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Clinoptilolite Adsorption Capability of Ammonia in Pig Farm

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Abstract

In this paper, clinoptilolite, as an adsorbing material, which adsorption capability of ammonia was studied. Clinoptilolite is a porous crystal material, which adsorption properties of clinotiolite are strongly related to the framework structure, which has performance for the physical adsorption and ion exchange. China is in rich of nature clinoptilolite, which is cheap and suitable for extensive application in pig house. The experiment indicated that clinoptilolite had a characteristic of "rapid adsorption, slow equilibrium", it took 3 hours to reach adsorption equilibrium, clinoptilolite's particle size, moisture content and dosage had important effects on saturation adsorption time and ammonia adsorption capacity. With decreasing the particle size, clinoptilolite adsorption capacity increased, and the higher ammonia concentration, the better adsorption effect in the "rapid adsorption" phase. Different clinoptilolite's moistures also played an important role for adsorption effect, in the "rapid adsorption" phase, the effect was the best when moisture content of clinoptilolite was 40%; in the phase of "slow equilibrium", wet clinoptilolite adsorption would be better than the natural, the rank was: 40%>50%>30%>20%>60%>the natural. By regression analyze, when moisture content was 42%, adsorption capability could be the best. Besides, clinoptilolite adsorption capacity was studied, per unit saturation adsorption capacity of 10g nature clinoptilolite was 0.09 mg/g, 20g nature clinoptilolite's was 0.13 mg/g. Therefore, it could be seen that increasing the amount of clinoptilolite would improve the total and units clinoptilolite adsorption capacity. Considering the significant sorption for ammonia, the method of clinoptilolite adsorption could be simple and economic, it should be foreseeable that clinoptilolite adsorption would have a good prospect for air purification in pig farm.

Key words: Clinoptilolite; Ammonia; Adsorption; Pigpen

1. Introduction

China is the most important country for pig breeding in the world whose amount of pigs coming out is about 47% of the world [1]. More and more attention has been attracted to odors pollution of large-scale pig farms increasing. It is reported that pollution discharge is about 30 thousand tons, nitrogen discharge is 108 tons, phosphorus is 30 tons

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yearly, ammonia emission amount is 35 kilograms, sulfured hydrogen is 32 kilograms, power is 58 kilograms, and a lot of heavy metal, pathogenic microorganism and harmful substances, which soil, water and air away from within 5 kilometers are polluted with for a large-scale piggery with ten thousand pigs [2]. It appears pig unnamed high fever and other diseases, which have blocked the development of the hog industry. Environmental problems of the pig house, especially the control of harmful gases, which have become the public subject concerned. Sources, distribution and control measures of harmful gases in pig houses have been quite concerned in the world, and ammonia is one of the most harmful gases [3]. Ammonia is a colorless gas with an irritating odor, the product of various nitrogen-containing organic matter decomposition [4], in pig houses mainly including pig feces, urine, grasses, feedstock and so on. Water-solubility for ammonia is good, which is often dissolved in the wet ground, walls as well as mucosa and conjunctiva of pigs and human. Chinese labor hygiene standards require that the maximum limit of ammonia is 30 mg/m^3 in the air, and livestock and poultry fields environmental quality standards require the highest ammonia concentration is 25 mg/m^3 [5], in piglets houses ammonia concentration is higher in the morning and evening, lower in the daytime and stable relatively. By testing Beijing Daxing District breeding swine farm, ammonia concentration is generally 15 mg/m^3 in piglet houses, ammonia concentration is up to 90 mg/m^3 before forced ventilation in the morning. High ammonia concentration makes the piglets weak, appetite decreasing and daily gain and productivity reduced. Fattening houses are basically closed for insulation in winter, and it was tested that ammonia concentration was significantly high in January, the highest was 14.69 mg/m^3; the highest ammonia concentration was 16 mg/m^3 in pregnancy houses in September, and 7.98mg/m^3 [5-6] in July, despite not exceeding the standard, when ammonia concentration is over 10 mg/m^3 in winter, it would do harm to fattening pigs to a certain extent, affecting the performance.

Therefore, abatement on ammonia in the pig house is more and more important. Conventional method of reducing the concentration is forced ventilation, which can meet ventilation requirements of fattening homes, but it will bring indoor temperature fluctuation in piglets and childbirth pig houses because forced ventilation, particularly in winter, would also cause great energy loss, make against of energy saving and waste reduction. At the same time, ventilation will let ammonia into outside directly, polluting the surrounding environment. So more convenient and cost-effective methods should be investigated and discussed on ammonia removal in pig houses, not only solving problems of environmental pollution in the pig house, but also meeting environmental requires for pig production to achieve energy saving and waste reduction. In the passage absorbing ammonia using simulated experiment apparatus, ammonia reducing device in the bottom of the glass, clinoptilolite in the upper part of the glass which was near to the outlet. When ammonia coming to being, the concentration was increasing and moving to the vent outlet, so ammonia concentration on the top was homogeneous. It is more benefit for absorbing ammonia because of clinoptilolite on the top of bottle and near the vents department. In the reality pig house, ammonia flow toward mechanical vents department, so in fact clinoptilolite should be placed near the vent department, which can absorb ammonia better, but only decreasing the ammonia concentration in the pig house, but also reducing the diffusion capacity of ammonia to the environment around, but only providing a good rearing environment for pigs.

The study on reducing ammonia concentration in the pig house is brought more and more attention. Hayes controlled the crude protein content of feed would decrease ammonia volatilization rate of 30%, the effect is obvious [7], but it can not be solved ammonia problem completely. By experimental study, Yongkun Liang discovered the biological filtration treating ammonia has a significant effect, removal rate of ammonia for low concentration could reach more than 95% [8], while in this paper sorption for high ammonia concentration were also studied. In this paper, in order to reduce and control ammonia emission to outside effectively, a kind of material with effective sorption was sought; these effects on removal ammonia were researched for help advice of wide application. Clinoptilolite is a kind of aluminosilicate crystal with uniform size and regular structure, and is a family of aluminosilicate mineral with frame structure of water content [9]. The zeolite has been found for more than 30 kinds in the nature, such as analcite, natrolite, clinoptilolite and so on, which has polarity and great sorption for the stench of smaller diameter material and unsaturated compound (ammonia and hydrogen sulfide, etc.), whose sorption and ion-exchange capability are higher than silica gel and activated carbon, particularly the high affinity for NH_3, H_2S, CO_2 and any other macromolecule. Clinoptilolite powder is used to cover dung for reducing bad odor of barns in the 1950s in Japan. Yuqiu Wang and other people assessed the potential of natural Chinese clinoptilolite for ammonia removal from the leachate solution of sewage sludge. In batch study the effects of relevant parameters, such as contact time, initial ammonia concentration and particle size of clinoptilolite, were examined respectively [10]. A study on ion exchange kinetics and equilibrium isotherms of ammonium ion on natural Turkish clinoptilolite (zeolite) was conducted using a batch experiment technique. The effects of relevant parameters, such as temperature, contact time and initial ammonium (NH_4^+) concentration were examined, respectively [11].

2. Materials and methods

2.1. Materials

2.1.1. Clinoptilolite

The experiment used clinoptilolite from Chifeng in Inner Mongolia region, selecting diameters of <0.16 mm, 0.16~0.35 mm and 0.35~0.63 mm, 10g, respectively, which were washed by distilled water and dried.

2.1.2. Ammonia concentration simulated

In order to simulate ammonia concentration, controlling ammonia concentrations were in three ranges of 36.4~40.0mg/m^3, 61.5~63.0mg/m^3 and 140.0~141.2 mg/m^3, respectively. By changing the ammonia dosage in the experimental bottle, to obtain different concentrations of ammonia, the relationship between the ammonia dosage and volatilization is in Tab. 1. Ammonia detection equipment used ammonia detector of Z-800XP.

Tab.1. The relationship between ammonia's volume and concentration

Ammonia dosage (mL)	0.2	0.5	1.0
Ammonia concentration (mg/m^3)	36.4~40.0	61.5~63.0	140.0~141.2

2.2. Experimental methods

2.2.1. Experimental apparatus

Factors and parameters of clinoptilolite adsorption for ammonia were studied, and the experimental apparatus was shown as follow:

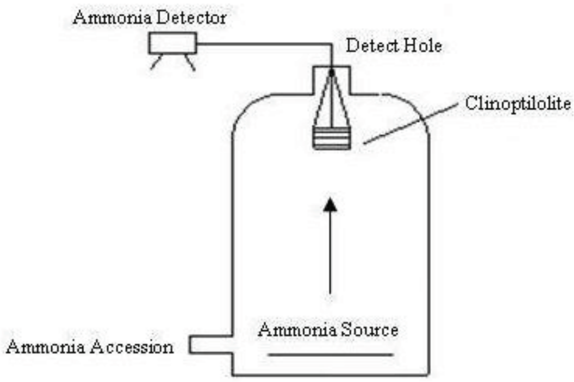

Fig.1. Experiment equipment of clinoptilolite

2.2.2. Experimental procedure

Different concentrations of ammonia were added into sealed glass bottle of 8L, to adjust the ammonia concentration in the bottle, clinoptilolite particles were placed on the steel net shelf so that the clinoptilolite and ammonia could contact completely. Experimental system was controlled by a certain direction flow under airproof, experimental temperature was set 20℃. Using ammonia detector monitoring the change of ammonia concentration in the device continuously, research and analysis on effective factors of clinoptilolite sorption and saturation adsorption were investigated, units was mg/L. Experiments were repeated three times. The transformation relationship between gas volume concentration and the mass concentration is:

$$X_1 = \frac{M \times X_2}{22.4} \quad (1)$$

In the formula, X_1——Mass concentration (mg/m^3)

X_2——Volume concentration (mg /L)

M ——Gas molecular weight measured (ammonia is 17)

3. Results and discussion

3.1. Adsorption capability of clinoptilolite

3.1.1. The structure of clinoptilolite

In 1756 Cronstedt who was a Sweden mineralogist, first discovered a white transparent fossil in the almond-shaped basalt pore, which was named zeolite for its foaming and boiling when heated. Zeolite is aluminosilicate mineral with water structure and a family of aluminosilicate mineral, the common minerals is natrolite, scolecite, analcime, clinoptilolite, mordenite and so on. The general chemical formulate is:

$(Na, K)_x\ (Mg, Ca, Sr, Ba)_y[Al_{x+y}\ Si_{n\cdot(x+y)}O_{2n}]mH_2O$

In the above formulate, n stands for electrovalence, x+y stands for the number of Al-O and Si-O tetrahedron, the value of x/y is between 1~5.

The framework of zeolite is the complicated three dimensional structures which are constituted by oxygen, silicon and aluminium. Basic structure cell is made of one silica atom (or aluminium) as the core, four oxygen atoms as vertices [13]. Different characteristics of different zeolites are reply on their different frameworks.

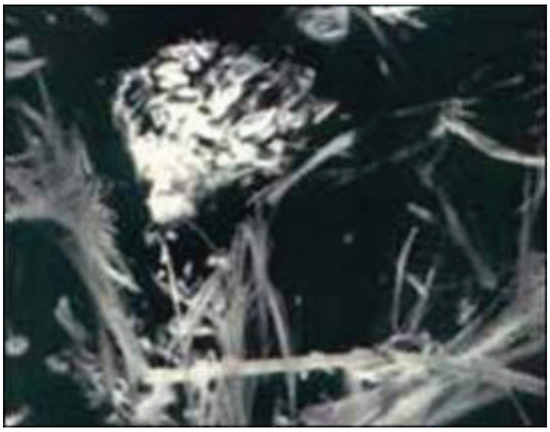

Fig.2. Configuration of natural zeolite

3.1.2. Adsorption capability of clinoptilolite

Clinoptilolite is a kind of porous crystal mineral. There are a lot of voids and holes in the clinoptilolite framework, which can adsorb and closure molecule with the very shape and size; it can be seen from the framework that electric charge numbers of Al-O tetrahedron are unbalanced, which needs to be compensated by alkali metals and alkaline-earth metals, when the number of electrical charge of trivalence aluminous is lower than the minus charge of around oxygenic. Therefore, clinoptilolite has a special characteristic of ion exchange, plentiful cations take up voids and holes in the framework, and the combination of cations and aluminium silicate is quite feeble, with strong liquidity, which can exchange with cations in the liquid easily, after exchanging the clinoptilolite structure would not be destroyed, that is the reason of its character of exchanging with cations [14]. Surface of various zeolites is between 400 and 800 m^2/g, such of which have good adsorption [15]. Besides, the diameter is between 0.6~1nm, pore canal diameter is between 0.3~1nm, the diameter of NH_4^+ is 0.286nm (NH_3 is smaller), so the adsorption effect of zeolite to ammonia is very good in the presence of dispersion force [16]. Because ammonia diameter is equivalent to pore and hole of clinoptilolite, molecule in the pore and hole of clinoptilolite which cause hole wall field superposition in the presence of dispersion force, forming super pore effect, increasing the adsorption effect. Besides, cations are in the holes of clinoptilite crystal lattice, meanwhile parts of trellis are with minus charge, so there is strong electric field around these ions. Clinoptilite has good adsorption effect because of combined action of dispersion force and electrostatic force [16]. In the paper, clinoptilite was studied, analyzing the adsorption to ammonia with different particle sizes but equivalent clinoptilite, adsorption of wet clinoptilite with different moisture contents, saturation adsorption and quantification unit of clinoptilite saturation adsorption.

3.2. The effect on different clinoptilolite particles for sorption capacity of ammonia

3.2.1. Clinoptilolite sorption capacity when ammonia concentration was 61.5~63.0 mg/m^3

The relationship of clinoptilolite adsorption course was drawn below, using the average values when ammonia concentration was between 61.5 and 63.0 mg/m^3, in Fig. 3.

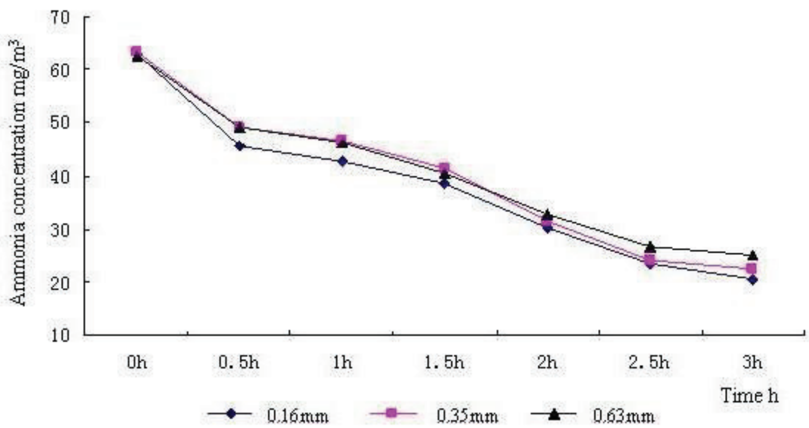

Fig.3. Experiment of adsorption in (61.5~63.0mg/m^3) concentration ammonia condition

It can be seen that in the first 0~0.5h, the ammonia removal efficiency is very significant, ammonia concentration in experimental bottle decreases linearly and the slope is more steep; in 0.5 to 1.5h, the curves decline become smooth gradually; a rapid adsorption process appears again from 1.5 to 2.5h, and sorption gradually reaches equilibrium till 3 hours, which reflects the clinoptilolite with a characteristic of "rapid adsorption, slow equilibrium". In the adsorption process, 0.5h and 1.5h were two important turning points as the "rapid adsorption" and "slow equilibrium", meanwhile gas species concentrated in the solid interface, and solid surface energy was decreased because of adsorption effect. Physical absorption was caused by dispersion force, electrostatic force and capillary force of clinoptilite surface, the same adsorption course with common porous materials [17].

Langmuir thought there are places which could adsorb molecule or atomic just like seats in the showplace. Adsorption seats could be distributed around the surface equably, but much more were non-uniform. When adsorption equilibrium was reached, molecule numbers which would be absorbed in the adsorption seats in unit time were equal to the leaving ones, that is to say, adsorption rate was the same with desorption ratio [18]. From the figure, it is known that adsorption rate was fastest and effect was best of clinoptilite with particle less than 0.16mm, which can show that the adsorption capacity was increasing to ammonia, with clinoptilite sizes decreasing, and adsorption capacity was more when adsorption equilibrium, which verified that clinoptilite was porous materials, less sizes, more surface area, more adsorption capacity, viewpoint of Langmuir were proved again.

According to the experimental data, the table of clinoptilite adsorption ratio could be drawn when ammonia concentration was between 61.5 and 63.0 mg / m^3, in tab. 2.

Tab.2. Ammonia adsorption ratios in different particles

Clinoptilite size (mm)	Ammonia concentration of (61.5~63.0 mg/m^3)							
	Rapid adsorption phase			Slow equilibrium phase			Total adsorption rate (%)	Average adsorption of unit clinoptilite (mg/g)
	Initial value (mg/m^3)	Value of 0.5h (mg/m^3)	Adsorption rate (%)	Value of 0.5h (mg/m^3)	Final value (mg/m^3)	Adsorption rate (%)		
<0.16	63.0	45.5	27.8	45.5	20.5	54.9	82.7	0.034
0.16~0.35	63.3	49.1	22.4	49.1	22.53	54.1	76.5	0.033
0.35~0.63	62.5	49.1	21.4	49.1	25.0	49.1	70.4	0.030

It could be seen from the table above that the best adsorption to ammonia was when the clinoptilite size was 0.16mm, the ratio of rapid adsorption phase was 27.8%, slow equilibrium phase was 54.9%, and the total was 82.7%, which were higher than the ratio of sizes of 0.16~0.35mm and 0.35~0.63mm, that is to say, the less of clinoptilite size, the higher ratio of adsorption to ammonia, and when ammonia concentration was 61.5~63.0 mg/m^3, the ratio of rapid adsorption phase was not high, and adsorption of slow equilibrium phase would play a major role. Besides, average adsorption capacities of unit quality clinoptilite were 0.034 mg/g, 0.033 mg/g and 0.030 mg/g, respectively. It would be harmful to the production performances when ammonia concentration was more than 10 mg/m^3 in the fattening pig house actually, that is to say, actual clinoptilite quantities needed to adsorb ammonia in the pig housing could be calculated, which were about 12.5g, 12.9g and 14.0g, respectively.

3.2.2. Clinoptilolite adsorption capacity when ammonia concentration was 140.0~141.2 mg/m^3

The experiment was repeated three times, and the curves were drawn below using the average values when ammonia concentration was between 140.0 and 141.2 mg / m^3, in Fig. 4.

Fig. 4 was similar with Fig. 3, even though clinoptilite adsorption was carried under the higher concentration; adsorption process took on the similar character as “rapid adsorption, slow equilibrium”, but still had some differences. The time of 0~0.5h was rapid adsorption phase, the effect of adsorbing ammonia was remarkable, the concentration of ammonia decreased linearly and the velocity was faster; from 0.5h to 2.5h, the adsorption curves gradually smoothed, and reached equilibrium till 3h. 0.5h was the time turning point from “rapid adsorption” to “slow equilibrium”, which were shown the characteristic of rapid adsorption once again.

Besides, when clinoptilite sizes were same, the higher original concentration of ammonia, the more adsorption capacity and faster adsorption rate in the rapid adsorption phase; in the slow equilibrium phase, the curves were smoother than the ones of slow concentration, and adsorption could be done in a short time. Under the condition of the same size, in the rapid adsorption phase, the higher original concentration of ammonia, more sufficient of clinoptilite, better adsorption effect, in the slow equilibrium phase, because there were a lot of ammonia in the clinoptilite that needed time for them moving toward the inner, leaving outside adsorption seats for ammonia un-adsorbed, which could be explained by Langmuir, so adsorption curves were smoother than the ones of slow concentration.

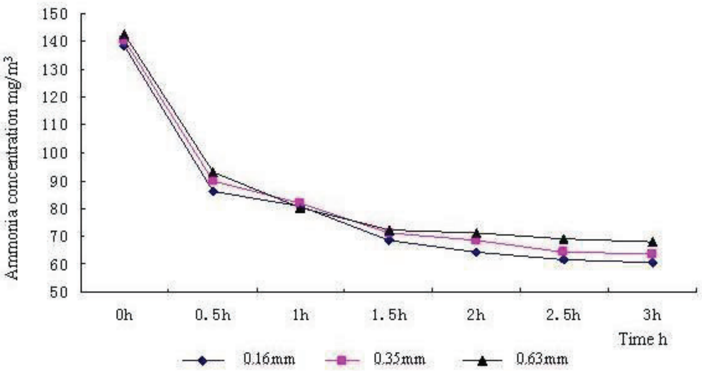

Fig.4. Experiment of adsorption in high concentration ammonia condition

According to the experimental data, the table of clinoptilite adsorption ratio could be drawn when ammonia concentration was between 140.0~141.2mg / m^3, in tab. 3.

It could be known from the table above that compared to 61.5~63.0 mg/m^3, when ammonia concentration increased to 140.0~141.2 mg/m^3, the ratio was improving remarkably in the rapid adsorption phase, while the one decreased quickly in the slow equilibrium phase, and the total ratio dropped. Average adsorption capacities of unit quality clinoptilite were 0.062 mg/g, 0.061 mg/g and 0.059 mg/g, respectively. According to national criterion, the highest concentration of ammonia in the animal building should be no more than 25 mg/m^3, so actual clinoptilite quantities needed to adsorb ammonia in the pig housing could be calculated. They were about 12.5g, 12.9g and 14.0g, respectively. In the experimental course, clinoptilite quantities were 10g all the same, under the condition of high ammonia concentration, the ratio of rapid adsorption phase increased remarkably, but in the slow equilibrium phase, because clinoptilite adsorption was in saturation and couldn't adsorb any more, total ratio decreased. In addition, when clinoptilite dosing quantities were the same, the higher ammonia concentration was, the more remarkable the rapid adsorption course of clinoptilite was, the higher adsorbing ratio was.

Tab.3. Ammonia adsorption ratios in different particles

Clinoptilite size (mm)	Ammonia concentration of (140.0~141.2 mg/m^3) Rapid adsorption phase			Slow equilibrium phase			Total adsorption rate (%)	Average adsorption of unit clinoptilite (mg/g)
	Initial value (mg/m^3)	Value of 0.5h (mg/m^3)	Adsorption rate (%)	Value of 0.5h (mg/m^3)	Final value (mg/m^3)	Adsorption rate (%)		
<0.16	138.4	86.2	37.7	86.2	60.5	29.8	67.5	0.062
0.16~0.35	140.4	90.1	35.8	90.1	64.0	28.9	64.7	0.061
0.35~0.63	142.4	93.1	34.6	93.1	68.1	26.8	61.4	0.059

3.3. The effect on different moisture contents of the clinoptilolite for ammonia absorption

Environment of pig housings is always hot and humid, so moisture factor can not be ignored. Clinoptilolite surface moisture content would certainly affect the sorption capacity of ammonia 0.35~0.63mm, 10g clinoptilolite particles were selected in the experiment, moisture contents were 20%, 30%, 40%, 50% and 60% after treated respectively, the trend curves of sorption experiment are in Fig. 5.

It could be seen from Fig. 5, clinoptilolite still showed the characteristic of "rapid adsorption, slow equilibrium". In the first 0~0.5h of rapid adsorption phrase, when clinoptilolite moisture content is 60%, the adsorption was the worst, but discrepancies were not obvious between nature clinoptilolite and other moisture contents; In the slow equilibrium phrase, adsorption of clinoptilolite with certain moisture content is better than nature clinoptilolite.

It also showed that moisture don't affect the sorption in a certain extent. Till 3 hours of adsorption equilibrium, the adsorption capacity of nature clinoptilolite was the lest, the rank was: 40%>50%>30%>20%>60%>nature clinoptilolite, it shows that moisture concentration could effect clinoptilolite adsorption to ammonia, and when moisture concentration was more than 40% and less than 40%, it would decrease the adsorption effect. The experiment expressed that in the rapid adsorption phrase, moisture concentration was too high to block clinoptilolite adsorption; in the slow equilibrium phrase, adsorption of nature clinoptilolite was the worst, the adsorption quantity was the least when reaching equilibrium, while other moisture ratios have differences which made the trend delay.

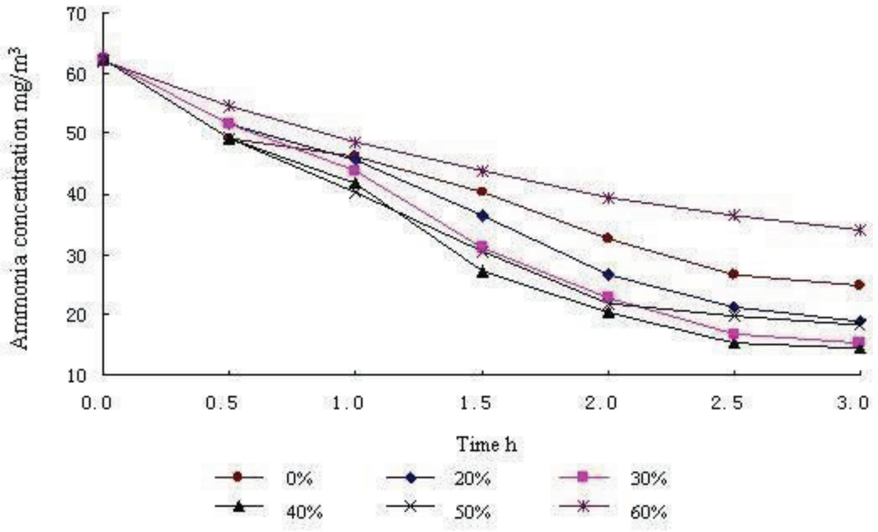

Fig.5. The adsorption in (61.5~63.0 mg/m^3) concentration ammonia condition with moisture ratio

According to experimental data, the table of ammonia adsorption ratio was drawn when ammonia concentration was 61.5~63.0 mg/m^3 in the Tab. 4.

Tab.4. Ammonia adsorption ratio at concentration of 61.5~63.0 mg/m^3

Moisture	Ammonia concentration of (61.5~63.0 mg/m^3)		
	Initial value (mg/m^3)	Final value (mg/m^3)	Adsorption rate (%)
Nature	62.2	25.0	59.8
20%	62.2	19	69.5
30%	62.2	15.2	75.6
40%	62.2	14.4	76.8
50%	62.2	18.2	70.7
60%	62.2	34.2	45.0

Using SPSS statistical procedures, through mathematical regression analysis, the curves for moisture content of ammonia adsorption are fitted under the concentration of 61.5~63.0mg/m^3 in Fig. 6. When the moisture content of clinoptilolite is 42%, adsorption quantity of ammonia is the largest.

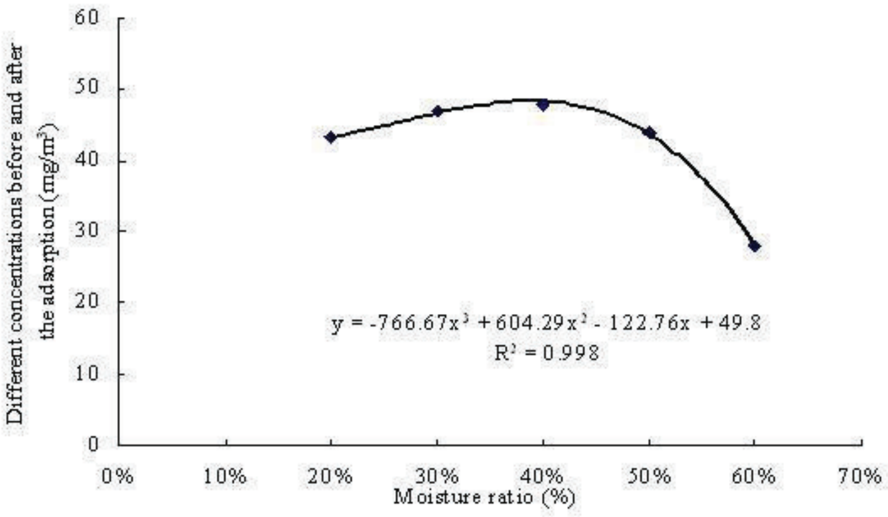

Fig.6. The adsorption capacity for ammonia concentration (61.5~63.0 mg/m^3) with different moisture ratios

When clinoptilolite with content moisture adsorbed ammonia, part of ammonia could transform water molecule in clinoptilolite into NH_4^+ (e.g. formula 2); at this time clinoptilolite adsorption included two courses physics adsorption and ion transformation. Physics adsorption course is related with framework structure of clinoptilolite, produced by external molecular force and electrostatic force, which is the same with common adsorption course of porous materials; and ion transformation course embodied adsorption to ammonia, which is the chemical transformation course between interior cations in clinoptilolite crystal structure and NH_4^+ in the solution, and this course can be described as:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$Z^{n-} \cdot M^{n+} + nNH_4^+ \leftrightarrow Z^{n-} \cdot nNH_4^+ + M^{n+} \quad (3)$$

In the formulas, Z stands for anion part of clinoptilolite, M stands for cation of clinoptilolite, n is charge number. But fluidity of cations inside clinoptilolite is large, and binding compound or complex can not be formed between cations and clinoptilolite crystal structure, so this ion transformation course is a special chemical adsorption, which depends on ion transforming force whose intension is much less than chemical bond [13]. clinoptilolite transformation has selectivity, different kinds clinoptilolite have different selectivity, the selecting ranking of clinoptilolite was: $CS^+>Rb^+>K^+>NH_4^+>Pb^{2+}>Ag^+>Ba^{2+}>Na^+>Sr^{2+}>Ca^{2+}>Li^+>Cd^{2+}>Cu^{2+}>Zn^{2+}$ [19], in the formula 3, M stands for alkali metal, such as Na, K, Li, and alkaline earth metal, such as: Ca, Mg, Ba, Sr, n is charge number of cation. From above, it could be illustrated that clinoptilolite adsorption to NH_4^+ is better than to Ba^{2+}, Na^+, Sr^{2+}, Ca^{2+} and Li^+, such as formula 2, better adsorption effect can be reached, from Fig. 6 it could be known that with the increasing of moisture content, the concentration of NH_4^+ was adding, and clinoptilolite adsorption quantity was improving. When moisture content was 42%, the quantity was the largest; at the same time NH_4^+ dissolved to solution saturation gradually. Moisture contents were increased continually, the concentrations of NH_4^+ were decreased, and adsorption quantity reduced.

It is generally thought that the temperature in piglet house can be controlled to 20~30℃, and pig house 15~20℃, and humidity 50~55%. Under this humidity, clinoptilolite adsorption quantity to ammonia can be improved to some degree.

3.4. Saturation of nature clinoptilolite for ammonia adsorption

3.4.1. Saturation of nature clinoptilolite particle for ammonia adsorption

The largest quantity of clinoptilolite adsorbing ammonia is related to the replacement time and the dosage. According to adsorbent saturation testing methods[20] clinoptilolite particles with 10g and 20g, 0.35~0.63 mm was got, 0.2 mL ammonia was dropped into experimental bottle gradually respectively, in order to increase the ammonia concentration in the bottle and make original concentration in the range of 36.4~40.0 mg/m^3. According to the above experimental results, ammonia could be adsorbed by clinoptilolite completely after 3 hours. The initial value, 2h adsorption value and the final value of 3h were recorded. Experiments repeated three times, and average values of every test points were analyzed in Tab. 5:

Tab.5. Data of ammonia adsorption capacity with 10 g nature clinoptilolite units: mg/m^3

sequence number	1	2	3	4	5	6
initial value	37.2	36.4	35.7	37.9	39.5	39.5
2 h	7.6	9.9	19.0	23.5	37.9	39.5
3 h	4.6	3.8	10.6	15.9	30	39.5

C_0: ammonia initial concentration, C_3: ammonia concentration of 3 hours

It could be seen that after the first 3 hours, ammonia concentration has decreased to 4.6 mg/m^3, and adsorption ratio was 87.6%; secondly, increasing the ammonia concentration in the bottle, adsorption ratio was 89.6% after 3 hours' adsorption; hereafter, increasing the ammonia concentration continually, this clinoptilolite could still adsorb ammonia, but its adsorption ratio decreased; it couldn't adsorb ammonia any more until the 6th, and ammonia concentration has not declined, it could be thought that clinoptilolite adsorption capacity has reached saturation.

The total concentration difference of ammonia adsorption:

$$\sum_{i=1}^{6} C_{0i} - \sum_{i=1}^{6} C_{3i} = 226.2 - 104.4 = 121.8 mg/m^3 \quad (4)$$

The total ammonia adsorption capacity: 121.8×8/1000 = 0.97 mg

Per unit ammonia adsorption capacity: 0.97/10 = 0.097 mg/g

According to unit adsorption capacity, in order to adsorb original concentration 37.2 mg/m^3, clinoptilolite needed in theory could be calculated as 3.1g. In the experiment using 10g of clinoptilolite to adsorb ammonia, it would be deduced that though a period of time after 3 hours' adsorption, clinoptilolite could adsorb the ammonia in the bottle completely; besides, in the range of adsorption capacity, clinoptilolite take on the character of continual adsorption, that is to say, in the adsorption phrase of "slow equilibrium", it could continue adsorbing until adsorption saturation when ammonia concentration was increasing.

Similarly, 20g, 0.35~0.63mm clinoptilolite particles were got; repeating the experiment above, measurement values are in Tab. 6.

Tab.6. Data of ammonia adsorption capacity with 20 g nature clinoptilolite units: mg/m^3

sequence number	1	2	3	4	5	6	7	8	9	10	11	12
initial value	35.7	33.4	35.7	39.5	41.0	37.2	36.4	37.9	33.4	38.7	36.4	37.9
2 h	7.6	6.8	9.1	9.1	9.9	8.3	10.6	27.3	23.5	26.6	31.1	35.7
3 h	0	0	0	0	0	0	0	3.8	15.9	25.0	28.8	35.7

C_0: ammonia initial concentration, C_3: ammonia concentration of 3 hours

It could be known that from Tab. 6 clinoptilolite ratio was 100% in the first seven experiments, that is 20g clinoptilolite could adsorb ammonia of 258.5 mg/m^3, 2.068 mg totally in 21 hours; clinoptilolite ratio was 90.0% for the eight times increasing ammonia concentration, after that the ratios has decreased sharply until clinoptilolite adsorption saturation for the twelve times, total adsorbing quantity was 334mg/m^3, 2.67 g, what's more, which was the 2.8 times more than the quantity of 10g nature clinoptilolite.

The total concentration difference of ammonia adsorption:

$$\sum_{i=1}^{12} C_{0i} - \sum_{i=1}^{12} C_{3i} = 443.2 - 109.2 = 334 mg/m^3 \quad (5)$$

The total ammonia adsorption capacity: 334/1000×8 = 2.67 mg

Per unit ammonia adsorption capacity: 2.67/20 = 0.13 mg/g

Through the experiment above, it indicated that under the condition of the same practical and similar original concentration, adding clinoptilolite dosage, the total adsorption quantity and unit saturation adsorption quantity can be both improved effectively. Because increasing the voids and holes could make adsorption effect better, adsorbing and closuring ammonia much more and faster, with adding clinoptilolite dosage; in the "slow equilibrium" phrase, when ammonia concentration was increasing, it could keep adsorbing until adsorption saturation in the range of clinoptilolite's adsorption capacity.

3.4.2 Saturation study of clinoptilolite particles with 40% moisture concentration for ammonia absorption

Kusakabe[21]et al. reported that gas molecule on clinoptilolite surface can generate ion transformation in some condition. The experiments above show that the best adsorption effect appears when moisture content is about 40%. Based on the adsorbent experiments of nature clinoptilolite, using the saturated clinoptilolite 10g, with particles of 0.35~0.63mm, dropping purified water to moisture content is 40%. Detail experiment data is shown in Tab. 7.

Tab.7. Data of ammonia adsorption capacity with clinoptilolite moisture content 40% units: mg/m^3

sequence number	1	2	3	4
initial value	37.2	37.9	36.4	39.5
2 h	15.2	17.5	30.4	38.7
3 h	13.7	15.2	28.8	38.7

C_0: ammonia initial concentration C_3: ammonia concentration of 3 hours

The total concentration ammonia adsorption:

$$\sum_{i=1}^{12} C_{0i} - \sum_{i=1}^{12} C_{3i} = 151 - 96.4 = 54.6 mg/m^3 \quad (6)$$

The total ammonia adsorption capacity: 54.6×8/1000 = 0.44 mg

Per unit ammonia adsorption capacity: 0.44/10 = 0.044 mg/g

By the experimen, clinoptilolite still had the character of adsorption capacity when dropping purified water on the saturated clinoptilolite in order to make its moisture content was 40%; 0.44mg ammonia was added to the former adsorption capacity, which shows that clinoptilolite is a kind of porous crystal mineral again. The process that nature clinoptilolite absorbing ammonia was seen as a physical adsorption process, after adding water to clinoptilolite, 0.44mg of ammonia was added, which explained that clinoptilolite has special character of ion transformation. A lot of cations take up certain places in the voids and pore of framework structure, but were little related to framework structure clinoptilolite because of its fluidity, which can be changed with NH_4^+ but not change the crystal structure [13]. Voids and holes in the aluminosilicate framework structure had exchangeable cations, so clinoptilolite exhibit well character of ion changing, absorbed NH_3 parts of NH_4^+ that filtered into holes of clinoptilolite in the water, that is, $NH_3+H_20 \rightarrow NH_4^++OH^-$, increasing adsorption quantity.

4. Conclusion

In this paper, the effect on clinoptilolite adsorption for ammonia was investigated, the impact of sorption of ammonia was discussed including the clinoptilolite particle size, moisture content, unit saturated adsorption capacities were calculated. The experiment results are as follow:

Clinoptilolite is good at adsorbing ammonia for the trait of porous media. In the adsorption process, clinoptilolite adsorption showed the characteristic of “rapid adsorption, slow equilibrium”. With the increasing of clinoptilolite particle size, particle surface area reduced, the adsorption capacity of ammonia also decreased, which may infer that: ammonia adsorption capacity would be greater for continuing to reduce the particle size, the effect would be more obvious, therefore, in order to obtain good absorption effect, clinoptilolite particle should be selected as small as possible.

Adsorption capability of wet clinoptilolite was bigger than the nature clinoptilolite’s, in a certain, with the increasing of moisture, adsorption capability also increased. In the experiment, when the moisture was more than 40%, adsorption capability decreased, and the rank was 40%>50%>30%>20%>60%>nature clinoptilolite. Nature clinoptilolite for ammonia adsorption can be considered as a physical adsorption course and no ion exchanging course; when wet clinoptilolite adsorbed ammonia, because of the integrating course of physical adsorption and ion exchanging course, made adsorption capability effect remarkable. Though mathematics regression analysis, the best adsorption effect was when the moisture of clinoptilolite was 42%.

In the saturation adsorption experiment, total adsorbing quantity of 10g clinoptilolite was 121.8mg/m^3, and per unit adsorption capacity is 0.097 mg/g; the quantity of 20g clinoptilolite was 334mg/m^3, and per unit adsorption capacity is 0.13 mg/g, it can be seen from that with the amount of clinoptilolite increasing, the unit and total clinoptilolite sorption capacity can be improved. Besides, dropping water on the saturated clinoptilolite 10g, making the moisture 40%, this could increase ammonia adsorption capacity of 0.44mg, which could illustrate the adsorption course was a integrating course of physical adsorption and ion exchange course again.

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References

[1] Yueping Zhao, Dewu Hu. Comprehensive treatment of main environment pollution of large-scale pig farm; 2006(211): 52–53.

[2] Sheng Hua, Shuqi Mei, Jinying Wu, Junhua Zhou. Environment protection technology of large-scale pig farm. Feed Industry; 2007, 28(17): 62–64.

[3] Sifa Dai, Like Wang. Observation of part harmful gases distribution in closed pig house. Journal of Anhui Agrotechnical Teachers College; 2004, 18(1): 7–10.

[4] G. Busca, C. Pistarino. Abatement of ammonia and amines from waste gases: a summary. Journal of Loss Prevention in the Process Industries; 2003, 16: 157–163.

[5] Zhiping Zhu, Hongmin Dong, Bin Shang, Guohu Kang, Haisheng Zhu, Xueping Tao et al.. Measurement of ammonia concentration and estimation on emission flux in pig house. Journal of Agro-Environment Science; 2006, 25 (4): 1076–1080.

[6] Zhiping Zhu, Hongmin Dong, Bin Shang, Guohu Kang, Haisheng Zhu, Yi Shi. Measurement of ammonia and nitrous oxide concentrations and estimation of the emission rates from gestation pig buildings. Transactions of the Chinese Society of Agricultural Engineering; 2006, 22: 175–178.

[7] Hayes E. T, Leek A.B.G., Curran T. P. The influence of diet crude protein level on odor and ammonia emission from finishing pig houses. Bioresource Technology; 2004, (91): 309–315.

[8] Yongkun Liang, Xie Quan, Jingwen Chen, Shuo Chen, Daming Xue, Yazhi Zhao. Biofiltration of ammonia-contaminated gas streams. Acta Scientiae Circumstantiae; 2000, 20(5): 518–522.

[9] Tiren Gu, Buyao Zhu, Wailang Li. Surface chemistry. Beijing: Science Press; 2003, 290.

[10] Yuqiu Wang, Shijun Liu, Ze Xu, Tianwei Han, Sun Chuan, Tan Zhu. Ammonia removal from leachate solution using natural Chinese clinoptilolite. Journal of Hazardous Materials; 2006, 136: 735–740.

[11] Dogan Karadag, Yunus Koc, Mustafa Turan, Bulent Armagan. Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. Journal of Hazardous Materials; 2006, 136: 604–609.

[12] Junmin Gao, Zegen Zheng, Yan Wang, Junfeng Dou. Application of Zeolite in Water Treatment. Journal of Chongqing Jianzhu University; 2001, 23(1): 114–117.

[13] Dongsheng Wen. Bioregeneration technology of natural zeolite applied in the pollution control of the storm runoff in Dianchi basin. China Environment science press; 2003, 21–25, 71–72.

[14] Fangming Chen, Qi Lu, Lijing Cao. Processing Technology of Natural Zeolite and Its Application in Water Treatment. Safety and Environmental Engineering; 2004, 11(1): 19–22.

[15] Jing Liu, Huifen Yang, Cunyi Song. Research on Application of Clinoptilolite in Deeply Sewage Treatment. Non-Metallic Mines; 2005, 28(2): 42–44.

[16] Chengalad Madhusoodana. Characterization and adsorption behavior of ZSM-5 zeolite film on cordierite honeycombs prepared by a novel in situ crystallization method. Journal of Porous Materials; 2001, (8): 265–271.

[17] Donghui Wen, Xiaoyan Tang. Mechanism for physical-chemical actions of natural zeolite on NH_4^+ in solution. China Environmental Science; 2003, 23(5): 509–514.

[18] Seiichi Kondo, Shi Chuan Da-hsiung, Abe Ikuo. Adsorption Science, LiGuoxi translated. Beijing: Chemical Industry Press; 2006, 37–39.

[19] Tsitsishvili G V, Andronikashvili T G. Natural zeolites. Chichester, England: Ellis Horwood Limited; 1992.

[20] Zongzhe Jing, Jinsheng Liang, Jing Wang. Purifying materials air purificationproperties of inorganic purifying materials activated by rareearth. China Building Material Science & Technology; 2000, (2): 9–12.

[21] Kusakabe K.,Kuroda T.,Uchino K.. Gas permeation properties of ion-exchanged faujasite-type zeolite membranes. AI ChE Journal; 1999, 45(6): 1220–1226.