Performance and mechanism of ferric tannate in nitrogen removal from wastewater

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Abstract. Ferric tannate (FT) has capacities on simultaneous adsorption of NH₄⁺-N and NO₂⁻-N. So far, no study has been reported on the mechanism of FT in the removal of NH₄⁺-N and NO₂⁻-N. In this work, FT was prepared for nitrogen removal, and the potential of FT in treating NH₄⁺-N and NO₂⁻-N from aqueous solution was investigated. The influence parameters e.g. substrate concentration and FT dosage on removing nitrogen from aqueous solution were optimized. The results showed that more N₂ generated when FT was added to the oxidation-reduction reaction between NH₄⁺-N and NO₂⁻-N. The concentration of NO₂⁻-N was higher than that of NH₄⁺-N would be conductive for the N₂ generation when adding FT. The Fourier Transform Infrared (FTIR) Spectrometer results showed that the structure of the FT (Fe-O) changed in the redox between NH₄⁺-N and NO₂⁻-N. The X-ray photoelectron spectroscopy (XPS) results showed that Fe³⁺ and Fe²⁺ coexisted in FT.

1. Introduction

At present, more and more contaminated wastewater which contained NH₄⁺-N and NO₂⁻-N are generated with the rapid development of industries, especially catalyst, chemical, and steel industries [1, 2]. Although nitrogen is a very important nutrient for algae, the excessive discharge of nitrogen will lead to eutrophication of receiving water bodies [3, 4]. The eutrophication of water will not only harm the environment, but also endanger the human health. And it has been reported that nitrite nitrogen causes blue baby syndrome, and is a precursor to the carcinogenic nitrosoamine [5]. Therefore, NH₄⁺-N and NO₂⁻-N removal from wastewater has attracted more interests recently.

Traditional methods, including biological treatment [6], ion exchange [7], adsorption [8-10] and catalysis etc., [11-14] have been applied to remove NH₄⁺-N and NO₂⁻-N from wastewater. Currently, long periods on bacteria acclimation for biological treatment and low total nitrogen (TN) removal when the influent biodegradable COD to TN ratio is low, which presents a problem in practical use [15]. Compared with the biological treatment, physical-chemical treatment has become a promising technology due to its high safety, high nitrogen removal, with practicable application [16]. Through the adsorbent and ion exchange resin can quickly remove nitrogen from wastewater, but they must be regenerated after adsorption nitrogen saturation, and the regenerated solution needs treatment and disposal. If the absorbent can be regenerated in situ, the adsorption will be an attractive alternative nitrogen removal technology.
Theoretically, the redox can occur between NO$_3^-$ and NH$_4^+$ according to their standard redox potential [17], which its products are N$_2$ and H$_2$O. To enhance NO$_3^-$ and NH$_4^+$ removal from wastewater simultaneously, a new material which had the ability of both NO$_3^-$ and NH$_4^+$ adsorption is needed. Previous a patent pointed that the colloidal particles of Fe(OH)$_3$, Ferric tannate (FT) and Fe$_2$O$_3$ could be used as catalysts during the process of NH$_4^+$-N reacted with NO$_2^-$N at room temperature [18]. However, to date, no research has been focused on factors of catalytic denitrification performance and mechanism on FT to remove NH$_4^+$-N and NO$_2^-$N.

Thus, the potential catalytic denitrification of FT to remove NH$_4^+$-N and NO$_2^-$N from aqueous solution simultaneously is investigated. The influence of various parameters (substrate concentration and FT dosage) on capacity and performance of the FT to remove nitrogen efficiently from aqueous solution were optimized. And before and after nitrogen removal, the FT were characterized through Fourier Transform Infrared (FTIR) Spectrometer and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. FT preparation

In this study, FT was prepared from the reaction of tannic acid and ferric chloride at ratio of 1:20 according to the reference [19].

2.2. Experiment procedure

The solution used in the test was mixture of ammonium chloride (~99.5%, Sinopharm Chemical reagent Co., China) and sodium nitrite (~99.0%, Sinopharm Chemical reagent Co., China). Ammonium (1000 mg/L) and nitrite (1000 mg/L) stock solution were prepared by dissolved ammonium chloride and sodium nitrite in deionized water, respectively. In these experiments, the concentrations of N in total were varied from 0 to 500 mg/L.

The adsorption-catalytic test was carried out in a 250 mL glass flask which had a working volume of 100 mL with the ratio of FT/ NH$_4^+$-N and FT/ NO$_2^-$N was 100 mg/mg and 50 mg/mg, respectively. There were two holes on the plug. The diameter of each hole was 50-70 mm. Two glass tubes connected with the flask through the holes for collecting samples and purging air. The gas of He was pumped into the flask to discharge all the air. Then the sealed flask was shocked at 200 rpm for 48 hours under ambient temperature, take the gas sample and the water sample from the flask every 2 hour. An additional flask that without ultrasound treatment was used as a control.

After filtration (microfiltration membrane pore size 0.45 μm, Beijing river the integrity of membrane technology development center, China), the concentrations of NH$_4^+$-N and NO$_2^-$N were determined.

2.3. Analysis and calculation methods

The concentrations of NH$_4^+$-N were measured using Nessler’S reagents spectrophotometer methods according to standard methods [20]. The concentrations of NO$_2^-$N were measured using hydrochloride naphthodiamide spectrophotometer methods on the basis of standard methods [20].

The content of N$_2$ was determined using the Agilent 6890N Gas Chromatograph equipped with TCD detector, and the gas of He was used as a carrier. During the procedure, temperature of the oven and the detector was 100°C and 250°C, respectively.

The functional group of the tannin acid and FT were measured using Fourier Transform Infrared Spectrometer (FTIR Spectrometer, Tensor 27, Germany) over the range of 400 ~ 4000 cm$^{-1}$ region [21]. In the test, the dried tannin acid and FTs were mixed potassium bromide (KBr) in the mass ratio of 1:20, respectively.

The binding energy of Fe and O on the surface of FT were obtained by XPS analysis. The sample of FT was packed carefully on XPS sampling template under the anaerobic condition to avoid surface oxidation. The XPS analysis was carried out using a Mutilab 2000 (ESCALAB250Xi, PANalytical co, Holland) with an Mg Kα X-ray (1253.6 eV) having a source power of 200 W. In the procedure of XPS
measurements, the sample chamber was evacuated (the base pressure was $3 \times 10^{-9}$ mbar) before changing the gas atmosphere. The flood gun for charge compensation was used and calibrated the binding energy on the carbon 1s peak at 284.6 eV.

Fe content of FT was determined by spectrophotometric method using a Reflectoquant RQflex plus 10 (Merck chemical (Shanghai) Co., Ltd, China). The measuring principle was as follows. In acid solution (pH 2.5-9), a red-violet complex formed when Fe$^{2+}$ ions react with a triazine derivative that is determined reflectometrically. Samples must be reduced by ascorbic acid before Fe$^{3+}$ ions and total iron (sum of Fe$^{2+}$ and Fe$^{3+}$) can be measured. The procedure of the sample pretreatment was as follows. At first, 0.01 g of the dried FT was dissolved in 10 mL HCl (10%), the solution was divided into two equal parts. 5 mL solution was measured by a Reflectoquant RQflex plus 10 to determine the content of Fe$^{2+}$. In order to measure the content of total Fe, the other 5 mL solution was dissolved in 5 mL ascorbic acid (100 mg/L).

The content of Fe$^{2+}$ was calculated according to equation (1).

$$Fe^{2+} \ (mg/L) = Total \ Fe - Fe^{2+}$$

Where Fe$^{2+}$ was measured by measuring the Fe(phen)$_{2}^{3+}$ (phen=1,10-phenanthroline) complex formed during acid condition, total Fe was measured by converting any Fe$^{3+}$ of FT to Fe$^{2+}$ using ascorbic acid as a reducer.

The adsorption performances were evaluated according to the amount of NH$_{4}^{+}$-N and NO$_{2}^{-}$-N absorbed on per mass of FT ($q_e$ in mg-N/g), which could be calculated according to equation (2).

$$q_e = (C_0 - C_e)/m$$

Where $q_e$ was the equilibrium contaminant adsorbed by FT (mg/g). $C_0$ was the initial concentrations (mg N/L), $C_e$ was the equilibrium concentration (mg N/L). $V$ was solution volume (L) and $m$ was the mass of FT used (g).

3. Results and discussion

3.1. The adsorption-catalytic denitrogenation performance on FT

The long reaction time (48 h) for FT in the study was chosen in the study, which might be due to the reaction time for NH$_{4}^{+}$-N and NO$_{2}^{-}$-N was unknown when FT added. To be on the safe side, the long reaction time (48 h) was chose for FT in the initial study.

![Figure 1](image)

**Figure 1.** The removal of NH$_{4}^{+}$-N and NO$_{2}^{-}$-N and N$_2$ production with the addition of FT.

In the present study, dosage of ferric tanate, concentration of NH$_{4}^{+}$-N and NO$_{2}^{-}$-N was 10.0 g/L, 100 mg/L and 200 mg/L, respectively. The results showed that N$_2$ increased when the concentration of
NH$_4^+$-N and NO$_2^-$-N decreased as time goes on (figure 1). In the procedure, NH$_4^+$-N reacted with NO$_2^-$-N as the equation (3).

$$\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + \text{H}_2\text{O}$$

(3)

After 24 hours, the concentration of NH$_4^+$-N and NO$_2^-$-N reduced to 30-35 mg/L and 125-128 mg/L, respectively. N$_2$ as product increased to 11.5-12.8 mg. And the removal rate of NH$_4^+$-N and NO$_2^-$-N was 64.6% and 39.0%. Meanwhile, the removal of NH$_4^+$-N and NO$_2^-$-N was 8.14% and 3.29%, respectively. And only 1.34 g N$_2$ generated in the control group. The results showed that more N$_2$ generated when FT was added to the oxidation-reduction reaction between NH$_4^+$-N and NO$_2^-$-N. Furthermore, according the result analysis, we confirmed the reaction time (10 h) for FT in the following study.

3.2. Adsorption of NH$_4^+$-N or NO$_2^-$-N on the FT

In order to investigate the nitrogen removal mechanism of FT, sequencing batch experiments for adsorbing NH$_4^+$-N and NO$_2^-$-N were conducted separately.

The adsorption capacity could describe well the distribution between liquid and solid phases at equilibrium [22, 23]. So the adsorption capacity of NH$_4^+$-N and NO$_2^-$-N on FT was measured in this work (figure 2). The maximum adsorption capacity of NH$_4^+$-N and NO$_2^-$-N were 13.4 mg/g and 10.0 mg/g (figure 2) under ambient temperature, respectively. And in the same experimental condition, the adsorption capacity of NH$_4^+$-N on FT was higher than NO$_2^-$-N. Thus, the results suggested that the FT showed better selectivity adsorption towards NH$_4^+$-N compared with NO$_2^-$-N. In addition, there was no N$_2$ generated in the processor. Hence NH$_4^+$-N and NO$_2^-$-N were removed by the adsorption of FT.

![Figure 2. Adsorption isotherms of NH$_4^+$-N and NO$_2^-$-N on FT.](image)

There were ferric ions and negative oxygen ions existed in FT, thus which can enhance NH$_4^+$-N and NO$_2^-$-N adsorption through the electrostatic interaction. The other important point is FT has the capacity of speeding this reaction up under ambient temperature. So the FT has the ability of regenerated in-situ when it used in NH$_4^+$-N and NO$_2^-$-N coexisted wastewater.

Therefore, in view of the cheaper cost and the simpler operation, FT is a good choice. More N$_2$ generated when FT was added to the reaction between NH$_4^+$-N and NO$_2^-$-N. Thus, the FT may be used as a promising material to remove nitrogen from wastewater in the future.

3.3. Factors influencing the reaction between NH$_4^+$-N and NO$_2^-$-N

The initial substrate concentration and the dosage of FT have important influence on the reaction of NH$_4^+$-N and NO$_2^-$-N. Therefore, it was necessary to investigate these significant factors. The experimental condition was listed as table 1, and the result of different initial substrate concentrations and different dosages of FT were illustrated as figures 3-6, respectively.
Table 1. The relative data in the experiments.

| Test | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|
| NH\textsubscript{4}+-N (mg/L) | 25  | 50  | 100 | 100 | 100 | 200 | 100 | 400 |
| NO\textsubscript{2}--N (mg/L) | 100 | 100 | 25  | 100 | 200 | 100 | 400 | 100 |
| NH\textsubscript{4}+-N/NO\textsubscript{2}--N | 1:4  | 1:2  | 4:1  | 1:1  | 1:2  | 2:1  | 1:4  | 4:1  |
| FT (g/L) | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  |
| V (mL) | 200  | 200  | 200  | 200  | 200  | 200  | 200  | 200  |

Figure 3. The variation of NH\textsubscript{4}+-N (a) and NO\textsubscript{2}--N (b) and conversion rate of N\textsubscript{2} (c) with the addition of FT.
Figure 4. The variation of NH$_4^+$-N (d) and NO$_2^-$-N (e) concentration and conversion rate of N$_2$ (f) with the addition of FT.

Figure 5. The variation of NH$_4^+$-N (g) and NO$_2^-$-N (h) concentration and conversion rate of N$_2$ (i) with the addition of FT.
3.3.1. Effect of the substrate concentration.

- The initial NH$_4^+$-N concentration was 100 mg/l, effect of the NO$_2^-$-N concentration on the reaction.

The results showed that the concentration of H$_2$O-N decreased to 99.3-64.3 mg/L and the removal quality of NO$_2^-$-N from 0.98 mg to 18.8 mg with NH$_4^+$-N to NO$_2^-$-N ratio decreased after 10 hours (figure 3). In the reaction, the production of N$_2$ was from 1.31 mg to 7.34 mg. And the most amount of N$_2$ (8.42 mg) generated at 1:2. The result indicated that the highest conversion rate of N$_2$ was achieved at 1:2 when the initial NH$_4^+$-N concentration was 100 mg/L.

- The initial NO$_2^-$-N concentration was 100 mg/l, effect of the NH$_4^+$-N concentration on the reaction.

The results showed that the concentration of NO$_2^-$-N decreased to 98.5-87.5 mg/L and the removal quality of NH$_4^+$-N from 0.70 mg to 5.20 mg with NH$_4^+$-N to NO$_2^-$-N ratio increased after 10 hours (figure 4). In the procedure, the production of N$_2$ was from 1.00 mg to 5.43 mg. And the most amount of N$_2$ (5.43 mg) generated at 1:2. The result indicated that the highest conversion rate of N$_2$ was attained at 1:2 when the initial NO$_2^-$-N concentration was 100 mg/L. While a closer look showed that the highest conversion rate of N$_2$ was obtained at NH$_4^+$-N to NO$_2^-$-N ratio 1:2 when the NO$_2^-$-N concentration kept constant.

- The initial amount of TN kept constant, effect of the NH$_4^+$-N to NO$_2^-$-N ratio on the reaction.

The initial content of TN in the group one (Test 1 and Test 3), group two (Test 7 and Test 8) were identical, respectively. After 10 hours reaction, the production of N$_2$ was 1.21 mg when the NH$_4^+$-N to NO$_2^-$-N ratio of 25:100, which was higher than the ratio of 100:25 (1.01 mg) when the initial TN
concentration was 125 mg/L. The production of $N_2$ was 7.14 mg when the NH$_4^+$-N to NO$_2^-$-N ratio of 100:400, which was higher than the ratio of 400:100 (4.66 mg) (figure 5) When the initial TN concentration was 500 mg/L. The results indicated that concentration of NO$_2^-$-N was higher than NH$_4^+$-N would be conductive to the $N_2$ generation with FT addition.

Results of the substrate concentration indicated that the concentration of NO$_2^-$-N was higher than NH$_4^+$-N would be conductive to the $N_2$ generation with FT addition. And in the present study, the optimum NH$_4^+$-N to NO$_2^-$-N ratio was 1:2, the removal rate of NH$_4^+$-N and NO$_2^-$-N was 64.3% and 7.0%, respectively. Meanwhile, the $N_2$ conversion ratio was 14.0%.

3.3.2. FT dosage. The addition of FT accelerated the reaction of NH$_4^+$-N and NO$_2^-$-N, and more $N_2$ generated. The effect of the dosage of FT on the redox between NH$_4^+$-N and NO$_2^-$-N was investigated.

In the study, FT dosages ranging from 0 to 20 g/L was optimized under optimum water conditions of NH$_4^+$-N 100 mg/L and NO$_2^-$-N 200 mg/L. The results showed that When the FT dosage was below 15 g/L, the production of $N_2$ increased as the increased addition of FT (figure 6). When the FT dosage continue increased (15-20 g/L), the production of $N_2$ and the removal of NH$_4^+$-N and NO$_2^-$-N no longer increased. Therefore, FT dosage was 15 g/L preferred for the further studies. And when the concentration of FT was 15 g/L, the highest removal rate of 68.0% for NH$_4^+$-N and 32.7% for NO$_2^-$-N could be reached. Meanwhile, the production of $N_2$ was 12.8 mg after 26 hours reaction.

3.4. The surface chemistry structure variation of FT

After the adsorption and adsorption-catalytic nitrogen removal reactions in the present study, FT were collected, and dried in a freezer dryer at minus 50°C. Then the structure analysis of FT was measured using FTIR spectroscopy. FTIR analysis permitted spectrophotometric observation of the material surface in the range 400-4000 cm$^{-1}$. The characteristic FTIR adsorption peaks could indicate some surface functional groups exist on the FT.

![Figure 7. FTIR spectra of FT before and after reaction.](image)

The smooth and broad adsorption peak at around 3500 cm$^{-1}$ appeared both the fresh and the used FT (figure 7), which was the characteristic FTIR adsorption peaks of adsorbed water or hydroxyl groups [24]. The broad Fe-O bands at around 567 cm$^{-1}$ and 459 cm$^{-1}$ appeared in the fresh FT, and the bands shifted to lower wavenumbers after either NH$_4^+$-N (559 cm-1 and 455 cm-1) or NO$_2^-$-N (557 cm-1 and 440 cm-1) adsorption. After experiments of adsorption-catalysis, the bands disappeared. The results implied that the structure of the FT (Fe-O) changed after it was added to the system where NH$_4^+$-N and NO$_2^-$-N coexisted.

3.5. The binding energy of O and Fe analysis in FT

The effects of chemical changes on the photoelectron peak shape using XPS have been of particular interest [25]. The technology of XPS was used to determine the chemical composition and the valence
state on the surface of substances [26]. In this study, the electron binding energy of O and Fe on the surface of FT were measured.

The O1s spectra were given as figure 8. In the fresh FT, the electron binding energy of O1s was 531.43 eV. After the FT was added to the system with NH4+-N or NO2⁻-N, or NH4⁺-N and NO2⁻-N coexisted, the electron binding energy of O1s was changed to 531.28 eV, 531.33 eV and 531.38 eV. The Fe 2p spectra were given as figure 8. In the fresh FT, the electron binding energy of Fe 2p was 710.93 eV. After the FT was added to the system with NH4⁺-N or NO2⁻-N, or NH4⁺-N and NO2⁻-N coexisted, the electron binding energy of Fe 2p was changed to 710.93 eV, 710.88 eV eV and 711.53 eV.

![Figure 8. XPS spectra of FT surface (m) O1s (n) Fe2p before and after reaction.](image)

There are four primary factors that affected the element’s electron binding energy as follows. (1) The spatial structure of the substance (2) The electronegativity of the substance (3) The oxidative state of the substance’s central ion (4) chemical environment of the element [27]. In this work, the electron binding energy of O1s on FT decreased. It might be the chemical environment of O1s had changed in the reaction, which led to the electron binding energy of O1s on the FT varied [28]. It was therefore suggested that the –O Fe was the core of the FT with the nitrogen removed function. And the difference in Fe 2p binding energy might be attributed to the oxidative state of Fe changed, or chemical environment of Fe changed [29]. The system with NO2⁻-N existed, NO2⁻-N would be combined with Fe ions of the FT through the electrostatic interaction. So the electronic cloud density of Fe ions on the FT increased, which could be observed from the binding energy of Fe ions decreased.

Furthermore, after and before adsorption-catalytic, the binding energy of Fe ions of FT were around 710 eV and 725 eV. Combined with the literature investigation and the standard XPS analysis method, it was found that Fe existed in FT as a form of Fe3O4 [30]. It might be concluded that the Fe3⁺ and Fe2⁺ coexisted in the FT, which could be determined in the next work.

### 3.6. The determination of the content of Fe in FT

FT that prepared in the study was difficult to dissolve in water. In the interest of analyzing the mechanism of the nitrogen removal using FT, before and after the reaction, the quantity change of FT was measured using the content of Fe (Fe3⁺ and Fe2⁺) in the substance with phenanthroline spectrophotometric method. The total amount of Fe in 1.5 g fresh FT was 0.1365 g, including a large quantity of Fe3⁺ (92.3%) and a small quantity of Fe2⁺ (7.70%) (figure 9). The result was consistent to the prediction of the XPS characterization with the Fe3⁺ and Fe2⁺ coexisted in the FT. And after the FT was added to the system which existed NH4⁺-N or NO2⁻-N, or NH4⁺-N and NO2⁻-N coexisted, the percentage composition of Fe3⁺ and Fe2⁺ was varied, while the total amount of Fe (Fe3⁺ and Fe2⁺) remained constant.

The percentage composition of Fe3⁺ in FT decreased quickly, and the percentage composition of Fe2⁺ increased obviously simultaneously in the first 2 hours in the system of NH4⁺-N and NO2⁻-N.
Later, the quantity of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} in FT transformed each other to a certain degree with time prolonging (figure 9). While in the system with NH\textsubscript{4}\textsuperscript{+}-N or NO\textsubscript{2}-N existed dependently, the percentage composition of Fe\textsuperscript{3+} in FT increased, and the percentage composition of Fe\textsuperscript{2+} decreased simultaneously with the time prolonging. And Fe\textsuperscript{3+} and Fe\textsuperscript{2+} in FT transformed each other without observed in the procedure. Therefore, only the redox reaction of NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N was coupled with the redox reaction between Fe\textsuperscript{3+} and Fe\textsuperscript{2+}. In the procedure, FT has the ability to improve the redox between NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N. And Fe ions which contained in the FT represented as the electron transfer.

![Figure 9. The content of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} of FT before and after reaction.](image)

4. Conclusions
More N\textsubscript{2} generated when FT was added to the oxidation-reduction reaction between NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N. Furthermore, the FT has good performance for ammonium and nitrite removal with up to 68.0% and 32.7% removal efficiency, respectively. The concentration of NO\textsubscript{2}-N was higher than NH\textsubscript{4}\textsuperscript{+}-N would be conductive to the N\textsubscript{2} generation with FT addition. When the FT concentration was 15 g/L, the production of N\textsubscript{2} was 12.8 mg, meanwhile the removal of NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N was 68.0% and 32.7%, respectively.

The FTIR results implied that the structure of the FT (Fe-O) changed after it be added to the system where NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N coexisted. XPS analysis found that Fe existed in FT as a form of Fe\textsubscript{3}O\textsubscript{4}, which meant the Fe\textsuperscript{3+} and Fe\textsuperscript{2+} coexisted in it. Results of the phenanthroline spectrophotometric method showed that in the system with NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N existed dependently, without observed Fe\textsuperscript{3+} and Fe\textsuperscript{2+} in FT transformed each other. And only the redox between NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N was coupled with the redox reaction between Fe\textsuperscript{3+} and Fe\textsuperscript{2+}. In the procedure, FT has the ability to improve the redox reaction of NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{2}-N, thus more N\textsubscript{2} generated. And Fe ions of the FT represented as the electron transfer.

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