Study on the ammonia nitrogen removal from tannery wastewater by natural and synthetic zeolite

Ding Shao-lan[*], *Li Ling, Zhang Ai-tao*

College of Resource and Environment, Shaanxi University of Science and Technology，Xi'an, Shaanxi 710021

Abstract: The removal of ammonia nitrogen by natural and synthetic zeolite from tannery wastewater were investigated, with the adsorption isotherms drawn, the effects of adding amount, temperature, pH, adsorption time, and salt to the adsorption process were analyzed. The results showed that the processes of ammonium adsorption by both zeolites were fitted to Freundlich adsorption isotherm. The best adsorption reached when pH=6, and the temperature affected much to neither zeolite. The addition of NaCl and Na_2SO_4 affected the ammonia removal by natural zeolite greatly, while relatively less than the synthetic one.

Key words: zeolite; tannery wastewater; ammonia nitrogen; salt

1 Introduction

As a refractory pollution, the tannery wastewater contains not only chromium, sulfide, but also oil, lignin and protein. It is usually treated by activated sludge. The microorganisms in sludge could largely decompose the organics to lower COD, but a new problem has also appeared that it also promoted organic nitrogen decomposition, resulting in ammonium concentration high as 200mg/L, or even higher. The discharge standard of water pollutants for leather and fur making industry (manuscript) has been proposed, in which the ammonium discharge concentration limit for present companies is 65 mg/L, and for the new-built companies is 35 mg/L. Therefore, it is necessary for further processing after the microbial treatment to meet emission requirements.

As a new non-metallic mineral, the natural zeolite has strong adsorption to ammonium with large specific surface and special structure. It is non-toxic, tasteless, and cheap, without any pollution to the environment. The natural zeolite could be used as a catalyst [1], or made into exchange column directly for further wastewater processing, and also it could be combined in biological units, such as biofilter and contacting oxidation to promote denitrogenation, which has been used widely in municipal wastewater, micro-polluted water, industrial wastewater treatment [2-5]. In this experiment, the effects of particle size, dosage, solution temperature, pH, salt content of tannery wastewater on ammonia treatment by natural zeolite were investigated, and the effects by synthetic zeolite were also studied.

2 Experiment
2.1 Materials

The natural zeolite (NZ) was from Jinyun, Zhejiang Province, and the main mineral was clinoptilolite, with some mordenite and heulandite. The chemical components were shown in Table 1;

*Corresponding author, Phone: 15829077070, E-mail: dingsl@sust.edu.cn

besides, there were some trace elements including sulfide, fluorine, and chromium. The ignition loss of NZ was 14.80%.

The synthetic zeolite (SZ) was from Shanghai Speciality Chemical CO., Ltd. with molecular formula as $Na_2O \cdot Al_2O_3 \cdot XSiO_2 \cdot YH_2O$, and the particle size at 20 to 40 mesh, i.e. 0.42 to 0.84 mm. The ignition loss of SZ was less than 15% to 30%.

Table 1 Main chemical components of NZ

Components	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	Sulfate
Content (%)	63.40	11.35	0.88	0.60	2.27	0.89	1.97	0.11	0.11	3.54

The ammonium solution was prepared with NH_4Cl, with concentration at 10 g N/L, and it was made into simulated wastewater according to the experiment.

2.2 Methods

2.2.1 The determination of adsorption isotherms

Put some zeolite in 250-ml flasks, add 150mL of ammonium chloride (NH_4Cl) solutions containing a range of NH_4^+ concentrations (ammoniacal concentration measured as nitrogen in ammonium form), keep agitating for 24h with covers, analyzing the ammonium concentrations before and after agitation, and the adsorption capacity q (mg NH_4-N g^{-1}) was calculated according to equation (1).

$$q = \frac{(C_i - C_0) \times V}{1000m} \tag{1}$$

Where C_0 is the ammonium concentration before adsorption (mg NH_4-N L^{-1}); C_i is the ammonium concentration before adsorption (mg NH_4-N L^{-1}); V is the volume of simulated wastewater (ml), and m is the zeolite dosage (g).

2.2.2 Effect of influential factors on adsorption

Put 150mL of simulated wastewater with a certain concentration in flasks, add some zeolite, adjust temperature, adsorption time, pH and the amount of salts, and keep agitating for 24h. The ammonium concentrations in solutions were analyzed with standard method (distillation and titration method, GB 7478-87), and the removal rate η was calculated according to equation (2).

$$\eta = \frac{C_0 - C_i}{C_0} \times 100\% \tag{2}$$

3 Results and Discussion

3.1 The determination of adsorption isotherms for both zeolites

By static adsorption experiment, the adsorption isotherms of both zeolites were shown in Fig. 1. According to the results, both isotherms were fit by Langmuir and Freundlich models, shown in Table 2.

According to the Langmuir model fitting results in Table 2, the ammonium adsorption capacities calculated for NZ and SZ were 19.23 mg/g and 19.88 mg/g respectively, but as shown in Fig. 1, the ammonium adsorption quantities for NZ and SZ had been higher than the calculated one when the ammonium equilibrium concentration was 4000 mg/L and 1500 mg/L, which inferred that the Langmuir model did not match the actual situation. The Langmuir equation assumes the uniformity of adsorbent surface, there be no interaction between the adsorbents, and limiting to monolayer adsorption. But the

zeolite showed very uneven surface, with much multilayer adsorption instead of monolayer, and so there existed much difference from the actual situation. According to Table 2, the adsorptions of both NZ and SZ were more fit with Freundlich isotherm, with higher correlation coefficient than the corresponding Langmuir isotherm, and the results were in coincidence with Wen Donghui's [6].
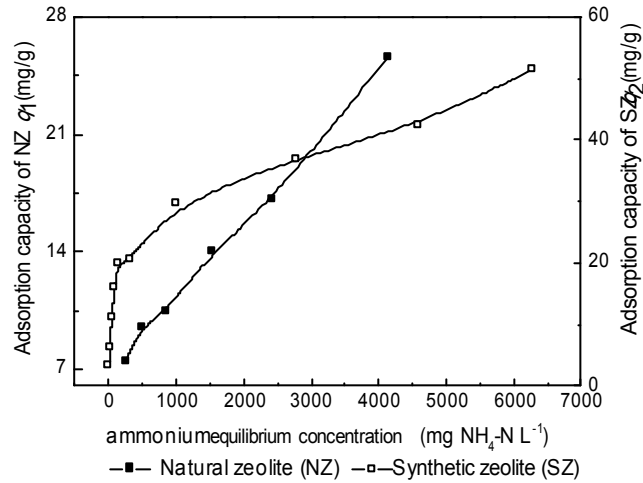

Fig. 1 The adsorption isotherms of NZ and SZ

Table 2 The adsorption isotherms of natural and synthetic zeolite

Isotherm Types	Zeolite Type	Adsorption Isotherm for Zeolite	q^0 (mg/g)	Linear Correlation Coefficient R^2
Langmuir Isotherm	NZ	$q = \dfrac{0.04473C}{1 + 0.002326C}$	19.23	0.865
	SZ	$q = \dfrac{0.6530C}{1 + 0.03285C}$	19.88	0.9748
Freundlich Isotherm	NZ	$q = 1.4818C^{0.3221}$	—	0.9548
	SZ	$q = 1.2750C^{0.5492}$	—	0.9933

3.2 Effect of NZ diameter on ammonium adsorption

The effect of diameter on ammonium adsorption was carried out with NZ. Add 5.0g NZ with a range of sizes into 150 ml of ammonium solution (the concentration was 200 mg NH_4-N L^{-1}), keep the temperature at 25℃, and the results were shown in Fig. 2.
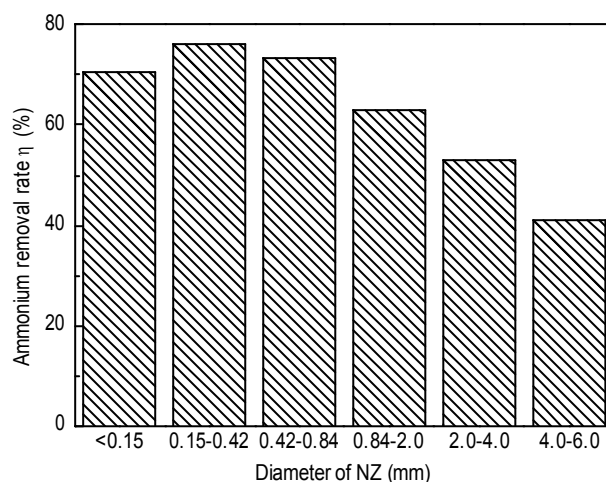
Fig. 2 Effect of diameter on ammonium adsorption by natural zeolite

Fig. 2 showed that the best removal efficiency was got when the diameter was 0.15 to 0.42mm, with the rate of 76.15%. The increase of diameter would result in a decline of adsorption efficiency. When the diameter was less than 0.15mm, the removal rate decreased either, which was caused by both the ion-exchange and physical adsorption of zeolites. When the diameter was smaller, the physical adsorption capacity would be reduced by the destruction of stereo chemical structure, besides, the zeolite powders would easily form agglomeration to reduce the dispersion in the wastewater and reduce the ammonium removal rate. When the diameter was bigger, the specific surface was relatively smaller, and so the removal rate decreased.

In the following experiments about the effects of influential factors on ammonium adsorption, NZ of sized at 0.42mm to 0.84mm was selected. The chosen NZ got the ammonium removal rate lower by about 3% than that of the NZ of sized at 0.15mm to 0.42mm.

3.3 Effect of zeolite dosage on ammonium adsorption

Add a certain amount of NZ and SZ respectively into 150 ml of ammonium solution (the concentration was 200 mg NH_4-N L^{-1}), keep the temperature at 25 ℃, and the results were shown in Fig. 3.
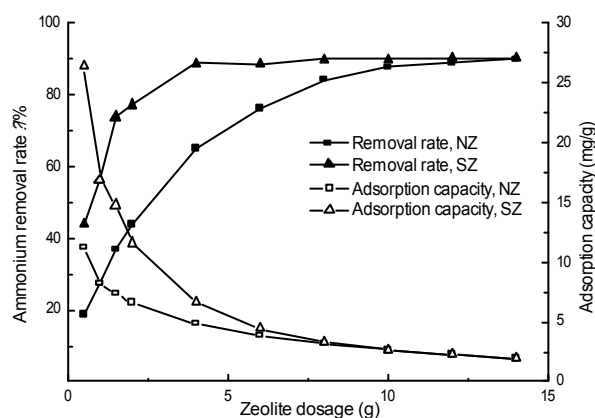

Fig. 3 Effect of zeolite dosage on ammonium adsorption

Fig. 3 showed that the ammonium removal rates improved with the increase of zeolite dosage. When the dosage ranged at 0.5g to 8g, the ammonium removal rate of SZ was higher than that of NZ When the dosage was more than 8g, the improvement of dosage on ammonium removal rate by NZ slowed down, and when it wan 12g, the removal rate was about 88%. As to the SZ, when the dosage was 4g, the ammonium removal rate was 88.26%, and it changed little with the increase of dosage. The ammonium

removal rate was 89.73% when the SZ dosage was 8g, and it reached 90.03% when the dosage was 15g.

When the dosage was less than 6g, the ammonium removal efficiency of SZ was far better than that of NZ, but the difference gradually reduced as more zeolites were used, and both of them reached a balance finally. The mechanism of ammonium adsorption on zeolite could be explained by its structure [7]. There was large specific surface, the electric field in the crystal lattice, the relatively strong surface static electricity and dispersion force in the NZ, besides, it had massive cavities and channels, accounting for about 50% of the overall structure, and they had uniform and fixed size, which helped in the ammonium adsorption to the zeolite. What's more, some Si^{4+} was replaced by Al^{3+} in the lattice, leaving residual negative charges, and it made NH_4^+ adsorbed to zeolite by ion exchange easier. Fig. 3 showed that the unit adsorption capacity reduced as the dosage increased, which made it necessary to consider both removal efficiency and economic factors in practical applications. The NZ was cheaper, while the SZ was relatively expensive, so 6.0g NZ or 2.0g SZ was used in the following experiments unless otherwise stated.

3.4 Effect of temperature on ammonium adsorption

Add 2.0g NZ and SZ respectively into 150 ml of ammonium solution (the concentration ranged at 50 to 500 mg NH_4-N L^{-1}), keep the temperature at 25℃ and 35℃ respectively, and the results were shown in Fig. 4.
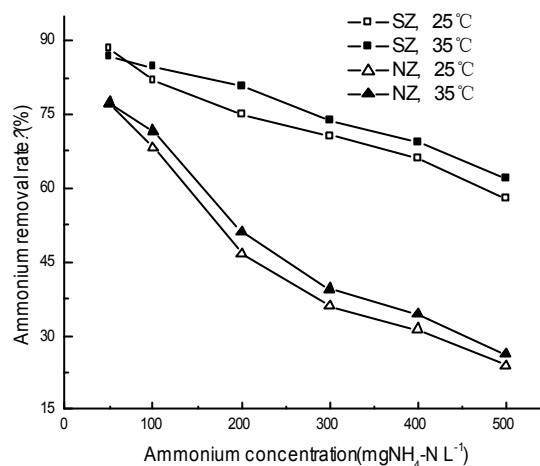

Fig. 4 Effect of temperature on ammonium adsorption

Fig.4 showed when the reaction temperature rose from 25℃ to 35℃, both the removal efficiencies of NZ and SZ increased, by about 3% to 5%. Since only the effect of temperature on the ammonium adsorption was considered, 2.0g NZ and SZ was used in this experiment, and so the ammonium adsorption to SZ was far better than NZ under the same ammonium concentration.

The temperature affected the adsorption in two aspects. First, the increase in temperature might speed up the ion movement, and it promoted the exchange reaction; Second, since the NH4+ hydrolysis, high temperature may conducive to the generation of $NH_3 \cdot H_2O$, decreasing the ammonium in water. By the combined effects, the temperature had less impact on adsorption. Lower temperature would improve the ion-exchange and selectivity of zeolite to ammonium [8]. Therefore, in the following experiment, the temperature was controlled at 25℃.

3.5 Effect of time on ammonium adsorption

Add NZ and SZ respectively into 150 ml of ammonium solution (the concentration was 200 mg NH_4-N L^{-1}), keep the temperature at 25℃, adjust adsorption time, and the results were shown in Fig. 5.
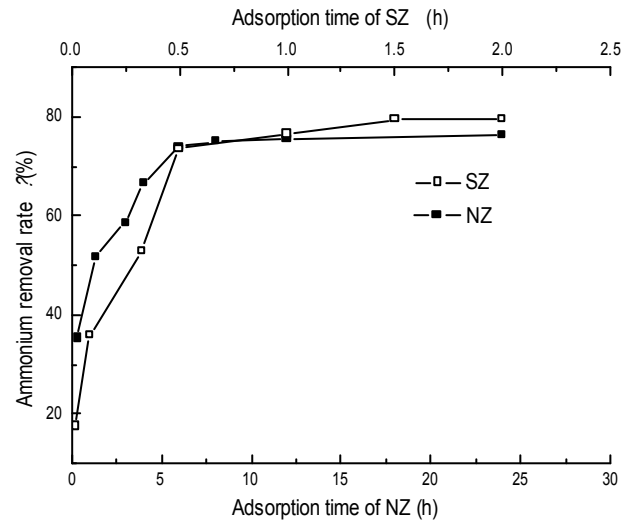
Fig. 5 Effect of time on ammonium adsorption

Fig. 5 showed that the adsorption rate of SZ was higher than that of NZ. The experimental results showed that NZ could reach high removal rate (>75%) when reacted for 6 hours, and it would rise slightly with time; as to SZ, the ammonium removal rate reaches high when reacted for 0.5 hours, and it might because of better structure and properties of SZ to NZ. As shown in Fig. 5, as time went on, both adsorptions reached a balance, with SZ higher than NZ. And it was consistent with the adsorption isotherms, which also confirmed larger adsorption capacity of SZ to NZ.

3.6 Effect of pH on ammonium adsorption

Add NZ and SZ respectively into 150 ml of ammonium solution (the concentration was 200 mg NH_4-N L^{-1}), keep the temperature at 25℃, adjust the pH of solution, and the results were shown in Fig. 6.
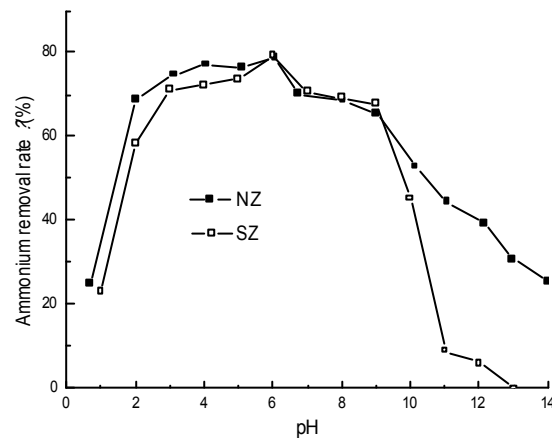

Fig. 6 Effect of pH on ammonium adsorption

Fig. 6 showed that there were some differences in suitable pH ranges of NZ and SZ. The suitable pH for NZ was 4 to 7, and its best efficiency was got when pH was 6; while the suitable pH for SZ was 3 to 9, and the best efficiency was also got when pH was 6. As to the tannery wastewater, the pH of effluent was 6 to 9 after physical and biological treatment, which meets the Integrated Wastewater Discharge Standard (GB 8978-1996), and also is in the suitable pH for SZ and NZ.

Fig.6 also showed that when pH<7, the adsorption of NZ was slightly higher than that of SZ; when pH<2 or pH>10, both zeolites declined greatly in removal rate, which meant that better adsorptions occurred in their suitable pH ranges. When in lower pH, the ion H^+ in wastewater might be competitive to NH_4^+ [9], and when in higher pH, the alkaline environment would promote the transformation of

ammonium into ammonia, resulting in worse ammonium removal efficiencies. In the experiment, it was found that SZ would dissolve under high pH, and it might also affect the ammonium removal.

3.7 Effect of salt dosage on ammonium adsorption

Massive salts will be used during leather-making process, take preparation section for example, common salt will be added for antisepsis, which will be discharged into wastewater as dissoluble ions, and would not be removed with COD et al, leaving high Na^+, Cl^-, SO_4^{2-}, and the leaving ions may affect the ammonium adsorption to zeolites. So, the effect of salt on ammonium adsorption was considered, as shown in Fig. 7.
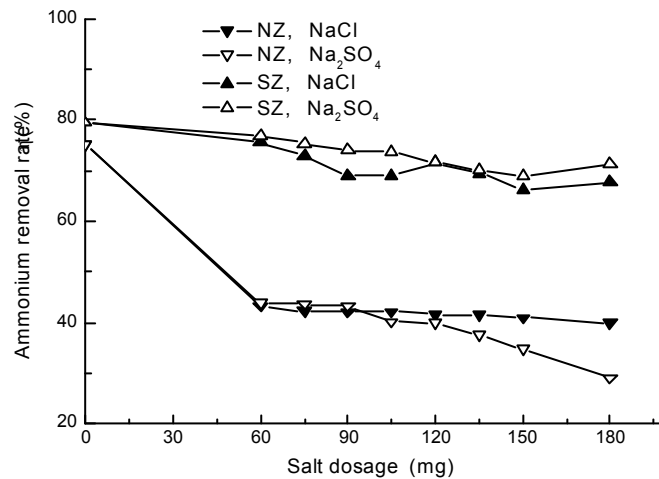

Fig. 7 Effect of salt dosage on ammonium adsorption

Fig. 7 showed that the addition of salt reduced the removal efficiency, and the impact was greater on NZ than on SZ. To NZ, when the salt dosage was 60mg, the ammonium removal rate declined to 45% from 75% obviously, while to SZ, it descended no more than 12%, much less than that of NZ. Fig.6 also showed that the effect of SO_4^{2-} on adsorption was greater than that of Cl^-, and quite the opposite for SZ.

The effect of salt on the ammonium adsorption was mainly due to the ion-exchange of zeolite. The Na^+ and Ca^{2+} exchange capacity of accouted for 97% of the overall exchange volumn. As Table 1 showed, Na^+ occupied 0.89% on the NZ, and there was 39.62g Na^+ in 6.0g NZ. When a lot of salt was added into the wastewater, the Na^+ quantity in solution was higher than that of on zeolite, and the ion exchange of Na^+ on zeolite and NH_4^+ in wastewater was restricted, resulting in huge decline in ammonium removal rate.

The existence of salt, on one hand, would affect the ion-exchange efficiency; on the other hand, the salts could be used for the regeneration of zeolites. Fu Wan-xia [10] used the mixture of NaCl and NaOH solution for the zeolite regeneration, and it was found that the best one-time regeneration occurred when pH was 11.99. The regeneration of zeolite by treated tannery effluent will be considered later, and the following study is in progress.

4 Conclusions

The ammonium adsorptions to both natural zeolte (NZ) and synthetic zeoltie (SZ) were more suitable to Freundlich model. The isotherm for NZ was $q = 1.4818C^{0.3221}$, with R^2 was 0.9548; and the isotherm

for SZ was $q = 1.2750C^{0.5492}$, with R^2 was 0.9933.

The ammonium removal rate increased 3% to 5% when the temperature rose from 25℃ to 35℃; The

adsorption rate of SZ was higher than that of NZ Both zeolites reached best adsorption efficiencies when pH was 6.

The addition of salt would greatly affect the ammonium adsorption to NZ, with a reduction high as 30%, while relatively less to SZ The effect of Na_2SO_4 on ammonium adsorption to NZ was greater than that of NaCl, but quite the opposite of SZ

Reference

[1] Zhi-xiang Zhang, Liang Chen, Nan Bao, et al. Photocatalytic oxidation of 2-chlorphenol using H-mordenite loaded TiO_2 film.Water Resources Protection, 2006, 22(2): 59-61.

[2] Michal Green, Adriaan Mels. Biological- ion exchange process for ammonium removal from secondary effluent [J]. Wat Sci Tech, 1996, 34(1- 2)：449- 458.

[4] Peng-an Luo, Zhi-chao Wu. Research of coking wastewater treatment with zeolite and biological combined processes. Industrial Water Treatment, 2004, 5: 21-24.

[5] Cintoli R .Ammonium by zeolite and treatment in UASB reactor of piggery wastewater[J]. Waster Science and Technology,1995，32(12)：73～81.

[6] Dong-hui Wen, Xiao-yan Tang, Qian-ru Ma. Research on the Adsorption Capacity for Ammonium of Natural Zeolite. Research of Environmental Science, 2003, 16(2): 31-34.

[7] Xi Zhang, Wei-zhong Wu, Dong-hui Wen, et al. Effect and Mechanism of Removal of Nitrogen in the Mimic Sewage Using Bio-zeolite System. Chinese Journal of Environmental Science, 2003, 24(5): 75-80.

[8] Gang Ren, Fu-yi Cui. Study of Modified Zeolite to Remove Ammonia Nitrogen in Water. Techniques and Equipment for Environmental Pollution Control, 2006, 7(3): 75-79.

[9] Koon J H, ufman W J. Ammonia removal from municipal wastewaters by ion exchange[J]. Journal Water Pollution Control Federation, 1975,47(3): 448-465.

[10] Wan-xia Fu, Ting yin. Selection and Optimization of Optimal Regenerated Catalyst for Zeolite. Journal of Beijing University of Civil Engineering and Architecture, 2007, 23(2): 1-3.