

In-situ Removal of Ammonia from Water of Live Transports of Fish

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Abstract—In-situ removal of ammonia from water is an important issue in live transports of fish. It has been believed that the adsorption of ammonia by a suitable adsorbent is an economic and possible method. In this study the zeolites (CVB 600 and CVB712) with low molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ were used as adsorbents to remove ammonia to reduce the concentration of ammonia in water with live fish. The mechanism of the adsorption of ammonia on these zeolites was obtained through the deduction of the Fourier Transform Infrared Spectroscopy (FTIR) spectra. According to the analysis of these IR spectra, two possible adsorption mechanisms were deduced: (1) NH_4^+ adsorption, which gave stretching vibration at 2836cm^{-1} and bending vibration 1460cm^{-1} . (2) $\text{O}_2\text{Al}^+\text{H-NH}_3$ adsorption: the adsorption at 3256cm^{-1} (NH asymmetry stretching vibration), 3060cm^{-1} (NH symmetry stretching vibration), 1642cm^{-1} (NH asymmetry bending vibration), 1098cm^{-1} (NH symmetry bending vibration) gave the evidences of the existence of $\text{O}_2\text{Al}^+\text{H-NH}_3$ on these zeolites. The interaction of ammonium with $\text{O}_2\text{Al}^+\text{H}$ is discussed in detail in this study. To reduce the cost of zeolites as adsorbents, the regeneration of used adsorbents was also studied. The original and used zeolites were heated at various temperatures to obtain their XRD spectra for further analysis. Experimental results showed that these zeolites used in our study ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio=5 and 11.5) will collapse over 350°C . It is suggested that temperature of the regeneration of these zeolites should be below 350°C .

Index Terms—adsorption, IR, XRD, interface

I. INTRODUCTION

Today, live fish transport is an important issue to be faced. However, water quality may pose a vital threat to fish in live transport [1]. Fish may be less capable of adjusting to rapid changes in pH and water quality [2]. Waste products accumulate in tanks during transport [3] and ammonia and CO_2 are the most likely to give concern. Especially ammonia toxicity may be a considerable risk [3]. High ammonia concentrations affect survival, decrease growth and lead to physiological malfunctions [4]. For example, a Total Ammonia uptake (TAN) of over 1 mg/l cannot be tolerated by cod in a rearing situation [2].

To solve this problem, many techniques such as biodegradation [5], catalytic oxidation [6], membrane separation [7], and ion-exchange adsorption by a cation exchanger [8] etc. are suggested for the removal of ammonia in the aqueous solution. Among them, ion exchange adsorption using zeolites is feasible and most popular because of its ease of operation and relative low cost. Sprynskyy *et al.* [9] assessed the ability of zeolitic tuff such as mordenite, which has a connected framework of SiO_4 and AlO_4 tetrahedra. These tetrahedra linked to each other by shared oxygen atoms. Each AlO_4 tetrahedron in the framework bears a net negative charge that is balanced by an extra framework cation. The smallest unit of the structure of zeolite is represented by $\text{M}_n[(\text{AlO}_2)_x(\text{SiO}_2)_y]\cdot w\text{H}_2\text{O}$, where n is the valence of cation M , w is the number of water molecules per unit cell, x and y are the total number of tetrahedral atoms per unit cell.

Zeolites are used widely in the petroleum refining and chemical industries as selective adsorbents, catalysts and ion exchangers. Many recent studies using zeolites as catalysts in pollution abatement are under studying overall the world. There are amount of research works have been published in the removal of ammonia from water [10]-[14]. Most of the zeolites used in these studies are natural zeolites. However, there are many synthesized zeolites recently. For example, Tsai *et al.* [15] used the synthesized zeolites to remove organic compounds from the aqueous solution by adsorption. Chun Jin *et al.* [16] discussed the synthesis of large spherical mesoporous silica. In this study we used the synthesized zeolite (CBV600 and CBV712) to remove ammonia from the aqueous solution.

To successfully apply zeolites in the removal of ammonia from the aqueous solution, it is necessary to understand the interfacial phenomena of the adsorption of ammonia on zeolites. Because FTIR is a common tool to analyze the adsorption phenomena [16], [17], in this study we observed the variations of IR spectra of original and ammonia-adsorbed zeolites. The variations of IR spectra were further analyzed to deduce the adsorption mechanism of ammonia on the surface of zeolites.

For practical utilization of zeolites on live fish transports, the reduction of the cost is inevitable. Therefore, we try to regenerate the used zeolites in this study. The original and ammonia-adsorbed zeolites were heated at various temperatures and their XRD spectra were obtained. With these XRD spectra the condition of regeneration of this zeolite was obtained.

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II. EXPERIMENTAL

A. Materials and Instruments

Zeolite: As discussed in the previous section, zeolites are inorganic materials based on an infinitely extending four-connected framework of SiO₄ and AlO₄ tetrahedra that are linked to each other by shared oxygen atoms. The structure of zeolite is shown as Fig. 1 In this study the synthesized zeolites CBV600 and CBV712 (supplied by PQ ZEOLITE B.V.) were used. Table I gives the characteristics of these two zeolites. The molar ratio of SiO₂/Al₂O₃ is 5 for CBV 600 and 11.5 for CVB712. The surface areas are 660 and 730 sqm/g respectively. CVB 600 has a weight loss of 1.88 and CVB is 10.2 weight percent at 1000 °C. In order to understand the stability of the structure, we treated the original and ammonia-absorbed zeolites at high temperature and observed the variation of the structures by XRD spectra.

NH₄OH solution with 26-30% NH₃.

pure water: with the electrical resistance greater than $1.8 \times 10^6 \Omega$.

FTIR: Shimadzu IR Prestige-zlwitha MCT detector.

XRD: NSRRC Powder X-ray Diffraction.

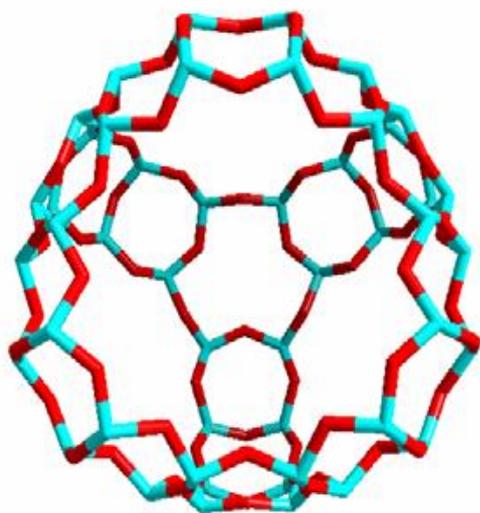


Figure 1. The structure of the zeolites

TABLE I. THE CHARACTERISTICS OF THE ZEOLITES USED IN THIS STUDY

Commercial code	CBV600	CBV712
Form	Powder	Powder
Unit Cell Size(angstroms)	24.33	24.35
SiO ₂ /Al ₂ O ₃ Molar Ratio	5.2	11.5
Na ₂ O (weight percent)	0.18	0.05
Crystal Size(μm)	0.4-0.6	0.4-0.6
Surface Area (sqm/g) (P/P0 =0.03)	660	730
LOI (weight percent) (@1000°C)	1.88	10.2

B. Experimental Procedure

The experimental procedure is as shown in Fig. 2. We used 0.6 g of zeolites in every experiment. Zeolites were soaked in the ammonia aqueous solution for an hour. Because zeolites are fine powder, they were collected by centrifugation in the experiments. The collected wet powders were dried at 70 °C. The dried powders were further calcinated at 350 °C, 450 °C, 550 °C, and 650 °C for two hours individually. FTIR and XRD were used to characterize these zeolite samples for further analysis.

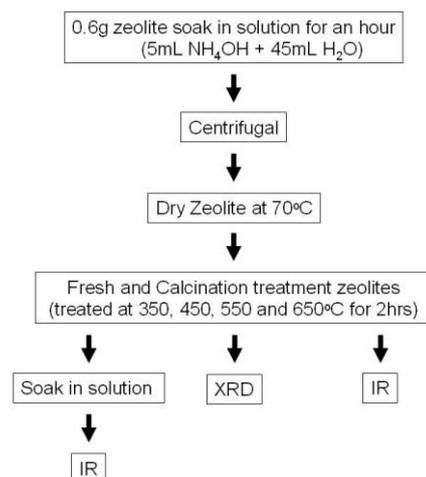


Figure 2. Experimental procedure

III. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 3 shows the XRD spectra of CBV600 zeolite and Fig. 4 is for CBV 712. They are used to display the crystalloid structures of these two zeolites with various treatments. It is clear that these zeolites soaked in NH₄OH solution at room temperature do not affect the structure of this zeolite. However, the soaked powders may collapse with the calcination over 350 °C and re-construct at 450 °C. CVB 712 will collapse once more at 550 °C. It therefore suggests that the regeneration of used zeolite should be conducted below 350 °C.

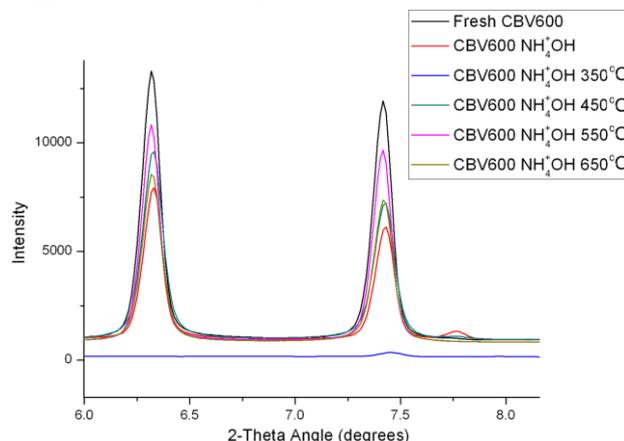


Figure 3. XRD spectra of CVB 600 zeolite

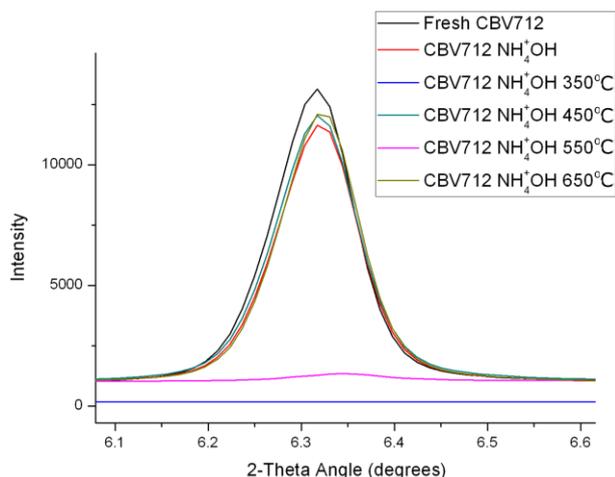


Figure 4. XRD spectra of CVB 712 zeolite

The IR spectra of original four types of zeolites (CVB600, CVB712, CVB720, CVB760) are shown in Fig. 5. CVB720 and CVB760 are high SiO₂ /Al₂O₃ zeolites. According to Chang's [18] experimental results, CVB 600 and CVB 712 have the greater capacity on the removal of ammonia than that of CVB720 and CVB760, therefore the following experiments were focused on these two zeolites.

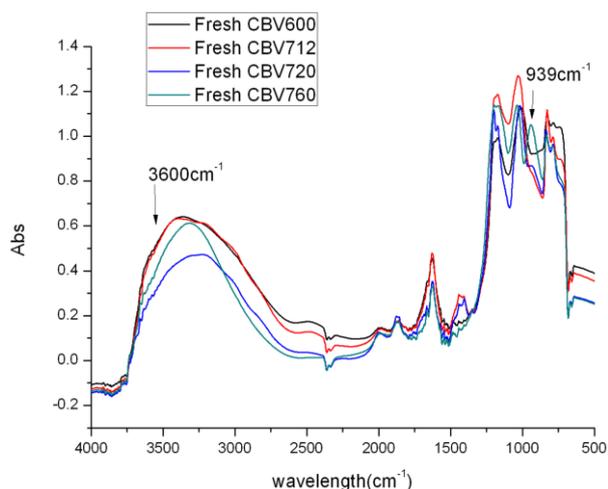


Figure 5. The IR spectra of original various CBV zeolites.

There are amount work shows that the adsorption at 3600 cm⁻¹ is the contribution of adsorbed water on the surface of the zeolite [19]. The adsorption within 700 cm⁻¹ ~ 1300 cm⁻¹ is the characteristics of most zeolites [10]. To understand the detailed phenomena of this region, a molecular simulation was conducted. Fig. 6 shows the molecular simulation results of the IR spectrum of SiOH with H₂O. It gives the evidence that the IR adsorption within 700 cm⁻¹ ~ 1300 cm⁻¹ is due to the interaction Si-O-H with water.

Fig. 7 is the IR spectrum of CVB600 and CVB712 zeolites soaked with NH₄OH. The adsorption of ammonia on zeolite gives IR adsorption at 3256 cm⁻¹, 3060 cm⁻¹, 2836 cm⁻¹, 1642 cm⁻¹, 1640 cm⁻¹, and 1098 cm⁻¹ respectively. The IR spectra of NH₃ are: asymmetric stretching vibration of N-H bond at 3414 cm⁻¹, symmetric

stretching vibration of N-H bond at 3336 cm⁻¹, asymmetric bending vibration of H-N-H angle at 1630 cm⁻¹, and symmetric bending vibration of H-N-H angle at 950 cm⁻¹. The shift of the IR spectra is worthy of concerning.

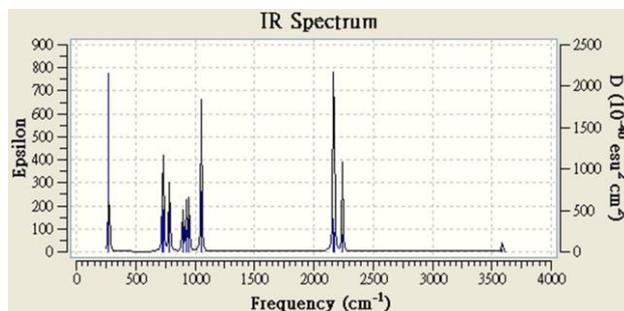


Figure 6. Molecular simulation IR spectrum of SiOH with H₂O

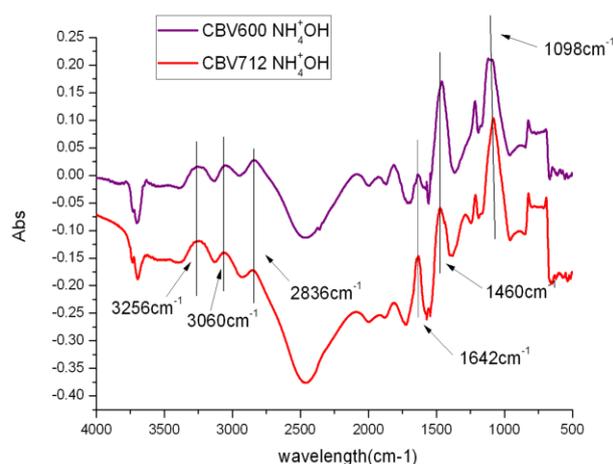


Figure 7. The IR spectrum of CBV600 and CBV 712 zeolite soaked with NH₄OH

To understand the effects of the adsorbed ion on the IR spectrum of NH₃, a molecular simulation was conducted (Fig. 8a, Fig. 8b). In comparison with the IR spectra of NH₃ and NH₄⁺, the asymmetric stretching vibration of N-H bond shifts from 3414 cm⁻¹ to 3368 cm⁻¹ and the asymmetric bending vibration of H-N-H angle from 1630 cm⁻¹ to 1587 cm⁻¹. It is clear that the attachment of the hydrogen ion to NH₃ induces a red shift of the IR spectrum.

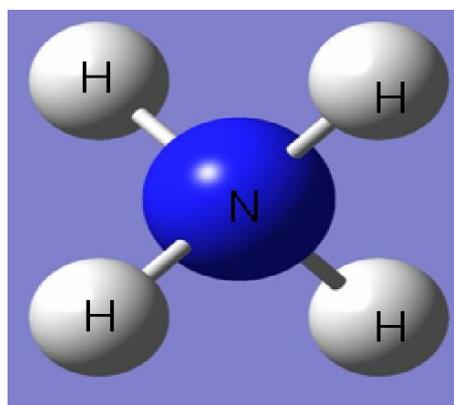


Figure 8a. Molecular simulation of NH₄⁺: blue-nitrogen, white-hydrogen.

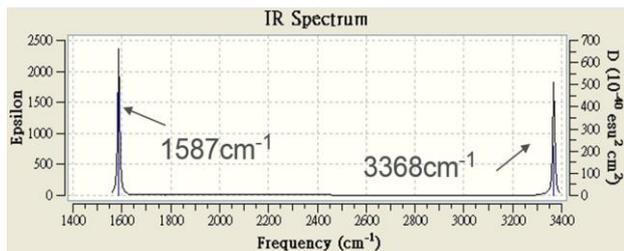


Figure 8b. Molecular simulation of NH₃.

The effect of the count ion on the IR spectrum was also studied. In this simulation sodium ion was chosen as the counter ion. Simulation results (Fig. 9a and Fig. 9b) showed that there are red shift for high frequency adsorption (3543 cm⁻¹ → 3454 cm⁻¹, 3400 cm⁻¹ → 3353 cm⁻¹) and blue shift for low frequency adsorption (1745 cm⁻¹ → 1753 cm⁻¹).

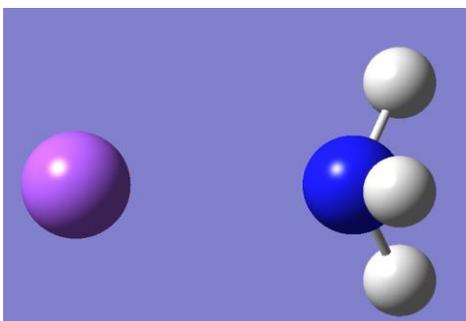


Figure 9a. Molecular simulation of NH₃ with Na⁺ as counter ion: pink-Na⁺, blue-nitrogen, white-hydrogen.

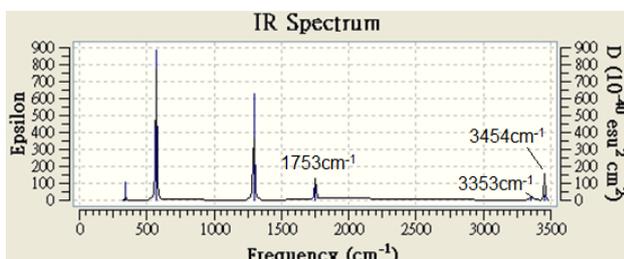


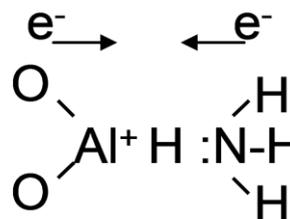
Figure 9b. Molecular simulation of NH₃ with Na⁺ as counter ion

It is well known that the frequency of the spectrum follows the Hooke's Law:

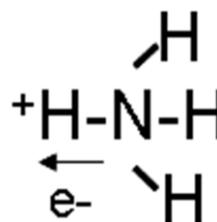
$$f = (1/2\pi c) \sqrt{(k/\mu)}$$

where μ is reduce mass $\mu = m_1 m_2 / (m_1 + m_2)$, where m_1 and m_2 are the masses attached. The reduce mass of N-H bond increases with the attached hydrogen ion or the counter ion and induces the decrease of the frequency and the red shift occurs.

According to the simulation results, the adsorption of NH₃ on zeolite is considered to be (O₂Al⁺H)(NH₃). In this structure, the adsorption at 3256 cm⁻¹ is NH asymmetry stretching vibration, 3060 cm⁻¹ is NH symmetry stretching vibration, 1642 cm⁻¹ is NH asymmetry bending vibration, and 1098 cm⁻¹ is NH symmetry bending vibration. In comparison with the experimental results, there were red shift for the high frequency adsorption and blue shift for the low frequency adsorption. It is consistent with the molecular simulation results. The structure (O₂Al⁺H)(NH₃) is depicted below:



With the donation of electrons from aluminum oxide and NH₃, this structure has the stronger N-H bond than that of NH₄⁺, and a blue shift occurs for the low frequency adsorption. The adsorptions at 2836 cm⁻¹ and 1460 cm⁻¹ are stretching vibration and bending vibration of NH₄⁺ individually. Because the lone pair electrons of ammonium were shared by the hydrogen ion, therefore the bond strength of N-H in ammonium was reduced as shown in the following structure.



IV. CONCLUSION

The present study demonstrates that

1. The adsorption of ammonia on the CBV600 and CBV712 zeolites (with SiO₂/Al₂O₃ molar ratio=5 and 11.5) gives two possible mechanisms:

- (1) NH₄⁺ adsorption: that appears stretching vibration at 2836 cm⁻¹ and bending vibration 1460 cm⁻¹.
- (2) (O₂Al⁺H)(NH₃) adsorption: that has red shifts for high frequency (3256 cm⁻¹ NH asymmetry stretching vibration and 3060 cm⁻¹ NH symmetry stretching vibration) and blue shifts for low frequency (1642 cm⁻¹ NH asymmetry bending vibration and 1098 cm⁻¹ NH symmetry bending vibration). It gives the evidences that adsorbed NH₃ interacts with the counter ion O₂Al⁺H.

2. XRD analysis showed that the structure of this type of zeolite may collapse when temperature is over 350 °C. Therefore, the regeneration of this zeolite should be conducted below 350 °C.

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REFERENCES

- [1] M. Iversen, B. Finstad, R. S. McKinley, R. A. Eliassen, K. T. Carlsen, and T. Evjen, "Stress responses in atlantic salmon (salmo salar l.) smolts during commercial well boat transports, and effects on survival after transfer to sea," *Aquaculture*, vol. 243, pp. 373-382, January 2005.

- [2] B. Björnsson and S. R. Ólafsdóttir, "Effects of water quality and stocking density on growth performance of juvenile cod (*gadus morhua* L.)," *ICES J. Mar. Sci.*, vol. 63, pp. 326-334, January 2006.
- [3] Z. Svobodová, P. Kalab, L. Dušek, B. Vykusová, J. Kolářová, and D. Janoušková, "The effect of handling and transport of the concentration of glucose and cortisol in blood plasma of common carp," *Acta Veterinaria Brno*, vol. 68, pp. 265-274, October 1999.
- [4] J. Tomasso, "Toxicity of nitrogenous wastes to aquaculture animals," *Rev. Fish. Sci.*, vol. 2, pp. 291-314, December 1994.
- [5] A. Pollice, V. Tandoi, and C. Lestingi, "Influence of aeration and sludge retention time on ammonium oxidation to nitrite and nitrate," *Water Res.*, vol. 36, pp. 2541-2546, May 2002.
- [6] H. Kušar, A. Ersson, M. Vosecký, and S.G. Järås, "Selective catalytic oxidation of NH_3 to N_2 for catalytic combustion of low heating value gas under lean/rich conditions," *Appl. Catal., B*, vol. 58, pp. 25-32, June 2005.
- [7] A. Bodalo, J. L. Gomez, E. Gomez, G. Leon, and M. Tejera, "Ammonium removal from aqueous solutions by reverse osmosis using cellulose acetate membranes," *Desalination*, vol. 184, pp. 149-155, November 2005.
- [8] M. Sprynsky, M. Lebedynets, A. P. Terzyk, P. Kowalczyk, J. Namieśnik, and B. Buszewski, "Ammonium sorption from aqueous solutions by the natural zeolite transcarpathian clinoptilolite studied under dynamic conditions," *J. Colloid Interface Sci.*, vol. 284, pp. 408-415, April 2005.
- [9] M. Sprynsky, M. Lebedynets, R. Zbytniewski, J. Namieśnik, and B. Buszewski, "Ammonium removal from aqueous solution by natural zeolite, transcarpathian mordenite, kinetics, equilibrium and column tests," *Sep. Sci. Technol.*, vol. 46, pp. 155-160, November 2005.
- [10] R. Anquetil, J. Saussey, and J. C. Lavalley, "Confinement effect on the interaction of hydroxy groups contained in the side pockets of h-mordenite with nitriles; a ft-ir study," *Phys. Chem. Chem. Phys.*, vol. 1, pp. 555-560, November 1999.
- [11] S. Balci and Y. Dinçel, "Ammonium ion adsorption with sepiolite: Use of transient uptake method," *Chem. Eng. Prog.*, vol. 41, pp. 79-85, January 2002.
- [12] L. Weatherley and N. Miladinovic, "Comparison of the ion exchange uptake of ammonium ion onto new zealand clinoptilolite and mordenite," *Water Res.*, vol. 38, pp. 4305-4312, December 2004.
- [13] M. Sarioglu, "Removal of ammonium from municipal wastewater using natural turkish (dogantepe) zeolite," *Sep. Sci. Technol.*, vol. 41, pp. 1-11, January 2005.
- [14] Y. Wang, Y. Kmiya, and T. Okuhara, "Removal of low-concentration ammonia in water by ion-exchange using na-mordenite," *Water Res.*, vol. 41, pp. 269-276, January 2007.
- [15] W. T. Tsai, K. J. Hsien, and H. C. Hsu, "Adsorption of organic compounds from aqueous solution onto the synthesized zeolite," *J. Hazard Mater.*, vol. 166, pp. 635-641, July 2009.
- [16] C. Jin, Y. Guo, S. Zhang, and W. Shen, "Synthesis of large spherical mesoporous silica using tween-80 and starch hydrolysis solution," *Adv. Sci. Lett.*, vol. 5, pp. 204-207, January 2012.
- [17] A. Wang, J. Cai, and Y. Chen, "Modeling the spectral absorbance of heavily doped silicon gratings," *Adv. Sci. Lett.*, vol. 4, pp. 1473-1477, April 2011.
- [18] C. Y. Chang, "The mechanism of the adsorption of ammonia on zeolite," M.S. thesis, Dept. Appl. Chem., National Chia-Yi Univ, Chiayi City, Taiwan, 2013.
- [19] J. W. Ward, "Spectroscopic study of the surface of zeolite y. Ii. Infrared spectra of structural hydroxyl groups and adsorbed water on alkali, alkaline earth, and rare earth ion-exchanged zeolites," *J. Phys. Chem.*, vol. 72, pp. 4211-4223, November 1968.



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