第 24卷 第 6期
2008年 12月
哈尔滨商业大学学报(自然科学版)
Journal of Harbin University of Commerce (Natural Sciences Edition)
Vol 24 No. 6
Dec 2008

Study on adsorption and biochemical regeneration of clinoptilolite for ammonia removal

ZHANG Bing[1], CUI Fu-yi[1], ZUO Jin-long[2], ZHANG Xue-hong[3]

(1. School of Municipal & Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China; 2. Department of Environmental Engineering, Harbin University of Commerce, Harbin150076, China; 3 Department of Resources and Environmental Engineering, Guilin University of Technology, Guilin 541004, China)

Abstract: In order to tackle the problem for remove ammonia from polluted water, clinoptilolite is used for adsorbing the ammonia from waster water, and chemical and biological regeneration for ammonia removal was investigated. The results showed that the data were fit to Langmuir isotherms for ammonium ion uptake onto clinoptilolite. For biochemical regeneration experiment, it was stable for the removal of NH_3—N by clinoptilolite column with removal efficiency over 80% after two months biochemical regeneration using the $NaHCO_3$ regenerant with Na^+ concentration of 2 000 mg/L and air-water ratio 5∶1 at 15～26.5 ℃. The clinoptilolite zeolite was suggested as a suitable material for adsorbing ammonia.

Key words: clinoptilolite; ammonia adsorptive capacity; ion exchange; biochemical regeneration

中图分类号: X703　　**文献标识码**: A　　**文章编号**: 1672 - 0946(2008)06 - 0657 - 05

斜发沸石去除氨氮及其再生的研究

张　兵[1],崔福义[1],左金龙[2],张学洪[3]

(1.哈尔滨工业大学 市政环境工程学院,哈尔滨 150090; 2.哈尔滨商业大学 环境工程系,哈尔滨 150076; 3.桂林工学院 资源与环境工程系,广西 桂林 541004)

摘　要:为了有效去除污水中的氨氮,采用斜发沸石进行污水中氨氮的吸附去除研究,同时探讨了化学再生和生物再生的效果.结果表明,氨氮在沸石上吸附符合 Langmuir吸附等温式;生物化学再生后沸石,经过 2个月稳定运行,采用 Na^+质量浓度 2 000 mg/L,气水比为 5∶1,温度为 15～26.5 ℃时,氨氮的去除效率可超过 80%.沸石可以作为一种有效的氨氮吸附材料并且可有效再生.

关键词:斜发沸石;氨氮吸附容量;离子交换;化学和生物再生

1　Introduction

Because the stringent nutrient levels are being required in the effluents to protect water body, removal of nutrient from discharged wastewater has been required in many wastewater treatment plants. Ammonia nitrogen in the effluent has harmful effects on water resources[1-3]. Thus wastewater with high ammonia concentration must be treated before arriving at the receiving water[4-6]. The three most widely used methods for removal of ammonia from polluted water are air stripping, ion exchange and biological nitrification denitrification[7-9]. The ion exchange method is preferred over the other methods since it is stable, suits

收稿日期: 2008 - 01 - 02.
基金项目:国家高技术研究发展计划(863)项目(2003AA601060),广西科技攻关项目(桂科攻 0428008 - 4N).
作者简介:张　兵(1974 -),男,博士研究生,研究方向:水处理与回用技术.

automation and quality control, and is easy to maintain[10-12].

As a kind of aluminum silicate minerals with a framework structure, zeolite has a high cation exchange capacities and high ammonia selective properties[13-16]. Furthermore it can act as a bio-carrier for nitrifying bacteria which oxidize ammonia to the nitrate anion [17-20]. Clinoptilolite is a natural zeolite that has been known for their ability to remove ammonia from polluted waters[20-22]. In this paper, clinoptilolite is used for adsorbing the ammonia from waster water, moreover chemical and biological regeneration for ammonia removal was investigated. This study specifically aimed to: 1) clinoptilolite for ammonia adsorption and ion exchange; 2) chemical regeneration and biological regeneration.

2 Materials and methods

2.1 Materials and wastewater quality

The clinoptilolite used in the experiments was provided by Academy of Geology and Mineral Resource of Guilin, China. The chemical analysis of the clinoptilolite sample is given in Table 1. The wastewater used in this project was secondary effluent from a Guilin water sewage treatment works and the average wastewater concentration was shown in Table 2.

Table 1 Chemical analysis of clinoptilolite

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
% by wt	70.03	15.78	0.37	0.26	0.38	9.55	1.77

Table 2 Raw water quality in the experiment

Parameter	pH value	COD	BOD_5	SS	NH_4^+—N
Average /(mg·L^{-1})	7.0～7.8	30～56	10～17	10～25	10～20

2.2 Experimental apparatus

The system is composed of the following items: 28 liter reactor made from 200 mm diameter transparent PVC pipe; the reactor is filled with 2000 g clinoptilolite, under the clinoptilolite was gravel bed with height of 100 mm. An acrylic plate was placed in the bottom of the column to support the clinoptilolite and distribute backwash water and supply air.

2.3 Experimental methods

During batch and continuous experiments, the ammonia nitrogen adsorptive capacities of virgin clinoptilolite and biofilm covered clinoptilolite were examined. The DO, ammonia of the influent and effluent was measured respectively, by adopting the Chinese EPA standard methods [23].

Preparation of biofilm covered clinoptilolite: Firstly, the activated sludge was pumped through the clinoptilolite column for several cycles, then the column operated in a batch mode (no outflow) and air was supplied for three days. When the biomass was found on the surface of clinoptilolite, the influent solution was shifted to cultured solution. The conditions were controlled as follows: DO was maintained at 2.0～2.5 mg/L, water temperature was kept at 20～25 ℃. Then biofilm covered clinoptilolite was washed with distilled water to remove the remaining regeneration solution. Shown in Figure 1.

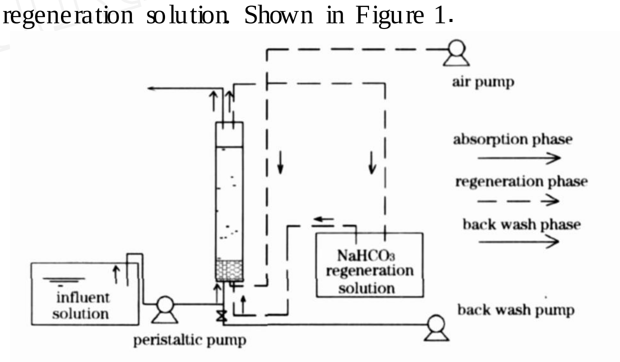

Figure 1 Schematic diagram of the ammonia removal experiment by clinoptilolite in laboratory

3 Results and discussion

3.1 Ammonia adsorption experiment

3.1.1 Batch experiment

The ammonia adsorption capacity of clinoptilolite of virgin clinoptilolite and biofilm covered clinoptilolite were shown in Table 3 and 4.

In general such ammonia exchange properties were described by Langmuir isotherm, and the Langmuir isotherm is defined as:

$$q = abC_e / (1 + bC_e). \quad (1)$$

Where q is the amount of NH_4^+ exchange per unit weight of clinoptilolite, C_e is the NH_4^+ concentration in the solution; The values of a and b are model parameters, a is the maximal NH_4^+ exchange per unit weight of clinoptilolite, b is the Langmuir energy constant

Usually the (1) equation also can be rearranged as follow:

$$1/q = (1/a) + (1/(abC_e)). \quad (2)$$

Table 3 Data of adsorbed ammonia by virgin clinoptilolite during static experiment

Number	Original concentration / (mg · L⁻¹)	Equilibrium concentraction C_e / (mg · L⁻¹)	Ammonia adsorption capacity q / (g · g × 10⁻³)	$1/C_e$	$1/q$
1	50	12. 20	3. 78	81. 97	264. 55
2	100	31. 20	6. 88	32. 05	145. 35
3	150	45. 10	10. 49	22. 17	95. 33
4	200	80. 60	11. 94	12. 41	83. 75
5	250	110. 10	13. 99	9. 08	71. 48
6	300	153. 60	14. 64	6. 51	68. 31

Table 4 Data of adsorbed ammonia by the biofilm covered clinoptilolite during static experiment

Number	Original concentration / (mg · L⁻¹)	Equilibrium concentraction C_e / (mg · L⁻¹)	Ammonia adsorption capacity q / (g · g × 10³)	$1/C_e$	$1/q$
1	50	14. 20	3. 58	70. 42	279. 33
2	100	40. 20	5. 98	24. 88	167. 22
3	150	55. 10	9. 49	18. 15	105. 37
4	200	91. 60	10. 84	10. 92	92. 25
5	250	124. 10	12. 59	8. 06	79. 43
6	300	169. 60	13. 04	5. 90	76. 69

The data of virgin clinoptilolite and biofilm covered clinoptilolite gave good fit for Langmuir isotherm. Two Langmuir isotherms were good linear form, and the linear form related coefficients were 0. 989 5 and 0. 967 4 respectively. The results showed that the data obtained from batch studies were fit to Langmuir isotherms for ammonium ion uptake onto clinoptilolite

According to Langmuir isotherms, the maximal NH_4^+ exchange per unit weight of virgin clinoptilolite was 20. 39 mg, and the maximal NH_4^+ exchange per unit weight of biofilm covered clinoptilolite was obtained 16. 75 mg It was concluded that no significant differences in the adsorption capacity were detected between virgin clinoptilolite and biofilm covered clinoptilolite.

3. 1. 2 Breakthrough experiment

Figure 2 presents the results of a breakthrough curve with the ammonia nitrogen concentration of 20 mg/L and hydraulic loading rate of 2 m³ / (m² · h). Figure 3 presents the results of a breakthrough curve with the ammonia nitrogen concentration of 10mg/L and hydraulic loading rate of 8 m³ / (m² · h).

As can be seen from Figure 2 and Figure 3, the hydraulic loading rate decreased from 8 m³ / (m² · h) to 2 m³ / (m² · h), although the influent ammonia concentration increased from 10 mg/L to 20 mg/L, the breakthrough value was 560 BV in the virgin clinoptilolite and 530 BV in the biofilm covered clinoptilolite respectively. The results showed that longer retention times caused the similar ammonia adsorptive capacity with virgin clinoptilolite or biofilm covered clinoptilolite, the clinoptilolite did not lose its adsorption capacity in spite of the biofilm covered. Thus during the ammonia adsorptive experiment, the results of batch and breakthrough experiments showed that the difference of ammonia adsorption capacity between biofilm covered clinoptilolite and virgin clinoptilolite was not obvious

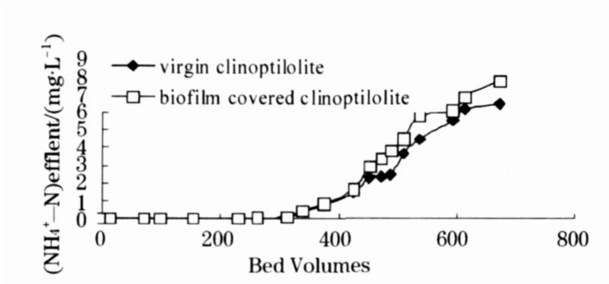

Figure 2 Breakthrough curve with hydraulic load of 2 $m^3/(m^2 h)$

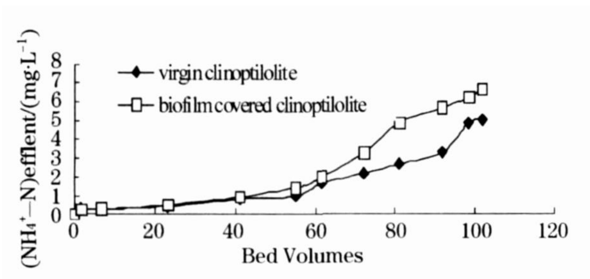

Figure 3 Breakthrough curve with hydraulic load of 8 $m^3/(m^2 h)$

3.2 Biochemical regeneration experiment

3.2.1 Desorption experiment

Three sodium bicarbonate regeneration solution with different concentration of 2 000 mg/L, 4 000 mg/L and 10 000 mg/L were provided to pass through clinoptilolite column by upflow style at a hydraulic loading rate of 2 $m^3/(m^2 \cdot h)$. The desorption curve are shown in Figure 4.

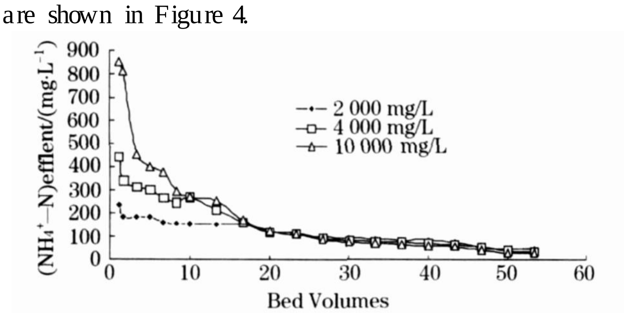

Figure 4 Desorption curve of adsorbed ammonia of clinoptilolite

The curve showed that the desorption rate with higher regeneration solution concentration was much higher than that one with lower concentration. During the desorption process, 21%, 15% and 9% of ammonia adsorbed in the each clinoptilolite column were desorbed at 10 BV with 10 000 mg/L, 4 000 mg/L and 2 000 mg/L of regeneration solution concentration respectively. The results indicated that regeneration solution with higher concentration had higher Na^+ gradient between clinoptilolite and solution. Thus the increased Na^+ concentration could result in more contact time with clinoptilolite.

3.2.2 Adsorption - biochemical regeneration experiment

The adsorption - biochemical regeneration experiments were run for two months with regeneration time of three days. At each stage, the influent ammonia concentration and hydraulic loading rate were kept at 20 mg/L and 2 $m^3/(m^2 \cdot h)$ respectively. Ammonia nitrogen concentration of 5 mg/L in the effluent was adopted as the breakthrough point, when breakthrough occurred, the adsorption capacity of ammonia nitrogen was determined. The experiment results were shown in Figure 5.

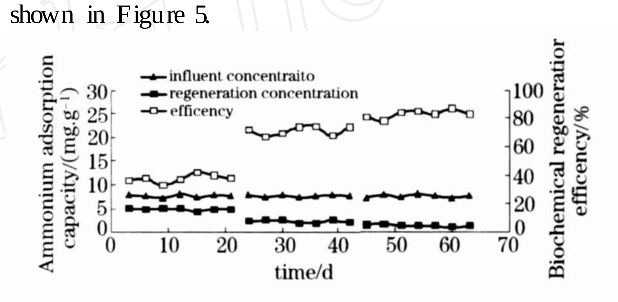

Figure 5 Biochemical regeneration efficiency of clinoptilolite column

Figure 5 showed that ammonia nitrogen removal efficiency was increased rapidly when temperature and aeration increased. The results indicated that higher temperature and air-water ratio had higher nitrification efficiency and temperature played more important role than air-water ratio. And the biochemical regeneration is actually a combination of chemical adsorption and ion-exchange as well as biological nitrification.

4 Conclusions

1) The results of batch and breakthrough experiments showed that the difference of ammonia adsorption capacities of virgin clinoptilolite and biofilm covered clinoptilolite was not obvious.

2) It was stable for the removal of NH_4^+—N by clinoptilolite column with removal efficiency over 80% after two months biochemical regeneration using the $NaHCO_3$ regeneration with Na^+ concentration of 2 000 mg/L and air - water ratio 5∶1 at 15～26.5

℃.

3) The results of regeneration experiment indicated that to increase dissolved oxygen concentration with favorable temperature would improve the bioregeneration capacity.

参考文献:

[1] LAHAV O, GREEN M. Ammonia Removal Using Ion Exchange and Biological Regeneration [J]. Water Research, 1998, 32 (7): 2019 - 2028.

[2] LAHAV O, GREEN M. Ammonia Removal from Primary and Secondary Effluents Using a Bioregenerated Ion - exchange Process[J]. Water Science and Technology, 2000, 42 (1): 179 - 185.

[3] ANNELIE H. Ion exchange of ammonia in zeolites: a literature review [J]. Journal of Environmental Engineering, 2001, 127 (8): 673 - 680.

[4] PIIRTOLA L, HULTMAN B, LOWEN M. Effects of detergent zeolite in a nitrogen removal activated sludge process[J]. Water Science and Technology, 1998, 38 (2): 41 - 48.

[5] ZORPAS A, CONSTANTINIDES T, VLYSSIDES A G, *et al*. Heavy metal uptake by natural zeolite and metals partitioning in sewage sludge compost[J]. Bioresource Technology, 2000, 72: 113 - 119.

[6] CELIK M S, OZDEMIR B, TURAN M. Removal of ammonia by natural clay minerals using fixed and fluidized bed column reactors[J]. Water Science and Technology, 2001, 1 (1): 81 - 88.

[7] AHMET D, AHMET G, EYYUP D. Ammonium removal from aqueous solution by ion exchange using packed bed natural zeolite [J]. Water SA, 2002, 28 (3): 329 - 335.

[8] RAHMANI A R, MAHVI A H, MESDAGHINIA A R. Investigation of Ammonium removal from polluted water by Clinoptilolite zeolite [J]. Environmental Science and Technology, 2004, 11 (2): 131 - 141.

[9] ELIK M S, ZGEMIR B, TURAN M, *et al*. Removal of ammonia by natural clay minerals using fixed and fluidised bed column reactors [J]. Water Science and Technology: Water Supply, 2001, 8 (1): 81 - 88.

[10] RYAN M, LAUTENCE W. Ammonium ion (NH_4^+) removal from secondary effluent through ion - exchange: the effect of biological activity and the presence of other cations[J]. Water Science and Technology, 1999, 40 (2): 143 - 149.

[11] INAN H, BAYKAL B B. Clinoptilolite: A possible support material for nitrifying biofilms for effective control of ammonium effluent quality[J]. Water Science and Technology, 2005, 51 (11): 63 - 70.

[12] JORGENSEN T C, WEATHERLEY L R. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants[J]. Water Research, 2003, 37 (8) 1723 - 1728.

[13] WANG Y Q, LIU S J, ZE X, *et al*. leachate solution using natural Chinese clinoptilolite[J]. Journal of Hazardous Materials, 2006, 136 (3): 735 - 740.

[14] ROBERTO L R, GELACIO A A, LINDA G G. Ammonia exchange on clinoptilolite from mineral deposits located in Mexico [J]. Journal of Chemical Technology and Biotechnology, 2004, 79 (6): 651 - 657.

[15] WANG Y F, LIN F, PANG W Q. Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite[J]. Journal of Hazardous Materials, 2007, 142 (1 - 2): 160 - 164.

[16] HANKINS N P, PLIANKAROM S, HILAL N. Removal of NH4 + ion from NH_4Cl solution using clinoptilolite: a dynamic study using a continuous packed - bed column in up - flow mode[J]. Separation Science and Technology, 2004, 39 (6): 1347 - 1364.

[17] WEATHERLEY L R, MILADINOVIC N D. Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite [J]. Water Research, 2004, 38 (20): 4305 - 4312.

[18] BELER B B, BAYRAM S, AKKAYMAK E, *et al*. Removal of ammonium from human urine through ion exchange with clinoptilolite and its recovery for further reuse[J]. Water Science and Technology, 2004, 50 (6): 149 - 156.

[19] MILADINOVIC N, WEATHERLEY L R. Intensification of ammonia removal in a combined ionexchange and nitrification column[J]. Chemical Engineering Journal, 2008, 135 (1 - 2): 15 - 24.

[20] ENGLERT A H, RUBIO J. Characterization and environmental application of a Chilean natural zeolite[J]. International Journal of Mineral Processing, 2005, 75 (1 - 2): 21 - 29.

[21] JORGENSEN T C, WEATHERLEY L R. Continuous removal of ammonium ion by ion exchange in the presence of organic compounds in packed columns[J]. Journal of Chemical Technology and Biotechnology, 2006, 81 (7): 1151 - 1158.

[22] HEDSTROM A, AMOFAH L R. Adsorption and desorption of ammonium by clinoptilolite adsorbent in municipal wastewater treatment systems [J]. Journal of Environmental Engineering and Science, 2008, 7 (1): 53 - 61.

[23] Chinese EPA. Water and Wastewater Monitoring Methods[M]. 3rd ed. Beijing: Chinese Environmental Science Publishing House, 1997.