
原 著

木材の鉄イオン含有酸性温泉水処理による アンモニア吸着剤の製造

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Production of Ammonia Adsorbents by Treatment of Woods in Acid Hot Spring Water with Iron Ions

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Abstract

The woods, Japanese cryptmeria (Sugi) and pine (Akamatsu), were treated in the boiled model hot spring water (MHS-water; filtrate of the suspension of Yubana from Matsukawa well, Iwate Prefecture in distilled water) and their ability for ammonia removal was investigated in 1,000 ppm NH₃ atmosphere at room temperature. First the ability for ammonia removal of the raw woods was found to increase with an increase in the moisture content. Then the woods treated in the MHS-water showed about 2.5-4 times greater ability for ammonia removal compared to the dry raw woods. As main cause of the increase in the ability, the increased pore space of the treated woods was considered. The residual acid components in the treated woods were also thought to enhance the ability by their neutralization action. In addition, the Fe ions (74.0 mg-total Fe/kg-wood) in the treated woods would also act as a catalyst for the decomposition of ammonia. Accordingly, the woods successively treated in a FeSO₄ solution after the pretreatment in the MHS-water exhibited the remarkably higher ability for ammonia removal. Finally, the wood materials treated in the actual hot spring water (from Matsukawa well) showed the same or slightly higher ability for ammonia removal compared to those treated in MHS-water.

要 旨

模擬温泉水で煮沸処理した杉と赤松を用い, 1,000ppmのアンモニア雰囲気中におけるアンモニア吸着能について研究を行った. その結果, 生の木材の場合, 水分率が高いほ

どアンモニアの除去率は高く、模擬温泉水で煮沸処理された木材は乾燥状態の未処理試料と比較して約2.5～4倍の高い除去能を示した。これらは模擬温泉水処理による木材内部の空隙率の増加に伴う比表面積の増加がアンモニアの吸着を促したものと考えられる。また、木材内部に残留する酸性化合物とアンモニアとの中和反応も除去を高めたものと考えられる。一方、模擬温泉水で処理された木材内部には約74.0mg/kgの鉄イオンが含まれていることから、模擬温泉水で処理した木材に硫酸第一鉄を含浸させたところアンモニアの除去能はさらに著しく向上した。このことから模擬温泉水で処理された木材中の鉄イオンが触媒的な働きをしてアンモニアを酸化分解することも考えられた。さらに、実際の温泉水で処理した木材は、合成温泉水で処理したものと同等あるいはそれ以上のアンモニアの除去能を示した。

Key words : Hot spring water, Wood material, Ammonia removal, Fe ion

キーワード：温泉水，木質材料，アンモニア除去，鉄イオン

1. Introduction

In recent years, stinking effluent gases from various factories accompanied with regional industrialization caused social problems for living in pleasant surroundings. Therefore, the developments of new methods for removal of such stinking gases invading environments are earnestly expected in many fields. Basically it is most important for protection of environment that the generation of stinking gases is prevented. However, in the case that stinking gases are once generated, it is necessary to remove them by the treatment using some chemical or physical materials harmless for environment.

There are some chemical ways of removing stinking gases based on neutralization and redox reactions. The chemical deodorant materials mainly composed of cellulose have recently been developed as a new way to remove stinking gases because of easier resolution into nature after the use of these materials (Kuwahara, 1993). As one of such chemical materials, the new type deodorants consisting of the natural fibers with metal complex such as phthalocyanine complex or Fe (II)-L-ascorbic acid compound have been developed (Inokari, 1986). In addition, many researchers have investigated the removal of stinking gas using antibiotics (Nakajima, 1993).

We have already reported that the wood materials treated in an acid hot spring water became lighter in weight and higher porous state compared to those obtained by the same treatment using distilled water (Sasaki, *et al*, 1997). Then, we have discussed the hydrolysis mechanism during such the treatment as well as the application of the treated woods from the viewpoint of utilization of thinning woods (Sasaki, *et al*, 1998). In this method there are original advantages that hot spring water or geothermal water can be utilized as both economical heat-source and natural chemicals for hydrolysis of woods.

This paper reports the synthesis of new wood materials for the removal of stinking gas such as ammonia based on the treatment of thinning conifers, Sugi and Akamatsu, in the acid hot spring water containing Fe ions and their ability for ammonia removal. The mechanism of ammonia removal by the resulting wood materials was also discussed herein.

2. Experimental

2.1 Wood materials

Sugi (*Cryptomeria japonica* D. Don) and Akamatsu (*Pinus densiflora* S.et Z.) gathered from the northern part of Iwate prefecture were used in this study. These wood samples, straight grain and heart wood, were prepared as 0.3g in weight (about 40(L) × 25(W) × 0.7(T)mm) and were left outdoors for over 6 months for giving a form stability.

2.2 Hot spring water

The model hot spring water (MHS-water) and the actual hot spring water were adopted in this study. The MHS-water was obtained by adding 5g Yubana in 1dm³ of a distilled water, boiling and finally filtrating the resulting suspension. Yubana is the deposit of the hot spring water at Matsukawa in Iwate prefecture. The hot spring water used here was obtained from the same well. The chemical components of the hot spring water and the MHS-water are shown in Table 1. The MHS-water contained larger amounts of Fe²⁺, Al³⁺ and SO₄²⁻ ions compared to the hot spring water, but smaller amounts of Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions. The pH values of the MHS-water and the hot spring water were the same as 2.7. As the content of chemical ingredients in the hot spring water was generally uncertain, the MHS-water was mainly used in this study.

Table 1 Analytical data of chemical composition of the hot spring water and MHS-water.

(1) Cation	Hot spring water ^{a)} (mg/l)	MHS-water ^{b)} (mg/l)
H ⁺	1.90	2.00
pH	2.7	2.7
Na ⁺	13.7	1.65
K ⁺	4.20	1.22
Mg ²⁺	6.80	0.46
Ca ²⁺	33.7	0.05
Fe ²⁺ , Fe ³⁺	17.6	46.74
Mn ²⁺	0.70	0.56
Al ³⁺	9.00	14.22
(2) Anion		
F ⁻	1.20	0.86
Cl ⁻	0.70	0.20
HS ⁻	Tr	0.54
SO ₄ ²⁻	366	862

a) From wells in Matsukawa, Iwate Prefecture

b) Filtrate of the suspension of 5 g Yubana from Matsukawa well in 1 dm³ of distilled water

2.3 Treatment of wood materials in MHS-water and hot spring water

The wood materials were treated with the boiled MHS-water or hot spring water (0.2dm³) in a beaker equipped with a reflux condenser for 10-40 hours. After the treatment, the wood materials were dried at 105 °C for 24 hours under vacuum and stored in a desiccater. The moisture contents in the treated woods was determined by the gravimetric analysis. As the other type samples, the Fe ion supported woods were prepared by soaking the treated woods in 10% FeSO₄ solution for 1 hour at room temperature after treatment in the MHS-water or the hot spring water. The post-treatment was the same as described above.

2.4 Ammonia removal by wood materials

The ammonia atmosphere was prepared by adding 1.2cm³ of ammonia solution (0.28%) in a 300cm³ beaker. The concentration of ammonia was measured using a gas detector (Gastec 801, measurable ranges: 10-1000ppm). In the experiments of ammonia removal, the wood sample was set up in

the beaker sealed with the pala film and the ammonia solution was poured into the beaker. After 5 minutes, the measurement of ammonia concentration was started using the gas detector which was inserted over the wood sample through a space between the pala film and the beaker. The initial concentration of NH_3 was about 1,000 ppm in all the experiments.

3. Results and Discussion

3.1 Relation between moisture content in raw woods and ammonia removal

At first, the ability for ammonia removal of the raw woods was investigated as a reference. The degrees of ammonia removal with Sugi and Akamatsu having various moisture contents are shown in Figs. 1. In both cases, the degree of ammonia removal became higher with an increase in the moisture content. However, the rate of ammonia removal was different between two woods samples. The rate of ammonia removal with Sugi was faster than that of Akamatsu in the early stage but not so changed after that. For example, the Sugi sample indicated 57% in the degree of ammonia removal after 10 minutes and 62% after 2 hours at the moisture content of 27%, while the Akamatsu sample indicated about 10% after 10 minutes and about 80% after 2 hours at the same moisture content. Thus the Akamatsu sample had higher ability for ammonia removal than the Sugi sample in spite of its slower rate.

The major difference in the rate of ammonia removal between the Sugi sample and the Akamatsu sample at early stage was thought to be depend on the difference in the vacant space (Sasaki, *et al*, 1997). The specific gravity was approximately 0.5 g/cm^3 for the Akamatsu sample and 0.3 g/cm^3 for the Sugi sample. Furthermore the vacant space was 60% for the Sugi sample and 25% for the Akamatsu sample, which indicated that the Sugi sample had larger specific surface area than the Akamatsu sample.

The effect of the moisture content on the degree of ammonia removal may depend on the solubility of ammonia because ammonia dissolves quite easily in water. However, in spite of the same moisture content in the Sugi sample and the Akamatsu sample, the degree of ammonia removal was different. Accordingly, the structural difference between the Sugi sample and the Akamatsu sample was

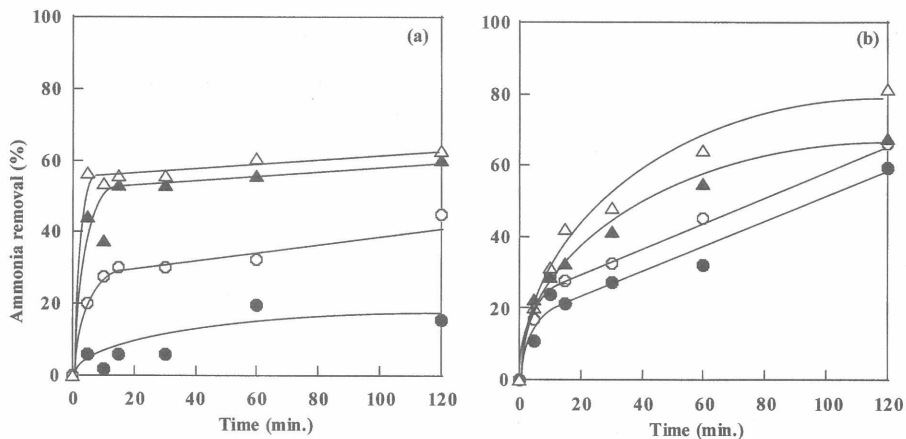


Fig. 1 Effect of moisture content in the raw wood samples on ammonia removal. moisture content (%); ● 0, ○ 7, ▲ 12, △ 27. Sugi; (a), Akamatsu; (b).

also thought to cause the different adsorbability.

It is well known that the structure of conifers is consisted of many tracheides and their cellular configuration is comparatively regular. Therefore, the moisture content in conifers is generally higher than that in broadleaf trees. Although Sugi has about 97.2% tracheides (Harada and Saeki, 1990), which is higher than that of Akamatsu, the equilibrium amount of adsorbed ammonia for the Sugi sample is lower than that of the Akamatsu sample. It was thought that as Akamatsu had the huge cells as resin canals (0.08 mm in diameter) in an axis direction of the woods, ammonia was easy to permeate into the inside of the Akamatsu sample deeper than that of the Sugi sample which, would cause a larger adsorbability of ammonia with the Akamatsu sample.

Figure 2 shows the degree of ammonia removal with the Akamatsu sample, when 0.3 and 0.9g of the wood samples were used. In the case of the sample having 0% moisture content, the ratio in the degree of ammonia removal of 0.3g samples to 0.9g samples was about 1.9, on the whole, which indicated that the surface area directly influenced the degree of ammonia removal. However, in the case of the sample having 10% moisture content, the ratio in the degree of ammonia removal was 3.2 at early stage, which was quite larger than that of the dry sample. This indicated that the moisture content in the woods influenced strongly on the ability for ammonia removal.

3.2 Effect of treatment of woods in MHS-water on ability for ammonia removal

In the previous section, it was confirmed that the raw woods without any treatment also had the adsorbability of ammonia gas. In this section, the effect of treatment of the woods in the MHS-water on their ability for ammonia removal was discussed. The degrees of ammonia removal with the Sugi sample and the Akamatsu sample treated in the MHS-water for different time periods are shown in Fig. 3. These data were obtained using the dry samples. It was first found that the treated Sugi and Akamatsu samples indicated at least about 4 and 2.5 times greater removal ability compared to the untreated woods, respectively. However, the degree of ammonia removal did not always increase with an increase in treatment time. The Sugi and Akamatsu samples treated for 40 hours indicated the lower degree of ammonia removal than the woods treated for 10-30 hours.

As has been reported in the previous paper (Sasaki, *et al*, 1999), the woods treated in the acid hot spring water became lighter in weight and higher in porous state compared to those obtained by the same treatment using only hot distilled water, because water-soluble components like saccharides and parts of hemicellulose were dissolved during the treatment in the hot spring water by acid hydrolysis. We (Sasaki, *et al*, 1997) also reported that after the treatment for 48 hours, the pore spaces of the Sugi sample had about 10% increase and the Akamatsu sample had 2.8 times larger pore spaces compared to the untreated wood.

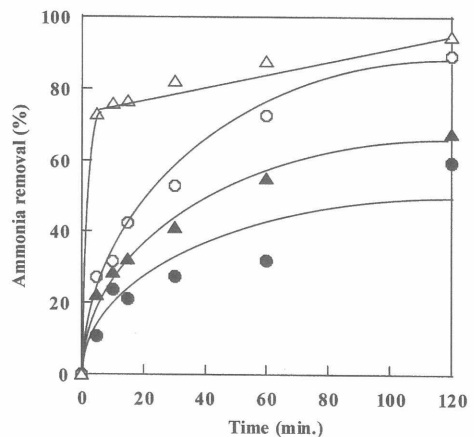


Fig. 2 Effects of moisture content and weight in the raw Akamatsu sample on ammonia removal.
moisture content (%); 0, sample weight (g); ● 0.3, ○ 0.9.
moisture content (%); 10, sample weight (g); ▲ 0.3, △ 0.9.

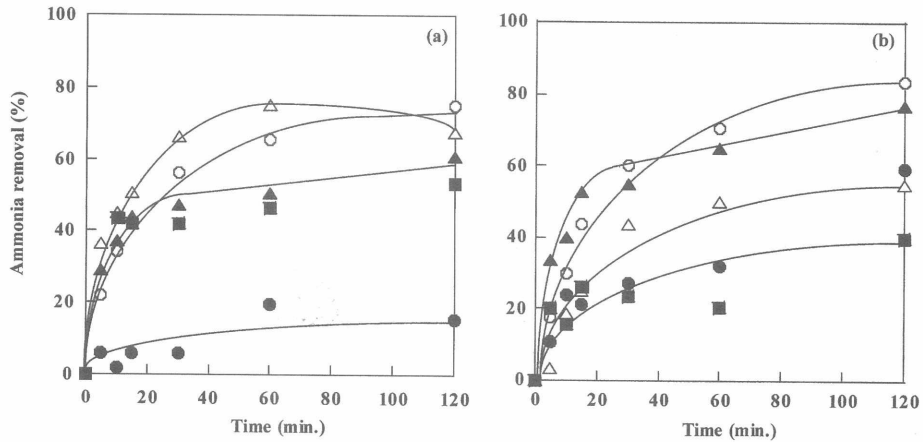


Fig. 3 Effects of treatment of the wood samples in the MHS-water on ammonia removal. treatment time (hr.); ● 0, ○ 10, ▲ 20, △ 30, ■ 40. Sugi; (a), Akamatsu; (b).

The cross sectional SEM micrographs of the untreated and treated woods in the MHS-water for 144 hours are shown in Fig. 4. There was serious damage to the cell shapes and cell walls to result smaller pore space for the treated woods. As another cause of the increase in the ability for ammonia removal, ammonia was thought to be neutralized with the acid ingredients in the pore space of the treated woods. Generally, the fiber structure of the wood was destroyed and the mechanical strength of the treated wood was decreased by the hydrolysis treatment in acid solutions. Since the similar phenomena would occur to the woods treated in the MHS-water, the degree of ammonia removal with the woods treated for long time (30-40 hours) was decreased by the excessive hydrolysis.

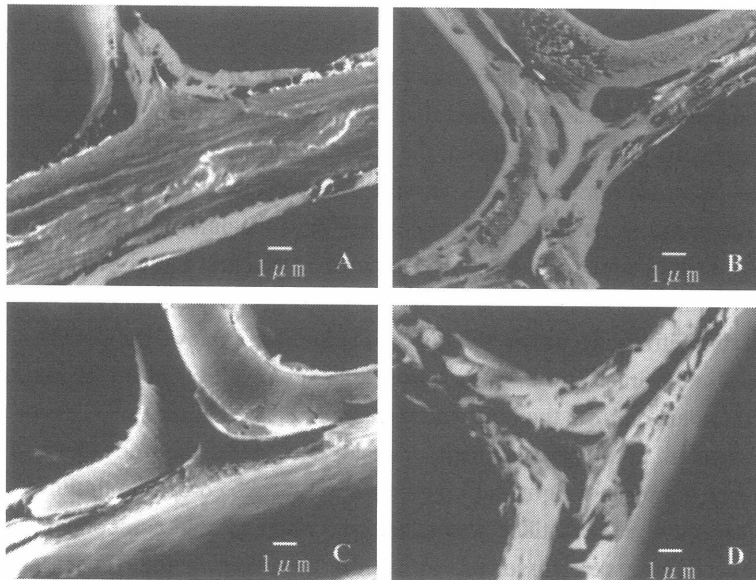
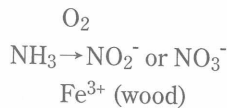


Fig. 4 Scanning electron micrographs of the woods treated in the MHS-water. Akamatsu; A untreated, B treated for 144 hrs. Sugi; C untreated, D treated for 144 hrs.

3.3 Effect of treatment of woods in iron (II) sulfate solution on ability for ammonia removal

As can be seen in Table 1, the MHS-water and the hot spring water contained iron and aluminium ions as a major cation and sulfate ions as a major anion. It is already known that some kinds of metal salts have the function to remove ammonia gas effectively (Shirai, 1985). For example, copper(I) salts using for dyeing are able to make a coordination bond with hydroxyl groups of cellulose and easily oxidized to copper(II) salts. Then when copper(II) salts on the fibers are reduced to copper(I) salts, ammonia is decomposed by the oxidation with copper(II) ion. Deodorizing fibers (Kuwabara, 1993) are produced by using the similar chemical reaction. It is also known that iron (II) sulfate is easily oxidized to iron (III) sulfate and make a coordinate bond with hydroxyl groups of cellulose. This iron (III) sulfate on the cellulose can work as an oxidation catalyst at room temperature (Katou, 1991) as well as serving neutralization action for ammonia. Accordingly, if the treated woods contain some iron (III) ion in their matrix, ammonia will be oxidized with oxygen on the catalytic points as follows:



Here the total iron content in the Sugi sample treated in the MHS-water was measured. The result is shown in Table 2. The woods treated for 48 hours have approximately 3.3 times greater amount of total iron compared to the untreated wood. Therefore, it was presumed that irons in the treated woods would accelerate the decomposition of ammonia.

Table 2 Total Fe ion content of the Sugi sample treated in the MHS-water.

Treatment time (hr.)	0	48	144
Total Fe (mg/kg)	22.6	74.8	74.0

In order to investigate the function of irons in the treated woods for ammonia removal, the woods treated in the MHS-water were soaked in iron (II) sulfate solution and subjected to the measurement of the ability for ammonia removal. The results are shown in Fig. 5. The degree of ammonia removal with the Sugi sample, which were treated once in iron (II) sulfate solution without the pretreatment in the MHS-water, was the same as that with the woods treated in the MHS-water for 10 hours. Furthermore, the Sugi sample treated two times in iron (II) sulfate solution indicated about 3 times higher degree of ammonia removal after 1 hour compared to that of the untreated woods. It suggested that the ability for ammonia removal was remarkably enhanced by the treatment in iron (II) sulfate solution after the pretreatment in the MHS-water.

The woods treated two times in iron (II) sulfate solution after the pretreatment in the MHS-water for 10 hours showed the highest ability for ammonia removal. Thus the degree of ammonia removal with the retreated Sugi sample after 1 hour was 2.6 times higher value compared to that of the untreated woods and 1.1 times higher value compared to that of the woods treated only in iron (II) sulfate solution. On the other hand, the Akamatsu sample treated in the MHS-water and then in iron (II) sulfate solution had about 3 times higher value in the degree of ammonia removal compared to the untreated woods and 1.3 times higher value compared to the woods treated only in iron (II) sulfate solution. Furthermore, the degree of ammonia removal of the twice retreated woods in iron (II) sulfate solution became higher than that of the once retreated woods. Consequently, it was concluded that the treatment of woods both in the MHS-water and in iron (II) sulfate solution gave the remarkably high ability for ammonia removal to the conifers such as Sugi and Akamatsu.

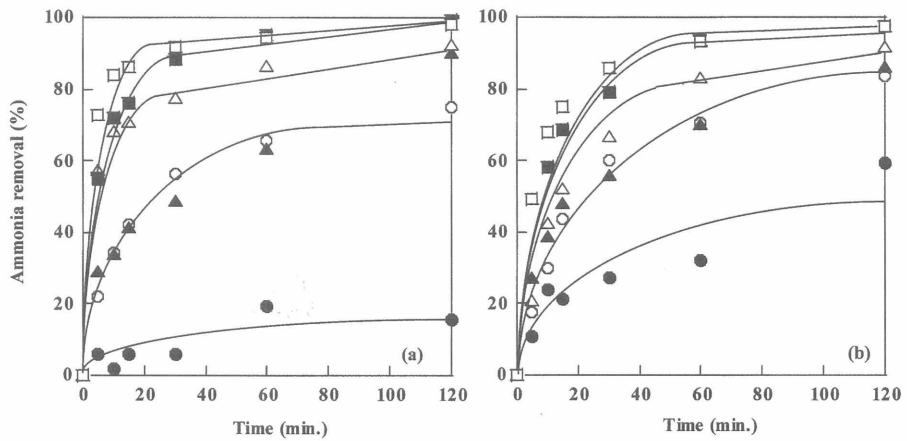


Fig. 5 Effects of treatment of the MHS-water pretreated wood samples in $FeSO_4$ solution on ammonia removal.
 Untreatment ; ●, Treatment in the MHS-water for 10 hrs. ; ○,
 Treatment in $FeSO_4$ solution ; ▲ 1 time, △ 2 times,
 Treatment in the MHS-water for 10 hrs. + $FeSO_4$ solution (1 time) ; ■,
 Treatment in the MHS-water for 10 hrs. + $FeSO_4$ solution (2 times) ; □.
 Sugi ; (a), Akamatsu ; (b).

Finally, a set of the experiments using the actual hot spring water was carried out. The woods were treated in the hot spring water for 10 hours and then retreated two times in iron (II) sulfate solution. Their abilities for ammonia removal were examined and the results are shown in Fig. 6. The degrees of ammonia removal of the woods treated in the hot spring water were similar to or higher than those of the woods treated in the MHS-water. Therefore, it was concluded that the actual hot spring water had at least the same ability to produce the wood materials as the MHS-water mentioned above.

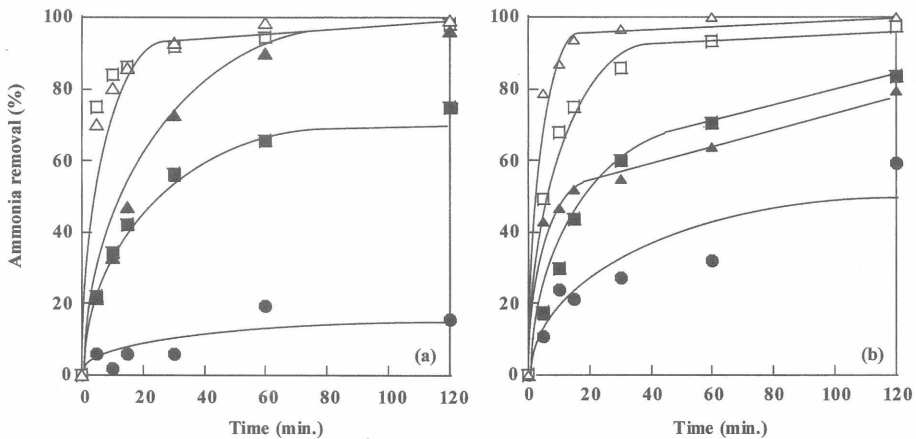


Fig. 6 Effects of treatment of the actual hot spring water pretreated wood samples in $FeSO_4$ solution on ammonia removal.
 Untreatment ; ●, Treatment in the MHS-water for 10 hrs. ; ○,
 Treatment in the hot spring water for 10 hrs. ; ▽,
 Treatment in the MHS-water for 10 hrs.+ $FeSO_4$ solution (2 times) ; □,
 Treatment in the hot spring water for 10 hrs.+ $FeSO_4$ solution (2 times) ; △.
 Sugi ; (a), Akamatsu ; (b).

4. Conclusions

The results of the study on the production of ammonia adsorbents by the treatment of the woods in the acid hot spring water with iron ions were summarized as follows:

- (1) The ability for ammonia removal of the raw woods such as Sugi and Akamatsu was increased with an increase in the moisture content of the woods.
- (2) The woods treated in the MHS-water had 2.5-4 times higher ability for ammonia removal compared to the untreated dry woods.
- (3) The increase in the pore space of the wood with the treatment in the MHS-water was thought to be mainly responsible for the increase in the ability for ammonia removal. The residual acid components in the treated woods would also react with ammonia gas by the neutralization. In addition, as the Fe ions in the treated woods was increased, the ability for ammonia removal was also enhanced by the catalytic action of Fe ions.
- (4) The woods successively treated in a FeSO_4 solution after the pretreatment in the MHS-water exhibited the remarkably higher ability for ammonia removal.
- (5) Practically no differences in the effect between the MHS-water and the actual hot spring water were observed here.

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