were characterized by N₂ adsorption–desorption, SEM, XRF, and EDS. SEM observations were carried out using a Zeiss Merlin Compact instrument. XRF analyses were conducted on a Thermo Scientific ARL PERFORM’X apparatus. EDS was measured by a Bruker Quantax analyzer. The diameter, SSA, and pore volume of the prepared samples were determined at /C₀₁95.8 °C by nitrogen gas sorption–desorption using a Micrometrics ASAP 2460 apparatus.

RESULTS AND DISCUSSION

NaCl modified Ms

The effects of varying the NaCl concentration and stirring time on the capacity of modified Ms to remove ammonium are shown in Figure 1 (initial ammonium concentration of 50 mg·N·L⁻¹). The capacity of the modified sieves to remove ammonium increased continuously with increasing NaCl concentration and stirring time. The capacity peaked at 3.41 mg·g⁻¹ when a 1.0 mol·L⁻¹ NaCl concentration and 180 min stirring time were used, and then stabilized with no further improvement with increasing NaCl concentration and stirring time. It can be concluded that a NaCl concentration of 1.0 mol·L⁻¹ and stirring time of 180 min were the optimum modification conditions for the NaCl modified Ms.

The EDS spectra analyses of raw Ms and NaCl modified Ms (Figure 4) showed that the Na content of the NaCl modified Ms (9.5%) was higher than that of the raw Ms (8.6%).
A higher sodium content resulted in an increased capacity to remove ammonium (Lei et al. 2008). We postulate that the Na\(^+\) ions displaced positive ions with a larger ionic radius, such as Ca\(^{2+}\), from the pores of Ms, thereby enlarging the pore diameters and increasing the capacity of the sieves to remove ammonium. At 1 mol L\(^{-1}\) NaCl concentration, the phenomenon became slow with the balance of ion exchange, and further increasing the NaCl concentration had a negligible impact on improving the removal of ammonium.

**Microwave modified Ms**

The effects of varying the microwave power and irradiation time on the capacity of modified Ms to remove ammonium are shown in Figure 2. It was found that raising the microwave power and irradiation time enhanced the removal of ammonium. When the microwave power used during modification was enhanced from 0 W to 400 W, the subsequent removal of ammonium was significantly improved from 2.37 mg g\(^{-1}\) to 3.40 mg g\(^{-1}\), which may be ascribed to the development of the pore structure on the surface of microwave modified Ms (Table 4). Small quantities of absorbed water inside the Ms could be completely desorbed as the microwave irradiation causes heating to 300–400 \(^\circ\)C. Following this, the Ms began to absorb microwave radiation, resulting in the elimination of impurities from inside the pore canals, the enlargement of pore diameter, an increase in micropores and an improved capacity to remove ammonium. When the microwave power surpassed 400 W, high-intensity microwaves may have caused some damage to the surface and inner structure of the modified Ms and...
changed the distribution of ions. This explains the gradual decrease in ammonium removal from 3.40 mg g\(^{-1}\) to 2.95 mg g\(^{-1}\) as the microwave power increased from 400 W to 800 W. Similar conclusions are reported for microwave treatment modifications to absorbent materials such as coal-based activated carbon (Ge et al. 2016), activated carbon derived from coconut husk and smectite (Foo & Hameed 2012; Franco et al. 2016).

The optimal microwave input power of 400 W found previously was used to probe the effect of microwave irradiation time on the capacity of Ms to remove ammonium. Prolonging the irradiation time from 1 min to 5 min resulted in an enhancement in the amount of ammonium removed, from 3.13 mg g\(^{-1}\) to 3.40 mg g\(^{-1}\). Following irradiation for periods longer than 5 min, the ammonium capacity of the sieves declined sharply with irradiation time. Similarly to the results seen previously during the optimization of microwave power, irradiation initially promotes the formation of inner pores while maintaining the open structure. However, above 5 min, the long-term accumulation of microwave radiation raises the inner temperature of the Ms, leading to overheating, which results in the collapse of the inner pores and structure of the Ms.

**NaCl-microwave modified Ms**

The experimental and model-predicted values for the capacity of Ms modified by NaCl solution and by microwave treatment to remove ammonium (mg g\(^{-1}\)), were taken as response value Y, and are presented in Table 2. A Box–Behnken design analysis with input factor variables NaCl concentration (X\(_1\)), microwave power (X\(_2\)) and microwave irradiation time (X\(_3\)), resulted in the following quadratic polynomial regression equation for predicting the optimum capacity of modified sieves to remove ammonium:

\[
Y = 2.0 + 0.65X_1 + 0.0050X_2 + 0.30X_3 - 0.00013X_1X_2 \\
- 0.0038X_1X_3 - 0.000057X_2X_3 - 0.15X_1^2 - 0.0000054X_2^2 \\
- 0.025X_3^2
\]

The results of an analysis of variance (ANOVA) for this response surface quadratic model are described in Table 3. The Model F-value of 42.90 means the model is significant (there is only a 0.01% chance that a ‘Model F-Value’ this large could occur because of noise). Values of ‘Prob > F’ less than 0.0500 indicate model terms are significant, while values greater than 0.1000 indicate model terms are not significant. ANOVA analysis implies that X\(_1\), X\(_2\), X\(_3\), X\(_1^2\), X\(_2^2\), X\(_3^2\) are significant model terms. There is a 9.62% chance that a ‘Lack of Fit F-Value’ of 4.31 could occur due to noise. The relationship between the values reached in practice and theoretical values by the quadratic polynomial regression equation is shown in Figure 3. It was observed that the maximum number of predicted responses and their residuals for each run were reasonably close to the diagonal line. The coefficient of determination (R\(^2\)) value is 0.9822, implying a good correlation between the experimental and model-predicted data of the response. The ‘Pred R\(^2\)’ of 0.7643 is in reasonable conformity to the ‘Adj R\(^2\)’ of 0.9593. The ‘Adeq Precision’ value of 18.391 indicates

<table>
<thead>
<tr>
<th>Source</th>
<th>Mean square</th>
<th>F-value</th>
<th>Prob &gt; F</th>
</tr>
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<tbody>
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<td>Model</td>
<td>0.080</td>
<td>42.90</td>
<td>&lt;0.0001**</td>
</tr>
<tr>
<td>X(_1)-NaCl concentration</td>
<td>0.15</td>
<td>82.31</td>
<td>&lt;0.0001**</td>
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<tr>
<td>X(_2)-microwave power</td>
<td>0.18</td>
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<td>&lt;0.0001**</td>
</tr>
<tr>
<td>X(_3)-microwave irradiation time</td>
<td>0.012</td>
<td>6.34</td>
<td>0.0400*</td>
</tr>
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<td>X(_1)X(_2)</td>
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<td>0.4317</td>
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<tr>
<td>X(_1)X(_3)</td>
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<td>0.7008</td>
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<td>X(_2)X(_3)</td>
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<td>2.08</td>
<td>0.1920</td>
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<tr>
<td>X(_1^2)</td>
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<td>16.09</td>
<td>0.0051**</td>
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<td>X(_2^2)</td>
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<td>64.34</td>
<td>&lt;0.0001**</td>
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<tr>
<td>X(_3^2)</td>
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<td>118.89</td>
<td>&lt;0.0001**</td>
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<tr>
<td>Lack of fit</td>
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<td>4.31</td>
<td>0.0962</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.0077</td>
<td></td>
<td></td>
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*Correlation is significant at the 0.05 level (two-tailed).
**Correlation is significant at the 0.01 level (two-tailed).
a tolerable signal to noise ratio. A ratio exceeding 4 is desirable. In conclusion, this model can be available for adequately describe the test data (Esfandiar et al. 2014).

A contour map is an intuitive way to express a regression equation. Three contour maps, each with two variables and with the absent third variable fixed at level 0, are illustrated in Figure 4. The contour centers are located within all three contour maps, intuitively reflecting the interaction effect between all factors. This also indicates that the most favorable conditions are within the range of the factor levels designed into this study. The interaction effect between the microwave power and irradiation time factors turned out to be the most significant (i.e. changing one of these variables influences the other most strongly), while the interaction effect between the NaCl concentration and microwave power ranked second, followed by that between NaCl concentration and irradiation time. When microwave power and irradiation time are fixed, the ammonium removal capacity increases with an increase in NaCl concentration. It was also observed that there was remarkably high ammonium removal capacity at the low microwave power of 400 W. However, after increasing microwave power beyond 400 W, there was a decrease in ammonium removal capacity at fixed NaCl concentration and irradiation time. A similar trend was observed at irradiation time intervals ranging from 2 to 8 min. Initially, the ammonium removal capacity increased at a rapid rate, and after the time interval of 5 min, no ammonium removal capacity increase was observed.

By using the RSM, the optimum capacity to remove ammonium (4.34 mg g⁻¹) was obtained when Ms had been treated with a 1.94 mol L⁻¹ NaCl solution, at a microwave power of 400 W, for 5.1 min. Three parallel tests were conducted using the optimized modification conditions to determine the validity of the Box–Behnken RSM. The average experimental removal value of 4.32 mg g⁻¹ is close to

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**Figure 4** Response contour lines of microwave power and NaCl concentration (a), microwave irradiation time and NaCl concentration (b), and microwave power and irradiation time (c) on ammonium adsorption by modified MS at an initial ammonium concentration of 50 mg N L⁻¹.
the model-predicted value, indicating that the model used here is credible. The costs of sodium chloride (NaCl > 98.5%) and Ms were estimated at 340 $/ton and 7,000 $/ton, respectively. Therefore, the chemical cost for this technique was 1.86 $/g N.

Nowadays, WWTPs need a new method to resolve the problem of ammonium exceeding standard limits under low wastewater temperature, which has the advantages of not influencing normal operation of WWTP, not stopping production, not reducing removal efficiencies of other pollutants, and so on. Based on this idea, we developed a new process, in which, the influent solution was fed to one column in upflow mode, using a peristaltic metering pump. Then zeolite in the column utilized its physical and chemical function to removal ammonium from wastewater. After a programmed period of time, the system switched to the regeneration mode. The regeneration solution with high salinity (5 g L⁻¹ Na⁺) was pumped to the column in the downflow mode. Meanwhile, the regeneration solution with ammonium desorbed was collected and pumped to the membrane bioreactor for bio-regeneration. Finally, the bio-regeneration solution (ammonium concentrations below 1 mg L⁻¹ during 210-d operation) came out of the MBR for reuse. The cyclic process went on. In our future study, NaCl-microwave modified Ms with high capacity to remove ammonium would be employed to replace zeolite on this new process.

**Raw and modified Ms characteristics**

SEM and EDS spectral analyses of the raw Ms, NaCl modified Ms, microwave modified Ms, and NaCl-microwave modified Ms are depicted in Figure 5. Compared with the smooth surface of raw Ms, modified sieves were found to be rougher, and relatively loose with numerous granules. The overall skeleton structure was not changed by NaCl or microwave treatment, and the main chemical elements of the skeleton structure (O, Si, Al and Na) were present. However, it was observed that the sodium content in the Ms surfaces increased from 8.6% to 9.3%, 9.3%, and 10.7%, respectively.

![Figure 5](https://iwaponline.com/wst/article-pdf/76/6/1378/449372/wst076061378.pdf)
following modification by NaCl, microwave, and NaCl-microwave treatments, respectively. The sodium content in the surface of Ms subjected to both NaCl and microwave treatments was found to be higher than that in Ms treated with either NaCl or microwave irradiation. These results are in good agreement with those obtained from XRF (Table 4). A higher Si/Al ratio corresponds to a better selectivity for ammonium (Alshameri et al. 2014b). From Table 4, it can be seen that the Si/Al ratio increases from 1.21 to 1.32, 1.24, and 1.32 following modification by NaCl, microwave, and NaCl-microwave treatments, respectively.

N₂ adsorption-desorption isotherms of the raw Ms, NaCl modified Ms, microwave modified Ms, and NaCl-microwave modified Ms are displayed in Figure 6. The adsorption isotherms above are all of type IV in terms of International Union of Pure and Applied Chemistry (IUPAC) classification, with the characteristic type H3 hysteresis loop (Ge et al. 2016; Korichi et al. 2012), which is associated with capillary condensation occurring in mesopores (Yu et al. 2015b). This indicates there are mesopores in all four samples (Hasan et al. 2015). The overall type IV appearance of the isotherms did not change after

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Chemical composition of raw Ms, NaCl modified Ms, microwave modified Ms, and NaCl-microwave modified Ms (Wt%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Si/Al</td>
</tr>
<tr>
<td>Raw Ms</td>
<td>1.21</td>
</tr>
<tr>
<td>NaCl modified Ms</td>
<td>1.32</td>
</tr>
<tr>
<td>Microwave modified Ms</td>
<td>1.24</td>
</tr>
<tr>
<td>NaCl-microwave modified Ms</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Figure 6 | N₂ adsorption–desorption isotherms of raw Ms (a), NaCl modified Ms (b), microwave modified Ms (c), and NaCl-microwave modified Ms (d).
modification. However, the NaCl and NaCl-microwave treated sieves showed a significant increase in the amount of nitrogen adsorbed and enhanced hysteresis. A corresponding lower quantity of mesopores was observed in the raw and microwave modified Ms samples (Yu et al. 2015a). The hysteresis loops of the NaCl and NaCl-microwave modified Ms closed when the relative pressure \((P/P_0)\) reached 0.4 on the desorption isotherm, indicating that there was also a range of smaller mesopores in these materials. The adsorption curves increased rapidly when the relative pressure \((P/P_0)\) approached 1.0, which showed that macropores were detected in all samples (Yu et al. 2015b).

Barrett-Joyner-Halenda (BJH) diameter distributions (adsorption branch) of the raw and three modified Ms are shown in Figure 7. Two types of mesopore structure clearly exist in the raw Ms. The narrower mesopores (diameter ~3 nm) are still present following modification. The wider mesopores (diameter ~30 nm) disappeared upon NaCl or NaCl-microwave modification, and new mesopores and macropores were detected with peak diameters of ~44 nm and 72 nm, respectively, in these samples.

Textural properties of the sieves are listed in Table 5. The total SSA of raw Ms was found to be 21.6 m² g⁻¹, with a total pore volume of 0.0459 cm³ g⁻¹, of which micropores contributed only 10.2% of the SSA and 1.9% pore volume, while mesopores and macropores were the major contributors to the SSA and pore volume. The total pore volume and their size distribution determine the capacity of the sieves to remove ammonium; only molecules with a diameter smaller than the Ms pore diameters can enter the inner structure of the sieves to undergo ion exchange. The average pore size of NaCl and NaCl-microwave modified sieves is reduced compared with raw Ms but is still larger than molecular ammonium. The total SSA and pore volume of these samples are also increased, increasing the number of adsorptive sites on the surface and thus promoting the adsorption of ammonium. Meanwhile, the total SSA of the Ms decreased following microwave modification, with a corresponding increase in total pore volume and average pore size. It is likely this can be attributed to dredging of the Ms’ pore canals during microwave irradiation, which consequently increased the total pore volume and average pore size. Microwave heating may also lead to partial overheating, which changes the partial pore size structure and creates new micropores. However, as micropore SSA means only a small proportion of the total SSA, the increase due to this effect is not pronounced.

### CONCLUSION

Raw Ms were modified to investigate their potential to remove ammonium from aqueous solution in batch experiments. Optimization of a single impact factor resulted in

### Table 5 | Textural properties of raw Ms, NaCl modified Ms, microwave modified Ms, and NaCl-microwave modified Ms

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET (m² g⁻¹)</td>
<td>Micropore (m² g⁻¹)</td>
</tr>
<tr>
<td>Raw Ms</td>
<td>21.6</td>
<td>2.2</td>
</tr>
<tr>
<td>NaCl-modified Ms</td>
<td>50.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Microwave modified Ms</td>
<td>19.8</td>
<td>3.0</td>
</tr>
<tr>
<td>NaCl-microwave modified Ms</td>
<td>48.7</td>
<td>1.8</td>
</tr>
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</table>


*Calculated by t-plot method.

†Single-point adsorption total pore volume of pores <40.4 nm diameter at \(P/P_0 = 0.95\).

‡BJH adsorption average pore diameter (4 V/A).
either 1.0 mol L\(^{-1}\) aqueous solution of NaCl stirred for 180 min, or irradiation with a microwave power of 400 W for 4 min, which yielded Ms with the capacity to remove 3.41 mg g\(^{-1}\) and 3.40 mg g\(^{-1}\) of ammonium, respectively. Ms modified by both NaCl treatment and microwave irradiation had the highest capacity to remove ammonium (4.32 mg g\(^{-1}\)), followed by NaCl modified Ms (3.41 mg g\(^{-1}\))، microwave modified Ms (3.40 mg g\(^{-1}\)), and raw Ms (2.37 mg g\(^{-1}\)). Optimization of the modification conditions using the RSM resulted in a 1.94 mol L\(^{-1}\) NaCl solution, a microwave power of 400 W and an irradiation time of 5.1 min. Modification under these conditions enhanced the ammonium capacity of the sieves from 2.37 mg/g (raw) to 4.32 mg/g, primarily due to the increased sodium content (24%), SSA (125%) and pore volume (34%) of the Ms. These NaCl-microwave modified Ms can be regarded as a good material for the ammonium removal from aqueous solution, and the results reported herein justify further studies on the ammonium removal from real wastewater.

**ACKNOWLEDGEMENTS**

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