Removal of Ammonia Nitrogen from Wastewater Using Modified Activated Sludge

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Abstract

The removal of medium-low N-NH$_4$ on activated sludge modified by ferric hydroxide suspension (FH-MAS) in batch studies was conducted as a function of pH, concentration of modifier, contact time, and initial concentration. The kinetics study showed that the sorption behavior fit well the pseudo second-order equation. An adsorption isotherms study indicated that FHMAS had a higher adsorption capacity for N-NH$_4$ than other adsorbents. The mechanism of removal of N-NH$_4$ by FHMAS was coexistence of adsorption and cation exchange. Initial N-NH$_4$ concentration being 116 mg/l in metallurgical wastewater was reduced to 11 mg/l after adsorption treatment.

Keywords: ammonium-nitrogen (N-NH$_4$) removal, activated sludge modified by ferric hydroxide (FHMAS), cation exchange, adsorption

Introduction

Eutrophication of surface water is primarily contributed by nitrogen and phosphorus contamination from industry wastewater, farmland fertilization, and municipal sewage, which has been a common environmental issue in many countries [1]. These nutrients cause diverse problems such as toxic algal blooms, loss of oxygen, fish kills, loss of biodiversity, loss of aquatic plant beds and coral reefs, and other problems.

Great efforts have been aimed at the removal of N-NH$_4$ from wastewater. Traditional methods include ammonia-stripping [2], chemical precipitation [3], biological denitrification [4], dry-ice [5], and so on. Ammonia stripping makes use of a stripping tower, consumes much energy, and is only suitable for treating high N-NH$_4$ concentrations. Chemical precipitation needs additional reagents that can introduce new pollutants to water bodies. Biological denitrification is the most common process in the treatment of N-NH$_4$ wastewater. But it is higher efficiency for the removal of low N-NH$_4$ concentration due to the requirement of an appropriate C/N ratio [6] and need for a long reaction time. It is inefficient, though, for the traditional ways to quickly treat medium-low N-NH$_4$ from wastewater. In recent years considerable attention has been aimed at the study of heavy metals removal from solution by adsorption using wastes, including fruit peels, straw, coconut coir, and so on [7-9]. Generally, the sorption capacities of crude by-products are low. To improve the adsorption capacity of these by-products, chemical modification has been used.

Surplus activated sludge is the by-product of sewage treated by the activated sludge process. Every year a large amount of activated sludge from a sewage plant

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is produced. In this study, activated sludge was used as the biosorbents to remove medium-low N-NH$_4$ from aqueous solution and wastewater. Because of its sorptional nature, ferric compounds often apply to the treatment of wastewater with heavy metals [10-11]. The objectives are to identify the NH$_4^+$ ion uptake capacity of the activated sludge modified by ferric hydroxide (FHMAS) to determine the kinetics, and assess the effects of pH, concentration of modifier, contact time, and N-NH$_4$ initial concentration on the removal. Then the adsorption isotherm of NH$_4^+$ is obtained, which contains the basic information for exploiting sludge as a water treatment agent.

Material and Methods

Adsorbate

Ammonium chloride (99.5%, analytical reagent, Tianjin Kermel Chemical Reagent Development Center, China) was used as the source of N-NH$_4$. Deionized water was used for the preparation of solutions. All other reagents such as ferric chloride, sodium hydroxide (NaOH), and hydrochloric acid (HCl) were analytical grade. Real N-NH$_4$ wastewater was obtained from a Metallurgical Plant of Ganzhou, Jiangxi, China.

Adsorbent

The activated sludge was obtained from a wastewater treatment plant of Ganzhou City, P. R. China. After being washed many times in distilled water, the sludge was dried at 110°C and sieved through a 245 μm sieve and stored dry until use, labeled as original activated sludge (OAS).

Adding NaOH solution to a certain concentration (0.05~0.30 mol/l) of ferric chloride solution, ferric hydroxide suspension was produced. With the ratio of 1 g OAS to 10 ml ferric hydroxide, suspensions were mixed uniformly and placed in an oven at 60°C for 12 h, and the suspension liquid was filtered and washing many times by distilled water until the effluent was cleared up. The filtered solid was dried at 110°C and stored for dry until use and labeled as activated sludge modified by ferric hydroxide (FHMAS).

Batch Experimental Procedures

The removal of N-NH$_4$ with FHMAS was performed in batch experiments. Prior to experiments, the pH value of N-NH$_4$ solution was changed from 3 to 10, with 0.1 mol/l NaOH or HCl solution. During the removal process, 0.3 g FHMAS or OAS was suspended in 100 ml wastewater containing N-NH$_4$ (100±5 mg/l). The mixture was agitated on a gyratory shaker at 250 rpm by 20 min. At the end of the experiment the suspension liquid was decanted and filtered through a 0.45 μm cellulose acetate filter and the supernatant was analyzed. Controls were also performed with no adsorbent to compare the efficiency of N-NH$_4$ removal with FHMAS and OAS.

All other experiments were conducted at pH 8. As for the factor of modifier concentration, samples were collected after 20 min contact with FHMAS and efficiency of N-NH$_4$ removal was analyzed. Based on the same ferric concentration, a different volume of ferric hydroxide suspension but no FHMAS added was also performed to compare the N-NH$_4$ removal with FHMAS. At the experimental process, the ferric ion concentration in solution also was analyzed.

In the contact time experiment, samples were withdrawn at pre-determined intervals and efficiency of N-NH$_4$ removal was analyzed. The percent efficiency of removal of N-NH$_4$ in solution was calculated by the use of the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

…where C_0 is N-NH$_4$ concentrations an the start of process (mg/l), C_t is N-NH$_4$ concentrations after time t (mg/l), and t is time of process.

At the mentioned optimum conditions, the effects of initial N-NH$_4$ concentration (20-250 mg/l) on the sorption of N-NH$_4$ was studied under the aspects of sorption isotherms. The amount of N-NH$_4$ adsorbed per adsorbent mass was calculated by the use of the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

…where q_t is the amount of N-NH$_4$ adsorbed on sludge at time t (mg/g), V is the volume of solution (l), and m is the adsorbent mass (g).

All experiments were fulfilled at room temperature (293±1 K). Each experiment was run in triplicate and mean values were calculated.

Analysis and Measurements

N-NH$_4$ was measured by WT-1 portable apparatus of N-NH$_4$ (Wuhan Water Environmental Protection Company, China), which was based on the standard method [12]. Fe^{3+} was determined based on the phenanthroline spectrophotometric method. pH was measured with a pH meter (pHS-25, Shanghai Leici Instrument Factory, China).

Results and Discussion

Effect of pH on N-NH$_4$ Removal

Ammonium is always a pH-dependent balance between soluble ammonium ion NH$_4^+$ and dissolved molecular ammonia NH$_3$ in wastewater [13]. In acidic and neutral media, N-NH$_4$ is presented as NH$_4^+$. In basic solution, non-volatile NH$_4^+$ is converted to NH$_3$. High pH favors ammonia volatilization by moving the equilibrium

between NH_3 and NH_4^+ to molecular ammonia, as shown in equation (3). In this study the pH from 3 to 10 was changed.

$$NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O \qquad (3)$$

In order to determine the desired pH for adsorption of N-NH_4 over FHMAS, the uptake of N-NH_4 as a function of hydrogen ion concentration was studied, as Fig. 1 showed. From Fig. 1 it can be seen that all three curves have the same trend, namely that inflection points appeared at pH 8. The net sorption removal of N-NH_4 by OAS was 9.1, 19.1, 23.9, 30.1, 40.3, 44.3, 42.1, and 40.6% after deducting results of the controls group at pH 3, 4, 5, 6, 7, 8, 9, and 10, respectively. The net sorption effect by FHMAS was 22.3, 32.6, 39.7, 47.9, 60.3, 68, 66.1, and 63.8% at pH 3, 4, 5, 6, 7, 8, 9, and 10, respectively.

Under three conditions the removal of N-NH_4 increased with pH of solution increasing. Ammonium chloride solution is a strong acid with weak base salt. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restricted the approach of NH_4^+ cation as a result of the repulsive force. Moreover, the ferric oxide layer on the surface of FHMAS was hydroxylated and positively charged at acidic water environment, which went against N-NH_4 adsorption.

It was observed that the presence of Fe^{3+} in solution was detected after contacting ammonium chloride solution with FHMAS, which inferred that ion-exchange between N-NH_4 and Fe^{3+} might exist.

All subsequent experiments were conducted with pH 8.

Effect of Concentration of Modifier on N-NH_4 Removal

The effects of concentration of modifier and ferric hydroxide suspension on the efficiency of N-NH_4 removal
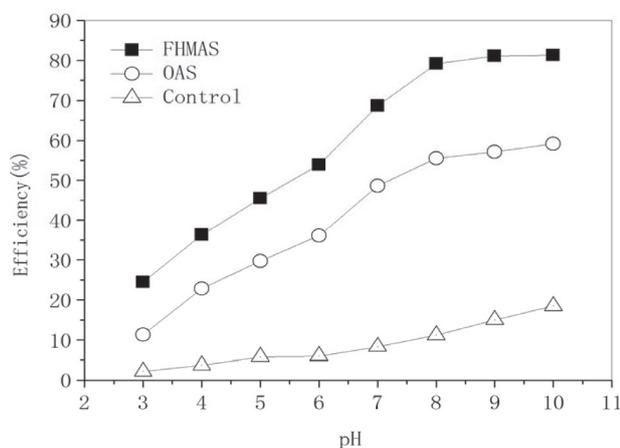
are shown in Fig. 2. The two curves in Fig. 2 show that the efficiency of N-NH_4 removal onto FHMAS was higher than that of ferric hydroxide suspension. The effect of removal always increases with the Fe^{3+} concentration increasing for FHMAS, indicated that perhaps increasing adsorption sites can increase the efficiency of N-NH_4 removal by adsorption.

After the experimental process, the analyzed Fe^{3+} concentration in solution showed that the content of Fe^{3+} increased with N-NH_4 efficiency of removal increasing by FHMAS, but Fe^{3+} concentration was almost zero by ferric hydroxide suspension, which inferred the existence of cation exchange in the experimental process with FHMAS. Analysis of the data showed that the number of removed N-NH_4 was more than that of Fe^{3+} in solution, which meant that cation exchange and adsorption are taking place at the same time.

Fig. 2 also showed that the efficiency of removal of N-NH_4 by FHMAS was first increased and then decreased with the concentration of increasing modifier. Maybe a small amount of ferric hydroxide can enhance the cation exchange capacity with NH_4^+. The excess ferric hydroxide may be part of the sludge pore blockage and lead to the decline of FHMAS adsorption capacity for N-NH_4.

All subsequent experiments were conducted with 0.15 mol/l ferric hydroxide suspension.

Kinetics Study

The efficiency of removal rate of N-NH_4 by FHMAS is shown in Fig. 3. The sorption process was rapid in less than 20 min and reached a plateau of some 87% in 30 min.

Various sorption kinetic models have been used to describe the removal of metals. The Lagergren first-order kinetic process has been used for reversible reaction with an equilibrium between liquid and solid phases. The rate equation for the reaction may be represented by the following expression:

Fig. 1. Effect of pH on N-NH_4 removal. Initial N-NH_4 concentration was 99.45 mg/l, concentration of modifier 0.10 mol/l, contact time 20 min, sorbent dose 3 g/l.
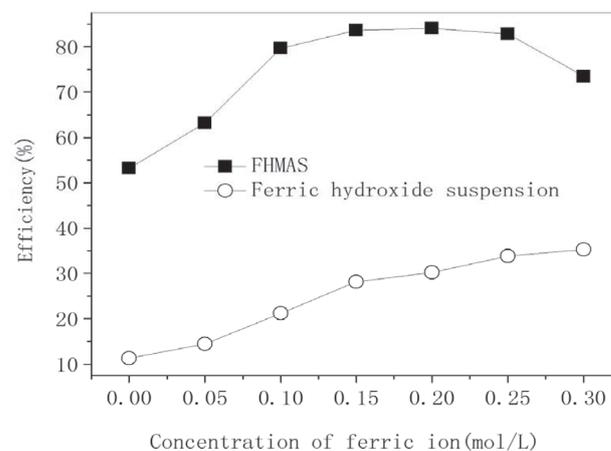
Fig. 2. Effect of concentration of modifier on N-NH_4 removal. Initial N-NH_4 concentration was 101.83 mg/l, pH 8, contact time 20 min, adsorbent dose 3 g/l.
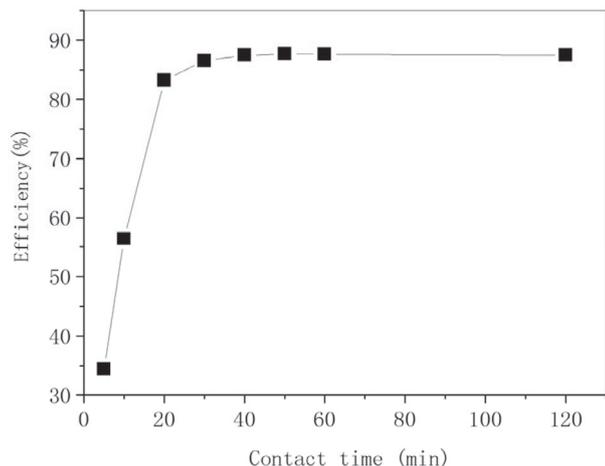
Fig. 3. Effect of contact time on N-NH$_4$ removal. Initial N-NH$_4$ concentration was 103.38 mg/l, pH 8, concentration of modifier 0.15 mol/l, adsorbent dose 3 g/l.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (4)$$

…where t is contact time (min), q_t is quantities of N-NH$_4$ adsorbed at time t (mg/g), q_e is quantities of N-NH$_4$ adsorbed at equilibrium (mg/g), and k_1 is sorption rate constant.

From Eq. (4), a plot of lg $(q_e$ -$q_t)$ versus t should give a straight line to confirm the applicability of the first-order kinetic model (Fig. 4), in which the correlation coefficient (R^2) was 0.76.

However, a pseudo second-order kinetic model has been considered to be the most appropriate over the past few years [14]. As a result, if a pseudo second-order equation is adequate, the rate equation for the reaction may be represented by the following expression:
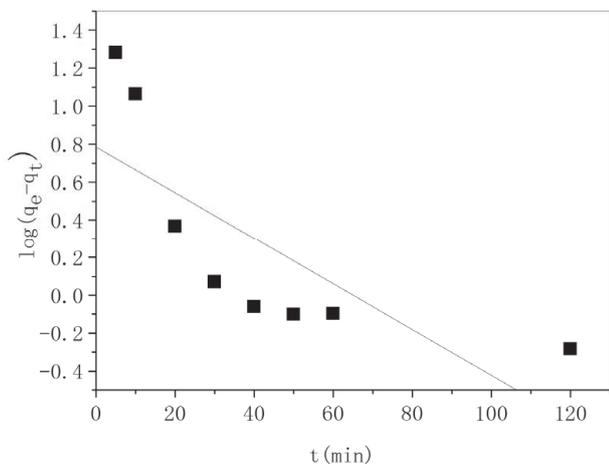
Fig. 4. Lagergren first-order Sorptional kinetics of N-NH$_4$ by FHMAS.
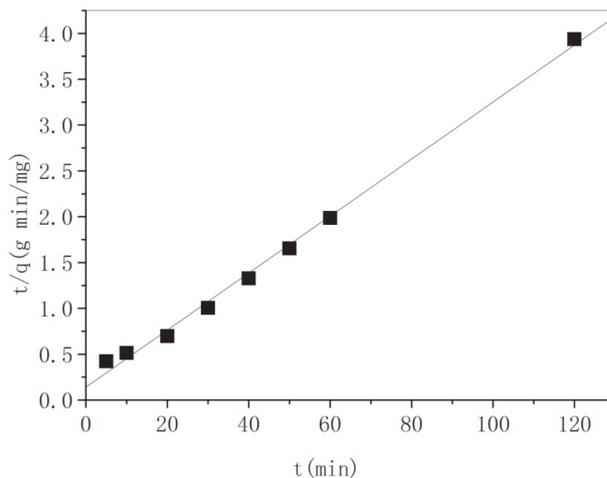
Fig. 5. Pseudo second-order sorptional kinetics of N-NH$_4$ by FHMAS.

$$\frac{t}{q_t} = \frac{1}{k_2} + \frac{t}{q_e} \qquad (5)$$

…where k_2 is sorption rate constant (mg/(g·min)). From Eq. (5), a plot of t/q_t versus t should give a straight line to confirm the applicability of the second-order kinetic model (Fig. 5).

Table 1 contains the sorptional kinetics parameters of N-NH$_4$ by FHMAS. From the correlation coefficient (R^2) of two lines it can been seen that the pseudo second-order kinetic ($R^2 = 0.99$) was more fitted than that of Lagergren first-order kinetic ($R^2 = 0.76$) for the sorption process.

Adsorption Isotherms

Langmuir adsorption isotherm model was tried to fit to the experimental adsorption data by linear estimation based on least-square method and the equation shown below:
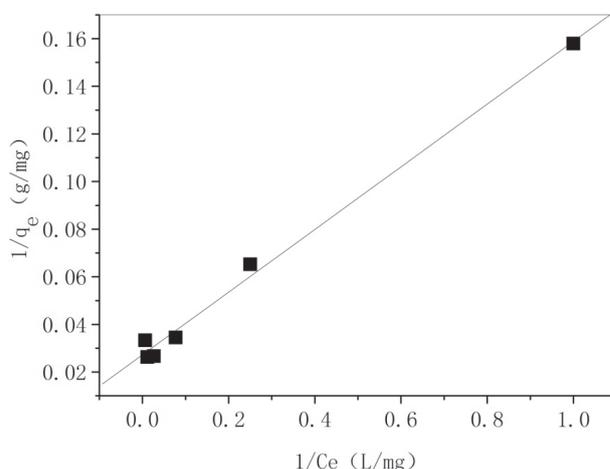
Fig. 6. Langmuir adsorption model of N-NH$_4$ by FHMAS.

Table 1. Sorptional kinetics parameters of N-NH$_4$ by FHMAS.

Sorptional kinetics	Fitted equation	Sorption rate constant	Correlation coefficient
Lagergren first-order kinetic	$\log(6.10 - q_t) = \log 6.10 - \dfrac{0.027}{2.303}t$	0.02	0.76
Pseudo second-order kinetic	$\dfrac{t}{q_t} = \dfrac{1}{7.10} - \dfrac{t}{32.15}$	7.10 mg/(g·min)	0.99

Table 2. Langmuir and Dubini-Radushkevich isotherm parameters estimated with the equilibrium adsorption data for N-NH$_4$ by FHMAS at 20ºC.

Langmuir			Dubini-Radushkevich			
q_m (mg/g)	B (l/mg)	R^2	q_m (mg/g)	$\beta*10^9$ (mol²/J²)	E (kJ/mol)	R^2
32.71	0.18	0.99	29.96	5.63	9.42	0.92

$$\frac{1}{q_e} = \frac{1}{bq_{max}C_e} + \frac{1}{q_{max}} \qquad (6)$$

...where C_e is equilibrium concentration (mg/l), q_{max} is maximum adsorption capacity (mg/g), and b is relative energy of sorption (l/mg). The value of q_{max} and b were calculated from the intercept and slope of the lines in diagram of ($1/q_e$) versus ($1/C_e$). As shown in Fig. 6, the regression correlation coefficients of plot of ($1/q_e$) versus ($1/C_e$) gave a straight line for N-NH$_4$ adsorption by FHMAS.

The Langmuir model fit well the experimental data based on the obtained determination coefficients ($R^2 = 0.997$) and isotherm parameters shown in Table 2.

The maximum adsorption capacity (q_{max}) of FHMAS, obtained in this research for N-NH$_4$, can be compared with other adsorbents' N-NH$_4$ uptake as shown in Table 3. It can be observed that the FHMAS had adsorption capacities for N-NH$_4$ of 7.43 times higher than that of the bentonite [15].

In addition, the Dubini-Radushkevich isotherm model (Eq. 7) was tried to fit to the experimental adsorption data by lineal estimation based on the least-square method:

$$q = q_m e^{-\beta \varepsilon^2} \qquad (7)$$

...where q_m is Dubinin-Radushkevich monolayer capacity (mg/g), β is constant related to adsorption energy (mol²/J²), ε is Polanyi potential (J/mol) related to equilibrium concentration C_e.

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (8)$$

...where R is gas constant (8.314 J/mol) and T is absolute temperature.

The constant β is related to the mean free energy of adsorption per mol of the adsorbate (E, kJ/mol) when it is transferred to the surface of the solid from the solution, and E can be estimated as follows:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (9)$$

Table 2 shows the Dubini-Radushkevich isotherm parameters for N-NH$_4$ by FHMAS. The q_m value shows less adsorption capacity in comparison to Langmuir isotherm. Moreover, the free energy of adsorption values (4-40 kJ/mol) suggests that physical the adsorption process occurs at the adsorbent surface [16].

Treatment of Metallurgical Wastewater

High concentrations of N-NH$_4$ are commonly present in industrial wastewater such as metallurgical, tannery, textile, landfill leachate, and fertilizer wastewater [17-19]. The real wastewater used in this study was obtained from a metallurgical plant in Ganzhou City, P. R. China. The metallurgical wastewater quality before and after treatment by FHMAS is listed in Table 4.

Table 3. Comparison of q_{max} of N-NH$_4$ on different adsorbents.

Adsorbent	q_{max} (mg/g)	References
Clinoptilolite	4.4	15
Artificial Zeoliteand	26.9	16
Kaolin	4.3	17
Na-based bentonite	3.0	18
Rare earth absorbent	6.5	19
Wheat shell	8.1	20
FHMAS	32.7	This study

Table 4. Water quality before and after treatment of metallurgical wastewater by FHMAS.

Items	pH	COD (mg/l)	N-NH$_4$ (mg/l)	Al (mg/l)	Fe (mg/l)	Mg (mg/l)	Pb (mg/l)	Zn (mg/l)
Before treatment	7.8	105	116	<0.05	0.148	<0.05	<0.05	0.061
After treatment	8	58	11	<0.05	9.41	<0.05	<0.05	<0.05
Emission standard [20]	6~9	70	15	–	–	–	0.2	1.0

After ammonia stripping the concentration of N-NH$_4$ was found to be about 116 mg/l. Conventional treatment methods could not effectively remove the medium-low concentration of N-NH$_4$. The FHMAS allows an alternative technique and showed encouraging performance on treating N-NH$_4$ from the wastewater. The results after treatment by FHMAS were list in Table 4. When ferric hydroxide 0.15 mol/l, dosage 3.5 g/l, and pH 8 contact 30 min at room temperature, initial N-NH$_4$ concentration and COD being 116 mg/l and 105 mg/l; ammonia in actual metallurgical wastewater was reduced to 11 mg/l and COD to 58 mg/l for N-NH$_4$ and COD after treatment by adsorption achieves pollutant concentration limits in solution for a new enterprise in the "Emission Standards of Pollutants from Rare Earths Industry" (GB26451-2011) [20]. From the adsorption capacity for N-NH$_4$ 30 mg/g, which was smaller than 32.7 mg/g at adsorption equilibrium for simulated N-NH$_4$ solution, it can be seen that some cations and organic constituents in metallurgical wastewater can affect the efficiency of N-NH$_4$ removal. And the concentration of Fe ion in wastewater increased because of cation exchange. Therefore, FHMAS was preliminarily feasible for treating N-NH$_4$ from real wastewater.

Conclusions

The presented research was carried out to explore a new adsorbent – modified activated sludge – for treating medium-low concentrations of N-NH$_4$ from wastewater. The experimental results showed that sludge modified by 0.15 mol/l ferric hydroxide can greatly improve the removal for N-NH$_4$. Influencing factors such as pH, concentration of modifier, contact time, and N-NH$_4$ initial concentration showed the serious influence of N-NH$_4$ removal. The kinetics study indicated that the sorption process was better described by the pseudo second-order equation than that of Lagergren's first-order equation. An adsorption isotherm study indicated that FHMAS had higher adsorption capacities for N-NH$_4$ than that of the clinoptilolite. The mechanisms of removal of N-NH$_4$ by FHMAS were coexistence of adsorption and cation exchange. Metallurgical wastewater containing medium-low concentrations of N-NH$_4$ was treated by FHMAS. Initial N-NH$_4$ concentration of 116 mg/l was reduced to 11 mg/l in 30 min by 3.5 g/l FHMAS at pH 8.

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