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1 **Synthesis and characterization of ferric tannate as a novel porous**
2 **adsorptive-catalyst for nitrogen removal from wastewater**

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4 Ruina Zhang, Lin Li, Junxin Liu*

5

6 Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18

7 Shuangqing Road, Haidian District, Beijing 100085, China

8

9 *To whom correspondence should be addressed. Tel. /Fax: +86 10 62849133. E-mail:

10 jxliu@rcees.ac.cn

11

12 **Abstract**

13 Ferric tannate has unique adsorption capacities on $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$
14 simultaneously. So far, no normative method is available for synthesizing ferric
15 tannate. In this work, an optimizing method for synthesizing ferric tannate by using
16 tannic acid and ferric chloride is established under the conditions of room temperature
17 and neutral pH. The optimal molar ratio of tannic acid and ferric chloride were
18 determined to be in the range of 1:20 and 1:25 based on the yield and stability of the
19 ferric tannate composite. Scanning electron microscopy, Brunauer–Emmett–Teller
20 method, X-ray diffraction, and Fourier transform infrared spectrometer were used to
21 characterize the ferric tannate composite. Results showed that the ferric tannate has a
22 rough and porous surface, a large surface area, and an amorphous structure.
23 Experiments of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ adsorption reflected that the ferric tannate
24 composite has a unique capacity of adsorption-catalyzed $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ to N_2 .
25 When the mass ratio of $\text{NH}_4^+\text{-N}$ /ferric tannate and $\text{NO}_2^-\text{-N}$ /ferric tannate were both
26 200, the removal of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were 98.1% and 96.2%, respectively, after
27 3.0 hours of reaction. The conversion rate of N_2 increased to 87.1%. Therefore, ferric
28 tannate can be used as a potential material for removing nitrogen from wastewater in
29 the future.

30

31 **Keywords:** Ferric tannate, Synthesis and Characterization, Adsorption performance

32

33 Introduction

34 Nitrogen in wastewater is acknowledged as one of the critical reasons causing severe
35 eutrophication of receiving water bodies. In order to satisfy the strict sewage
36 discharge standards, many technologies for wastewater nitrogen removal have been
37 extensively developed, such as biological nitrogen removal, chemical oxidation,
38 adsorption, and ion exchange. Currently, biological nitrogen removal through
39 combination of aerobic nitrification and anoxic denitrification is widely applied in
40 wastewater treatment plants. However, this approach requires a large amount of
41 oxygen for nitrification, and a sufficient amount of organic substrates to maintain
42 denitrification, which results in high energy consumption.¹ Another biotechnology,
43 anaerobic ammonium oxidation (Anammox), is recognized as a promising alternative
44 for nitrogen removal. In the Anammox process, NO_2^- -N is converted to nitrogen gas
45 (N_2) with NH_4^+ -N as electron donor; this process consumes less energy and does not
46 require additional carbon substrates as electron donor.² However, anammox bacteria
47 exhibits extremely slow growth rate, limiting its widely practical applications.^{3,4}

48 Chemical approach for nitrogen removal represents a greater reaction rate and
49 higher removal efficiency, but this approach requires additional oxidants or reductants,
50 thereby causing high costs and complicating operational procedures.^{5,6} Adsorption
51 and ion exchange approaches, such as activated carbon and zeolite, can quickly
52 remove NH_4^+ -N, NO_2^- -N, and NO_3^- -N from wastewater. However, the adsorbent and
53 ion exchange resins must be regenerated after the saturation of adsorbed nitrogen, and
54 the regenerated solution needs further disposal, leading to higher environmental and
55 economical costs.⁷⁻¹¹ Thus, adsorption would be an attractive alternative approach for
56 wastewater nitrogen removal if the adsorbent resin can be regenerated in-situ.

57 Theoretically, the redox reaction for N_2 production occurs between NH_4^+ -N and
58 NO_2^- -N based on their standard redox potential,¹² but the reaction rate depends on the
59 reaction conditions significantly. Chemical kinetics indicate that the reaction rate can
60 be accelerated through increasing the concentrations of reactants.¹³ Adsorption can
61 transform reactants from liquid into solid, causing the reactants to be concentrated on
62 the surface of adsorbents.¹⁴ A very recent patent implied that the presence ferric
63 tannate (a kind of magnetic nanoparticles) is capable of accelerating this reaction at
64 room temperature.¹⁵ Furthermore, a highly cross-linked network of ferric tannate was
65 found to exhibit a rough and porous surface,¹⁶ capable of absorbing both negative and
66 cationic ions due to its ferric ions and negative oxygen ions. In addition, N_2H_4 and
67 NH_2OH are intermediate products in the reaction of NO_2^- -N and NH_4^+ -N,¹⁷⁻¹⁹ while
68 ferric ions can convert N_2H_4 and NH_2OH to N_2 .²⁰⁻²² Thus, ferric tannate may be used
69 as a novel solution for nitrogen removal. Even though tons of previous studies were
70 illustrated on the development and applications of magnetic nanoparticles in nitrogen
71 removal,²³⁻²⁵ no literature clearly demonstrated that these magnetic nanoparticles
72 including the ferric tannate, could efficiently eliminate NH_4^+ -N and NO_2^- -N
73 simultaneously, as well as accelerate the redox reaction between these two substances.

74 Additionally, no approach has been developed to date for synthesizing the ferric
75 tannate that can be efficiently used in wastewater treatment.

76 Therefore, this study aims to develop an optimized approach for synthesizing
77 ferric tannate, which can accelerate the reaction between NH_4^+ -N and NO_2^- -N. Tannic
78 acid and ferric chloride were used as the raw materials to synthesize ferric tannate
79 under the combined condition of room temperature and neutral pH. Moreover, Fourier
80 transform infrared spectrometry (FTIR) and Brunauer–Emmett–Teller (BET) were
81 used to analyze the functional groups and surface morphology of the produced ferric
82 tannate. This study also investigated the potential nitrogen removal performance of
83 ferric tannate in wastewater treatment. The objective of this study is to synthesize a
84 material that can accelerate the reaction between NO_2^- -N and NH_4^+ -N.

85 **Materials and methods**

86 **Materials**

87 Tannic acid and ferric chloride (FeCl_3) were used to synthesize ferric tannate. Tannic
88 acid ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$, molar mass: 1701.18 g/mol) was purchased from Sigma-Aldrich Co.,
89 USA, with a pure grade of $\geq 99.5\%$. FeCl_3 , NH_4Cl , and NaNO_2 were purchased from
90 Sinopharm Chemical Reagent Co., China, with a pure grade of $\geq 99\%$. NaHCO_3 was
91 purchased from Tianjin Jinke Fine Chemical Research Institute, China, with a pure
92 grade of $\geq 99.5\%$. The solutions of tannic acid, FeCl_3 , and NaHCO_3 were prepared
93 with distilled water at concentrations of 0.1, 1, and 0.65 mol/L, respectively.

94 **Synthesis of ferric tannate**

95 Tannic acid is an abundant polyphenolic compound. Its orthophenolic hydroxyl
96 structure can cause complexation reactions with ferrous and ferric ions, which form a
97 hybrid with metal-organic framework. The chemical structures of tannic acid and
98 ferric tannate are shown in Fig.1.^{26, 27} In view of the complexity of the chemical
99 structure of tannic acid, six molar ratios of tannic acid and FeCl_3 (1:10, 1:15, 1:20,
100 1:25, 1:30, 1:40) were chosen to investigate the influence of varying proportions on
101 ferric tannate yield. The synthesis of ferric tannate was performed in a conical flask
102 with a volume of 150 mL. An amount of 10 mL of 0.1 mol/L tannic acid solutions was
103 mixed with various volumes of 1 mol/L FeCl_3 solution. The pH of the mixture was
104 adjusted to 7 by using 0.65 mol/L NaHCO_3 solution. The reaction products were
105 separated via sedimentation, and the resultant precipitation was washed with
106 deionized water for four times, centrifuged (3000 rpm, 2 min), and dried in a freezer
107 dryer at $-50\text{ }^\circ\text{C}$.

108 **Characterization of ferric tannate**

109 The ferric tannate yield (y_e) was calculated by the following equation (eq. 1):

$$110 \quad y_e = \frac{m_{ft}}{(m_t + m_{fe})} \times 100\% \quad (1)$$

111 where m_{ft} is the weight of the ferric tannate (mg); m_t and m_{fe} are the weights of
112 tannic acid and ferric chloride (mg), respectively.

113 To determine the stability of ferric tannate yield, 0.2 g ferric tannate composition,

114 which was prepared with different ratios as mentioned earlier, was placed into six
115 shake flasks. Then, each shake flask was charged with 200 mL of deionized water.
116 After 1 h of continuous stirring, the mixture in each shake flask was filtered through a
117 0.45 μm pore size filter. The filtrate was measured with a UV-vis spectrophotometer
118 (UV-1700, Hitachi Co., Japan) in 200 nm to 500 nm wavelength.

119 Field emission scanning electron microscopy (FE-SEM), which was coupled with
120 an energy dispersive X-ray spectroscopy (EDS) detector (SU-8020, Hitachi Co.,
121 Japan), was employed to observe the surface physical morphology and major
122 elements of ferric tannate.

123 An automatic micropore and mesopore analyzer (ASAP 2020 HD88, USA) was
124 operated to analyze the specific surface area and pore size distribution of ferric
125 tannate. Moreover, the specific surface area and pore size distribution of the ferric
126 tannate were determined with N_2 adsorption isotherm at 77 K by using Micromeritics
127 ASAP 2010 accelerated surface area analyzer and BET method.²⁸

128 Fourier transform infrared spectrometer (FTIR, Tensor 27, Germany) was applied
129 to measure the functional group of tannin acid and ferric tannate with potassium
130 bromide pellet method in the range of 400 cm^{-1} to 4000 cm^{-1} region.²⁹

131 X-ray diffraction (XRD; X'Pert PRO MPD, PANalytical, Holland) was used to
132 analyze the purity and crystallinity of ferric tannate, ferric chloride, and tannic acid
133 with $\text{Cu-K}\alpha$ radiation ($\lambda=0.015418\text{ nm}$) in the 2θ range of 10° to 80° . The XRD data
134 were collected in a scan mode with a step length of 0.5 with a scanning rate of $6^\circ/\text{min}$.
135 The accelerating voltage and the applied current were 45 kV and 45 mA, respectively.

136 **Determination of the nitrogen removal performance**

137 Several batch tests were conducted in stoppered conical flasks to estimate the nitrogen
138 removal performance of the synthesized ferric tannate. Stock solutions were prepared
139 by dissolving NH_4Cl or/and NaNO_2 in deionized water. For each time, 0.1 g ferric
140 tannate and 50 mL stock solutions were mixed in a flask, which was then shaken with
141 a shaker at 200 rpm at room temperature. In the procedure of the nitrogen removal by
142 using ferric tannate, the pH was 7, which was adjusted with HCl or NaHCO_3 .³⁰

143 In adsorption isotherm studies, the stock solutions with different initial
144 concentrations of $\text{NH}_4^+\text{-N}$ or $\text{NO}_2^-\text{-N}$ were added into 100 mL conical flasks, and the
145 equilibrium time was set to 2 h. The samples were separated via filtration.

146 In the experiments, both concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the reaction
147 solution were 50 mg/L. The amounts of 100 mL stock solution and 1.0 g ferric tannate
148 were added into a 150 mL stoppered conical flask. Then, the flask was shaken at 200
149 rpm for 3.0 h at room temperature, and the 500 μL water samples and 50 μL gas
150 samples were collected every 20 min. In the study, the data of NH_4^+ and NO_2^-
151 adsorption on the ferric tannate at room temperature were achieved through three
152 groups of parallel tests.

153 The concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were measured according to standard
154 methods.³¹ The Agilent 6890N Gas Chromatograph equipped with TCD detector was
155 used to analyses the content of N_2 .

156 The adsorption amount of $\text{NH}_4^+\text{-N}$ or $\text{NO}_2^-\text{-N}$ on the ferric tannate at equilibrium,
157 q_e (mg-N/g), was calculated with the following equation (eq. 2 and eq. 3):

$$158 \quad q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

$$159 \quad \text{Removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (3)$$

160 Where q_e is the equilibrium amount of adsorption on the adsorbent surface
161 (mg/g), C_i and C_e are the initial and equilibrium concentrations of $\text{NH}_4^+\text{-N}$ or $\text{NO}_2^-\text{-N}$
162 (mg-N/L) in the solution, respectively. V is the volume of the solution (L), and m is
163 the weight of the ferric tannate (g).

164 The Langmuir adsorption equation and the Freundlich adsorption equation can
165 be linearised according to the equation.³²

166 Due to the inherent bias resulting from linearisation of the isotherm model, the
167 error analysis was employed as a criterion for the fitting quality. This statistical
168 analysis is based on the sum of the squares of the differences between the
169 experimental and the Langmuir model and Freundlich model calculated data. The
170 error was calculated as the following equation (eq. 4 and eq. 5):

$$171 \quad \text{Relative error} = \frac{\sum_{i=1}^n \left| \frac{q_i - q_{sim}}{q_i} \right|}{n} \times 100\% \quad (4)$$

$$172 \quad \text{Standard deviation} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\left| \frac{q_i - q_{sim}}{q_i} \right| - \frac{1}{n} \sum_{i=1}^n \left| \frac{q_i - q_{sim}}{q_i} \right| \right)^2} \quad (5)$$

173 where q_i the equilibrium capacity of the adsorbent obtained from experiment
174 (mg/g), q_{sim} was the simulated adsorption capacities which calculated with Langmuir
175 equation and Freundlich equation (mg/g).

176 A low value of the relative error or standard deviation indicates that experimental
177 data fit better to the value from the model. In order to confirm the best-fit isotherms
178 and kinetic models for the adsorption system, there is a need to analyse the data set
179 using the Nash-Sutcliffe efficiency (NSE).^{33, 34} As a dimensionless goodness-of-fit
180 indicator, the values of NSE could be widely used and potentially reliable statistic for
181 assessing the goodness of fit of isothermal adsorption models. $\text{NSE} = 1$ indicated a
182 perfect fit, $0.75 \leq \text{NSE} \leq 0.9$ suggested a good fit, $0.65 \leq \text{NSE} \leq 0.749$
183 suggested a acceptable fit. NSE is calculated as follows (eq. 6):

$$184 \quad \text{NSE} = 1 - \frac{\sum_{i=1}^n (q_i - q_{sim})^2}{\sum_{i=1}^n (q_i - \bar{q})^2} \quad (6)$$

185 Where q_i is the equilibrium capacity of the adsorbent obtained from experiment
186 (mg/g), q_{sim} is the simulated adsorption capacities (mg/g), \bar{q} was the average
187 adsorption capacities (mg/g).

188 **Synthesis of ferric tannate**

189 As expected, the reaction of tannic acid with FeCl_3 resulted in the formation of an
190 abundant precipitate ferric tannate. Table 1 presents a summary of the results of the
191 ferric tannate yield in the six proportions of tannic acid and FeCl_3 , which showed an
192 obvious response between the ratio of tannic acid and FeCl_3 and ferric tannate yield.

193 Increasing the proportions of tannic acid and FeCl_3 from 1:10 to 1:30 resulted in the
194 gradual increase of ferric tannate yields. The highest yield, 82.6%, appeared in the
195 case of 1:30. Moreover, ferric tannate yields are nearly equal in the cases of 1:20, 1:25,
196 and 1:40.

197 The stability of the ferric tannate composition in liquid will be highly important
198 to apply nitrogen removal from wastewater. Therefore, the dissolution of the ferric
199 tannate compositions in water was determined. The UV-visible adsorbance spectra of
200 the soak water of the ferric tannate composition are shown in Fig.2. The results
201 showed that nothing could be dissolved in the cases of 1:15, 1:20, and 1:25, but the
202 adsorption peak appeared at 302 nm in the case of 1:10 and at 303 nm in the cases of
203 1:30 and 1:40, which indicated that some substrates were dissolved into the water.

204 The preceding results indicated that the molar ratio of tannic acid to ferric ion
205 was responsible for the formation of the ferric tannate complex. With strong
206 reducibility, the phenolic hydroxyl in tannic acid can reduce Fe^{3+} to Fe^{2+} .³⁵⁻³⁷ In the
207 case of 1:10, the excess tannic acid can produce a dissolved ferrous tannate, whose
208 adsorption peak appeared at 302 nm.³⁸ In the cases of 1:30 and 1:40, the ferric ion was
209 in excess, which could lead to the formation of $\text{Fe}(\text{OH})_3$. Therefore, the adsorption
210 peak at 303 nm is probably the ferric ion dissolution.³⁹ Therefore, based on the yield
211 and stability of the ferric tannate composition, the optimal molar ratios of tannic acid
212 and FeCl_3 to synthesize ferric tannate are between 1:20 and 1:25.

213 **Characterization of ferric tannate**

214 According to the results of the preceding experiment, the synthesizing sample in the
215 case of 1:20 was selected to characterize ferric tannate composite. FE-SEM images of
216 the ferric tannate composite are illustrated in Fig.3. The ferric tannate composite had a
217 rough and porous surface structure. The adsorption isotherms of N_2 on the ferric
218 tannate composite were used to deduce the surface characteristics. The results showed
219 that the BET surface area, pore volume, and average pore diameter were $97 \text{ m}^2/\text{g}$,
220 $0.073 \text{ cm}^3/\text{g}$, and 66.58 nm, respectively. In general, a large surface area and pore
221 diameter can increase the adsorption capacity of the material.^{40, 41}

222 The SEM-EDS spectrum of the ferric tannate composite is shown in Fig.4. The
223 composite mainly consists of C, O, and Fe elements, and the percentage contents of C,
224 O, and Fe in the ferric tannate composite are 23.06%, 46.83%, and 29.91%,
225 respectively. However, the ratio of C and O from the SEM-EDS spectrum is
226 anomalous compared with the chemical formula of tannic acid ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$). A
227 possible explanation is that ferric ion occurs partially hydrolysis reaction at neutral pH
228 condition, which leads to an increase of O in the ferric tannate composite.^{35, 42, 43}
229 However, this finding should be verified at further research.

230 The XRD patterns of the tannic acid, FeCl_3 , and ferric tannate composite was
231 shown in Fig.5. XRD data indicate that FeCl_3 has many diffraction peaks because of
232 its crystalline structure.⁴⁴ The diffraction peaks of the tannic acid and ferric tannate
233 composite appear in $2\theta=20^\circ$ to 30° range, which demonstrate that they have
234 amorphous structure.

235 The FTIR spectra of the tannic acid and ferric tannate composite are illustrated in
236 Fig.6. Two broad adsorption bands in the 3600 cm^{-1} to 3100 cm^{-1} range that indicated
237 the presence of phenolic hydroxyl group were observed, and the band at 1320 cm^{-1}
238 exhibits a characteristic of the bending vibrations of O-C in phenolic hydroxyl group.
239 The sharp band at 1400 cm^{-1} in the spectra of the ferric tannate composite is very
240 pronounced, which ascribed to C=O of benzoic acid vibration adsorption peaks. This
241 phenomenon can be explained by the chelation and redox reaction of Fe^{3+} with
242 phenolic hydroxyl, which results in a coexistence of Fe^{3+} and Fe^{2+} in ferric tannate.^{27,}
243 ³⁵ The interaction between Fe^{3+} and the phenolic hydroxyl group has effect on the
244 O-C bond stretch vibration, in which the band shifted from 1320 cm^{-1} in the spectra
245 of the tannic acid to 1338 cm^{-1} to 1375 cm^{-1} in the spectra of the ferric tannate
246 composite.⁴⁵⁻⁴⁷ During the combination process of Fe^{3+} with the phenolic hydroxyl
247 group, oxygen anion was formed.

248 **Valuation of the nitrogen removal performance of ferric tannate composite**

249 Some batch tests adsorbing $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were conducted separately to
250 estimate the nitrogen removal performance of the synthesized ferric tannate. The data
251 of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ adsorption on the ferric tannate composites, only $\text{NH}_4^+\text{-N}$ or
252 $\text{NO}_2^-\text{-N}$ in the solution, were shown in Fig.7. Langmuir and Freundlich models were
253 usually used to describe the equilibrium isotherm data. The results from linear of
254 these isotherms of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ on the ferric tannate composites were listed in
255 Table 2. Compared with the correlation coefficient value of the linear plot of the
256 Freundlich isotherm, that of Langmuir model was in better agreement with observed
257 data ($R^2=0.990$ for $\text{NH}_4^+\text{-N}$ adsorption and $R^2=0.957$ for $\text{NO}_2^-\text{-N}$ adsorption). The
258 maximum adsorption capacities of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ calculated from the Langmuir
259 equations were 13.6 mg/g and 10.2 mg/g at room temperature, respectively. The
260 results indicated that the adsorption capacity of ferric tannate toward $\text{NH}_4^+\text{-N}$ was
261 better than that toward $\text{NO}_2^-\text{-N}$.

262 In the study, the values of NSE (Table 3) indicated that the Langmuir models of
263 $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ being considered very good ($0.9 \leq \text{NSE} \leq 1$). The Freundlich
264 models of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ being considered good ($0.8 \leq \text{NSE} \leq 0.9$) and very
265 good ($0.9 \leq \text{NSE} \leq 1$), respectively.

266 Adsorption performances of ferric tannate toward $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were
267 different and varied significantly with time. Fig.8 showed the adsorptive behaviors for
268 $\text{NH}_4^+\text{-N}$ or/and $\text{NO}_2^-\text{-N}$ of ferric tannate. The concentration of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$
269 decreased with time, while the production of N_2 increased at the same time (Fig.8).
270 When the mass ratio of $\text{NH}_4^+\text{-N}$ /ferric tannate and $\text{NO}_2^-\text{-N}$ /ferric tannate were both
271 200, the removal of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were 98.1% and 96.2%, respectively, after
272 3.0 hours of reaction. The conversion rate of N_2 increased to 87.1%. Results showed
273 that after the addition of ferric tannate, the removal of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ increased
274 obviously with N_2 production increased simultaneously, which indicated that ferric
275 tannate would be benefit for the reaction between $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$, and lead to
276 more N_2 generation. These results indicated that the ferric tannate had a unique

277 capacity to absorb anions and cations simultaneously, and an adsorption-catalyzed
278 reaction occurred on the ferric tannate with the adsorption of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$.
279 The adsorption-catalyzed reaction between $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ could refresh the
280 adsorption site of ferric tannate, and the continuous adsorption of $\text{NH}_4^+\text{-N}$ and
281 $\text{NO}_2^-\text{-N}$ on ferric tannate could be promoted. Thus, the removal amount of $\text{NH}_4^+\text{-N}$
282 and $\text{NO}_2^-\text{-N}$ was enhanced. Therefore, the ferric tannate may be used as a promising
283 material to remove nitrogen from wastewater in the future.

284 In the practical use, the dosage of ferric tannate will be adjusted with the
285 concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the wastewater, for the purpose of more
286 $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ converted to N_2 .

287 **Conclusions**

288 A novel method to synthesize porous ferric tannate composites was demonstrated by
289 using tannic acid and ferric chloride under the conditions of room temperature and
290 neutral pH. According to the yield and stability of the ferric tannate composite, the
291 optimal molar ratio of tannic acid and FeCl_3 is between 1:20 and 1:25. Combined with
292 the characterization of SEM and BET, the characteristics of porous surface and large
293 surface area of the ferric tannate composite were confirmed. XRD analysis confirmed
294 that the ferric tannate composite has amorphous structure. The adsorption test results
295 indicated that the adsorption of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ on the ferric tannate composite
296 agrees well with that obtained Langmuir model. Moreover, the maximum adsorption
297 capacity of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ calculated from the Langmuir equations were 13.6
298 mg/g and 10.2 mg/g at room temperature, respectively. Furthermore, ferric tannate has
299 a unique capacity to absorb $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ simultaneously. In addition, an
300 adsorption-catalyzed reaction can occur on the ferric tannate with the adsorption of
301 $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$, which enhances the removal of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$. When the
302 mass ratio of $\text{NH}_4^+\text{-N}$ /ferric tannate and $\text{NO}_2^-\text{-N}$ /ferric tannate were both 200, the
303 removal of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were 98.1% and 96.2%, respectively, after 3.0 hours
304 of reaction. The conversion rate of N_2 increased to 87.1%. Therefore, ferric tannate
305 may be used as a promising material to remove nitrogen from wastewater in the
306 future.

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398

399 **Figure captions**

400 **Fig.1** Schematic diagram of chemical structures of (a) tannic acid and (b) ferric
401 tannate.

402 **Fig.2** UV-visible absorbance spectra of the soak water of the ferric tannate composite.

403 **Fig.3** SEM of for 1:20 tannic acid/FeCl₃ (a) ferric tannate composition and (b) its
404 microstructure.

405 **Fig.4** SEM-EDS spectrum of the ferric tannate composite (1:20 tannic acid/FeCl₃).

406 **Fig.5** XRD spectra of the tannic acid, FeCl₃ and ferric tannate composite (1:20 tannic
407 acid/FeCl₃).

408 **Fig.6** FTIR spectra of tannin and ferric tannate (1:20 tannic acid/FeCl₃).

409 **Fig.7** Adsorption isotherm of NH₄⁺-N and NO₂⁻-N on ferric tannate.

410 **Fig.8** The removal of NH₄⁺-N and NO₂⁻-N and the conversion rate of N₂ with the
411 addition of ferric tannate.

412

413

Table 1 Yield of ferric tannate at different ratio of tannic acid and FeCl₃.

Ratio(Tannic acid/FeCl ₃)	1:10	1:15	1:20	1:25	1:30	1:40
Yield (%)	71.3	75.4	78.4	79.2	82.6	78.4

Table 2 Langmuir and Freundlich isotherm parameters for NH_4^+ -N and NO_2^- -N adsorption by ferric tannate.

	Langmuir parameters			Freundlich parameters		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F [(mg/g)/(mg/L) ⁿ]	n	R^2
NH_4^+ -N	0.079	13.9	0.990	7.06	0.109	0.860
NO_2^- -N	0.009	10.2	0.957	2.84	4.53	0.952

Table 3 The data of error estimation and NSE

	Error estimation (%)				NSE			
	Langmuir		Freundlich		Langmuir		Freundlich	
	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻
Test1	1.51±1.24	1.46±1.44	3.50±2.28	2.94±2.07	0.972	0.994	0.854	0.992
Test2	1.58±0.901	1.67±1.19	3.51±2.32	2.74±2.29	0.976	0.996	0.849	0.991
Test3	1.89±1.19	2.42±1.44	3.85±2.63	1.60±1.43	0.965	0.994	0.824	0.997

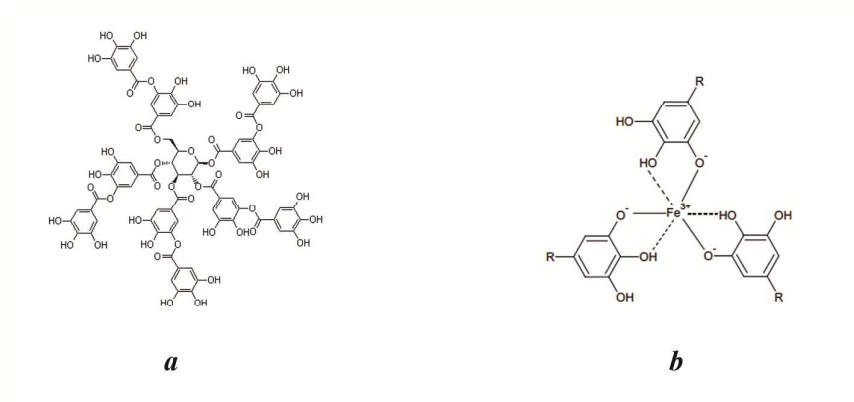


Fig.1 Schematic diagram of chemical structures of (a)tannic acid and (b) ferric tannate

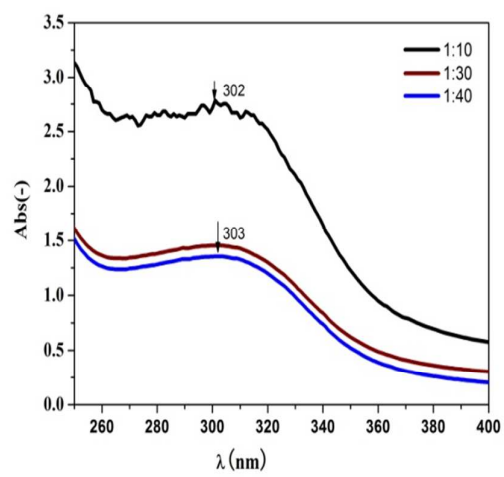


Fig. 2 UV-visible adsorbance spectra of the soak water of the ferric tannate composite.

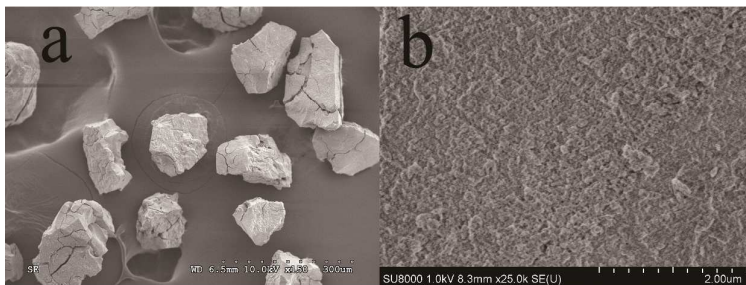


Fig. 3 SEM of for 1:20 tannic acid/ FeCl_3 (a)ferric tannate composition and (b)its

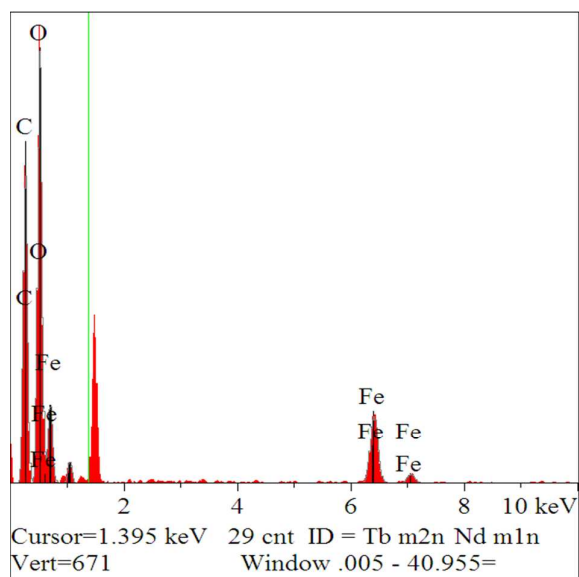


Fig.4 SEM-EDS spectrum of the ferric tannate composite (1:20 tannic acid/ FeCl_3)

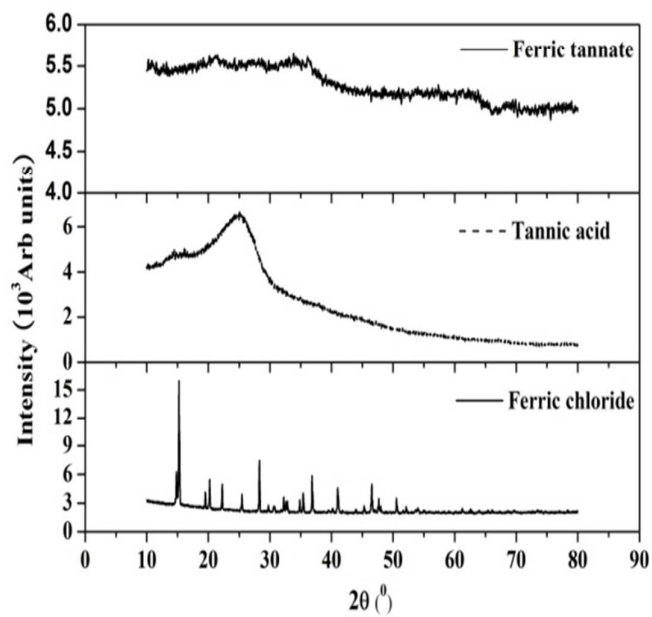


Fig. 5 XRD spectra of the tannic acid, FeCl_3 and ferric tannate composite (1:20 tannic acid/ FeCl_3).

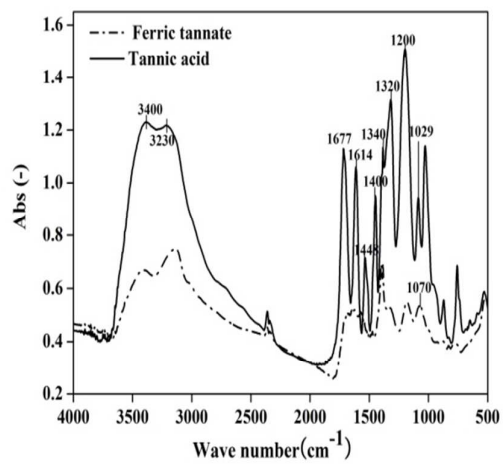


Fig.6 FTIR spectra of tannin and ferric tannate (1:20 tannic acid/FeCl₃)

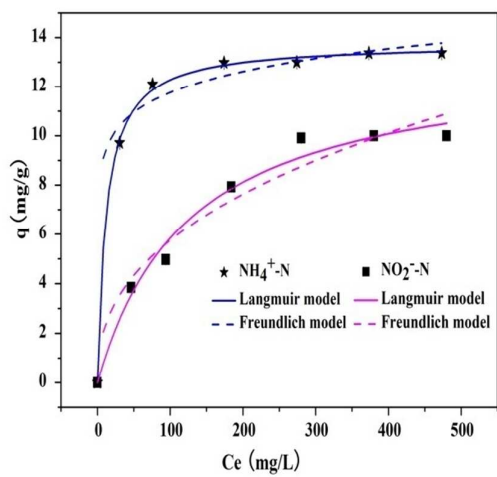


Fig.7 Adsorption isotherm of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ on ferric tannate

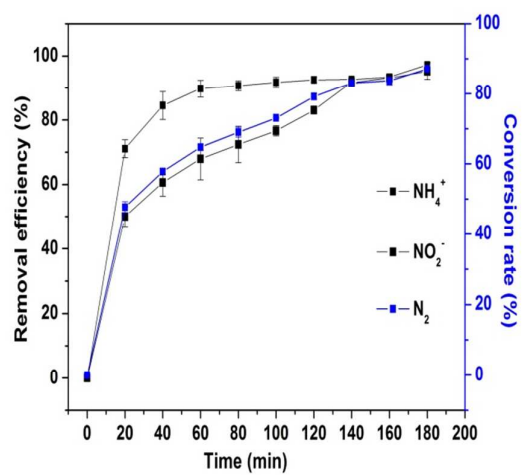


Fig.8 The removal of NH_4^+ -N and NO_2^- -N and the conversion rate of N_2 with the addition of ferric tannate