

Kinetics Study of Ammonia Removal from Synthetic Waste Water

Edison Muzenda, John Kabuba, Freeman Ntuli, Mansoor Mollagee

Abstract—The aim of this study was to investigate ammonium exchange capacity of natural and activated clinoptilolite from Kwazulu-Natal Province, South Africa. X – ray fluorescence (XRF) analysis showed that the clinoptilolite contained exchangeable ions of sodium, potassium, calcium and magnesium. This analysis also confirmed that the zeolite sample had a high silicon composition compared to aluminium. Batch equilibrium studies were performed in an orbital shaker and the data fitted the Langmuir isotherm very well. The ammonium exchange capacity was found to increase with pH and temperature. Clinoptilolite functionalization with hydrochloric acid increased its ammonia uptake ability.

Keywords—Activated clinoptilolite, Ammonium exchange, Equilibrium, Functionalization, Langmuir isotherm

I. INTRODUCTION

THE ammonium ion and ammonia can coexist in an aqueous solution according (1)



The equilibrium presented in (1) depends on pH and temperature. The nitrogen present in the ammonium ion and in the ammonia - water solution is referred as ammoniacal nitrogen. High concentrations of nitrogen compounds in industrial effluent can cause various environmental problems [1]. The ammonium present in wastewater can be removed by ion exchange process [2]. Ion exchange processes using organic resins as exchanger are very expensive compared to zeolites [2]. The use of natural zeolite for the removal of ammonium is considered to be a competitive and effective process due to its low cost and relative simplicity of application and operation [2]. Zeolites are crystalline aluminosilicates with a framework structure and have excellent cation exchange properties. Zeolite $[(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Ba}) (\text{Al}, \text{Si}) \text{O}_2] \cdot \text{X} \cdot \text{nH}_2\text{O}$, (crystalline) are remarkable for their continuous and partly reversible dehydration as well as base exchange properties. Zeolites have high cation exchange capacity, cation selectivity, higher void volume, and great affinity for ammonium. Clinoptilolite is the most commonly used natural zeolite in ion exchange. The ion exchange removal of ammonium using clinoptilolite has been studied

extensively as it is the most abundant natural zeolite [2]. Literature reveals that pH, temperature [3], conditioning of clinoptilolite [4, 5] and competing ions [6] influence the ion exchange of ammonium. The main objective of this paper was to investigate the removal of ammonia ions from synthetic solutions through ion exchange using South African Clinoptilolite.

II. MATERIALS AND METHODS

The natural clinoptilolite used in this study was supplied from the Vulture Creek, Kwazulu-Natal Province of South Africa. The clinoptilolite was grounded and sieved into 0.25 - 0.5 mm and 2-2.83 mm particle sizes ranges. The pulverized sample was placed in an oven at 105°C for 24h to drive off moisture. The powder was then characterized using X-ray powder diffractometer (XRD) Phillips X'pert Model 0993, X-ray fluorescence spectroscopy (XRF, Phillips Magix Pro) and BET (Tristar 3000). The analysis was performed under a nitrogen atmosphere. For porosity and surface area analysis, 2g of sample was first degassed and nitrogen gas was flushed through for 4h at 120°C. Clinoptilolite grains of sizes in the range of 2.8 mm to 5.6 mm were used for adsorption studies. A fraction of these grains was treated with HCl at concentration of 0.02M and 0.04M at room temperature for a period of 8 hours. The clinoptilolite was then washed in deionised water to remove any foreign impurities and then oven dried at 50°C for 24hours. The Nessler method was used to determine ammonia concentration. Ammonia chloride stock solution was prepared by dissolving 1g NH_4Cl in 1 litre of deionized water. Synthetic waste water samples were prepared by diluting appropriate amounts of ammonia chloride stock solution to distilled water.

III. RESULTS AND DISCUSSION

A. Clinoptilolite Characterization

The results of X-ray fluorescence analysis are presented in Table 1. The characterization as confirmed by [7] showed that clinoptilolite contained exchangeable ions of sodium, potassium, calcium and magnesium. This zeolite has a Si/Al ratio of 5.96 (mol/mol) and the corresponding ratio of (Na+K) / Ca of 3.4. XRF results also confirmed that the zeolite was a high silica content clinoptilolite enriched with Mg, K and Na.

E. Muzenda, J Kabuba, F. Ntuli and M. Mollagee are with the Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, Johannesburg 2028, Tel: +27115596817, Fax: +27115596430, Email: emuzenda@uj.ac.za.

TABLE I
CHEMICAL COMPOSITION OF THE NATURAL CLINOPTILOLITE

Component	Content (%)
TiO ₂	0.2
MgO	1.1
Na ₂ O	1.3
CaO	1.5
Fe ₂ O ₃	1.5
K ₂ O	3.8
Al ₂ O ₃	12.4
SiO ₂	74

B. Langmuir Isotherm

The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent, and there is no interaction between the adsorbate molecules [8]. The isotherm equation is represented as (2)

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (2)$$

Where C_e is the equilibrium concentration of Cu in solution, q_e is the amount adsorbed at C_e , Q_{\max} is the maximum adsorption capacity and K_L is the binding constant of Langmuir which is related to the energy of adsorption. A plot C_e/q_e against C_e gives a straight line with slope and intercept of $1/Q_{\max}$ and $1/K_L Q_{\max}$ respectively. The values of K_L and Q_{\max} at different temperatures are shown in Table II. The R^2 values for the K_L show that the experimental results fitted the Langmuir isotherm well.

TABLE II
ISOTHERM CONSTANTS, MAXIMUM ADSORPTION CAPACITIES AND REGRESSION DATA

T (°C)	Q_{\max}	K_L	R^2
20	1.58	0.094	0.992
30	1.97	0.083	0.986
40	2.32	0.059	0.961
50	2.5	0.071	0.937

C. Effect of pH

pH has a significant effect on ammonium removal by clinoptilolite, since it affects both ammonium ion chemical speciation and clinoptilolite characteristics [9].

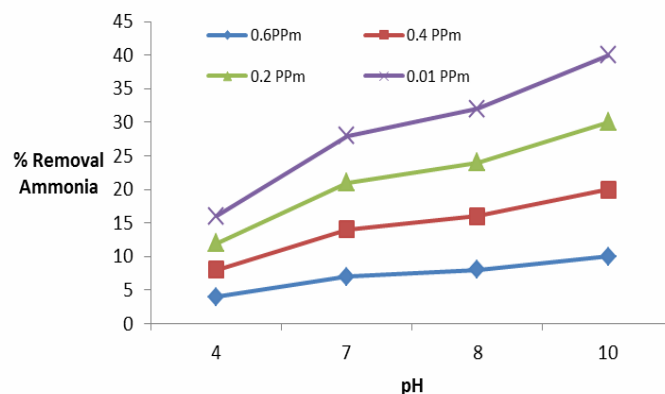


Fig. 1 Effect of pH on the adsorption of NH_4^+ at 293 K

Adsorption studies showing the effect of pH on NH_4^+ removal at 293 K were performed for a period of 24 hours (Fig 1). The uptake capacity of natural zeolite increased with increasing pH. Previous studies have shown that adsorption capacities decrease at pHs higher than 10 [10]. At low pH, the NH_4^+ ions compete with hydrogen ions for exchange sites where as at pHs higher than 10 ammonium ions are transformed into ammonia gas. The effect of the pH on the exchange capacity of the clinoptilolite can be attributed to the electrostatic interactions between the surface of the clinoptilolite and NH_4^+ ions in solution.

D. Effect of Temperature

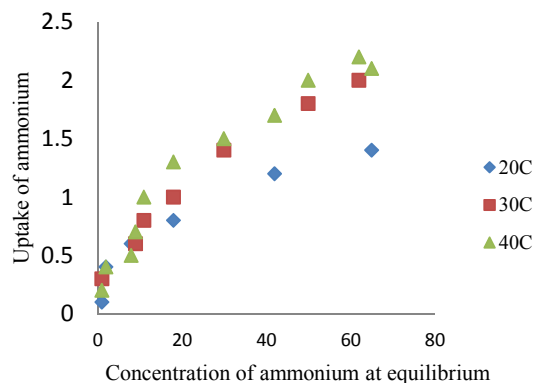


Fig. 2 Effect of the temperature on the adsorption isotherm of ammonium on clinoptilolite at pH 6

The effect of temperature on the ammonium uptake was performed at varying temperatures of 20, 30 and 40°C at pH 6. The sorption dependence on temperature is shown in in Fig. 2. The direction and magnitude of the influence of temperature depends on the specific solute-sorbent systems [11].

E. Effect of HCl Conditioning

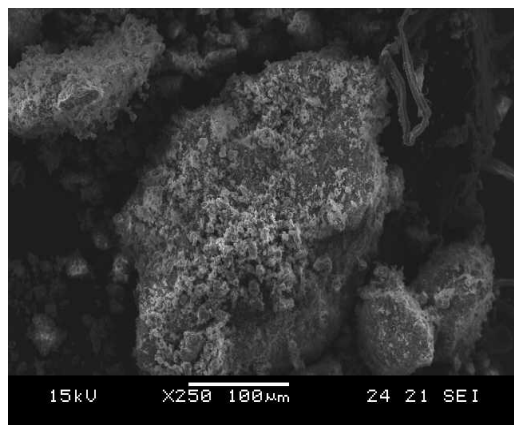


Fig. 3 SEM of original Clinoptilolite at X250 magnification

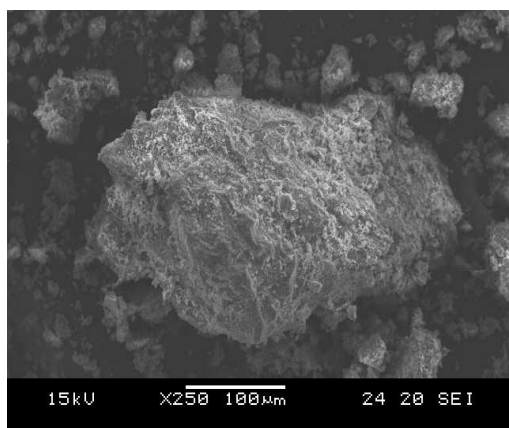


Fig. 4 SEM of activated clinoptilolite at X250 magnification

The SEM micrographs of natural and activated zeolite are shown in Figs 3 and 4 respectively. A more open structure of natural zeolite is observed accounting for the difference in adsorption performance compared to the morphologically modified acid treated zeolite, Fig. 5 [12]-[14]. Acid treatment leads to de-cantination, de- alumination and the dissolution of amorphous silica fragments blocking the channels.

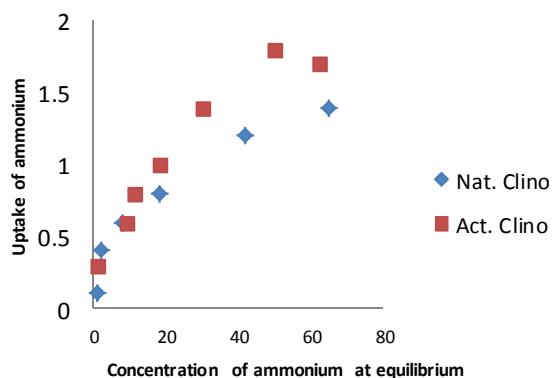


Fig. 5 Ammonium exchange capacities of natural clinotilolite and the activated clinoptilolite at @ 20°C and pH 4

IV. CONCLUSION

The clinoptilolite used in this study had high silicon content. The uptake of ammonium was found to be influenced by temperature, pH and acid conditioning. The sorption isotherms fitted the Langmuir model.

REFERENCES

- [1] R. Leva-ramos, J. E. Monsivais-Rocha, A. Aragon-Pina, M. S. Berber-Mendoza, R. M. Guerrero-Coronado, P. Alonso-Davila, J. Mendoza-Barron, "Removal of ammonium from aqueous solution by ion exchange on natural and modified Chabazite," J. Environ. Man., vol. 91, pp. 2662-2668, 2010.
- [2] A. Hedstrom, "Ion exchange of ammonium in zeolites: a literature review. J. Environ., Eng. vol. 127, pp. 673-681, 2001.
- [3] R. Leva-ramos, G. Aguilar-Armenta, L. V. Gonzalez-Gutierrez, R. M. Guerrero-Coronado, J. Mendoza-Bason, "Ammonium exchange on clinoptilolite from mineral deposits located in Mexico," J. Chem. Technol. Biotechnol., vol. 79, pp. 651-657, 2004.
- [4] V. K Jha, S. Hayashi, "Modificaton on natural clinoptilolite zeolite for its NH₄⁺ retention capacity," J. Hazard. Mater., vol. 141, pp. 483-488, 2009.
- [5] P. Vassileva, D Voikova, "Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions," J. Hazard. Mater., vol. 170, pp. 948-953, 2009.
- [6] Y. F. Wang, F. Lin, W. Q. Pang, "Ammonium exchange in aqueous solution using Chine natural clinoptilolite and modified zeolite," J. Hazard. Mater., vol. 142, pp. 160 – 164, 2007.
- [7] B. B. Mamba, D. W. Nyembe and A. F. Mulaba-Bafubiandi, "The effect of conditioning with NaCl, KCl and HCl on the performance of natural clinoptilolite's removal efficiency of Cu²⁺ and Co²⁺ Synthetic solutions," Water SA, vol. 36, no. 4, pp. 437-444, 2009.
- [8] M. Zhang, H. Zhang, Dan Xu, L. Han, D Niu, B.Tian, J Zhan, L. Zhan and W. Wu, "Removal of Ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method," Desalination (2011) doi: 10.1016/j. desal. 2010.12.021.
- [9] A. M. Yusofa, L. K. Keata, Z. Ibrahim, Z. A. Majiza, N. A. Nizamb, "Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powered and granulated forms of mordenite," J. Hazard.Mat., 2010, vol. 174, pp. 380-385, 2010.
- [10] H. Huang, X Xiao, Bo Yan, L. Yang, "Ammonium removal from aqueous solution by using natural Chinese (Chende) zeolite as adsorbent". J. Hazard. Mat. Vol. 175, pp. 247-252, 2010.
- [11] B. N. K. Njoroge and S. G. Mwamachi, "Ammonia removal from an aqueous solution by the use of a natural zeolite," J. Envir. Eng. Sci., vol. 3, pp. 147-154, 2004.
- [12] O. Korkuna, R. Lebeda, J. Skubiszewska, T. Vrublevs'ka, V.M. Gun'ko and J Ryzkowski, "Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite," Microporous and Mesoporous Materials, vol. 87, pp. 243-254, 2006.
- [13] V. O. Vasylechko, G. V. Gryshchouk, L. O. Lebedynets, R. Lebeda and J. Skubiszewska-zieba, "Investigation of usefulness of Transcarpathian zeolites in trace analysis of waters. Application of mordenite for the pre concentration of trace amounts of copper and cadmium," Chem. Anal. (Warsaw), vol. 44, no. 6, pp. 1013-1024, 1999.
- [14] M. A. Hernandez, "Nitrogen-sorption characteristics of the micro porous structure of clinoptilolite-type zeolites," J. Porous Mater., vol. 7, no. 4, pp. 443-454, 2000..



Edison Muzenda is the Research and Postgraduate Coordinator and Head of Environmental and Process Systems Engineering Research Unit in the School of Mining, Metallurgy and Chemical Engineering at the University of Johannesburg. Dr Muzenda holds a BSc Hons (NUST, ZIM, **1994**) and a PhD, Chemical Engineering (Birmingham, UK, **2000**). He has more

than **15** years experience in academia which he gained at different Institutions: National University of Science and Technology Bulawayo, University of Birmingham, Bulawayo Polytechnic, University of Witwatersrand and University of Johannesburg. He is a recipient of several awards and scholarships for academic excellence. His research interests in phase equilibrium measurement and computation, energy, environment, separation processes as well waste minimization and utilisation. He has published more than **60** international peer reviewed papers in international scientific journals and conferences. He serves as reviewer of a number of reputable international conferences and journals. He has also chaired several sessions at International Conferences. The author is a member of the International Scientific Committee, Scientific and Technical Committee & Editorial Review Board of Natural and Applied Sciences, Africa Representative and International Scientific Secretariat for the World Academy of Science Engineering and Technology; Water Institute of SA; International Association of Engineers; AMIChemE



John Kabuba is Lecturer in the Department of Chemical Engineering at the University of Johannesburg. Mr. Kabuba has ten years experience in Tertiary Education and has been lecturing at the University of Johannesburg since 2006. He holds a B.Eng. Degree and Master's Degree in Chemical Engineering. He is currently pursuing a Doctor's Degree in Extraction Metallurgy at the University of

Johannesburg. His research interests include Thermodynamics, Neural Networks, Mineral processing, Oil extraction and Environmental Technology.



Freeman Ntuli holds a PhD in Chemical Engineering from the University of Cape Town. Currently, he is a Senior Lecturer in the Department of Chemical Engineering at the University of Johannesburg.

His main areas of research are in hydrometallurgy, crystallization and environmental process engineering. His research involves gaseous reduction processes, leaching processes, reduction crystallization and modelling of particulate processes.



Mansoor Mollagee is currently the Head of Department in Chemical Engineering at the University of Johannesburg and has been in academia for the last 15 years.

Main research interests – Computational Fluid Dynamics and Dispersion Modelling