

Integrated effects of selected ions on 2,4,6-trinitrotoluene-removal by O_3/H_2O_2

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Abstract

Considering the components of 2,4,6-trinitrotoluene (TNT)-containing water, this paper aims to research the integrated effects of ions on TNT-removal by O_3/H_2O_2 through the selection of CO_3^{2-} , HCO_3^- , Cu^{2+} and Al^{3+} . In view of TNT-removal rate and its constant, we find that the test with HCO_3^- or $HCOO^-$ or Cu^{2+} results in lower TNT-removal rate and its constant than control test. Therefore, it may conclude that HCO_3^- or $HCOO^-$ and Cu^{2+} has a potential to inhibit the efficacy of O_3/H_2O_2 , and that their inhibitions increase with an order from $HCOO^-$ to Cu^{2+} and to HCO_3^- . However, Al^{3+} is an exception, because it has a potential to improve the efficacy. When the two selected ions coexist, HCO_3^- and $HCOO^-$ inhibit the efficacy. The inhibition is greater than that of either one alone, and also greater than their sum, and thus the integrated effect of HCO_3^- and $HCOO^-$ follows the synergistic effect. The inhibition of Cu^{2+} and $HCOO^-$ coexistence also is greater than that either alone, but smaller than their sum, and thus their integrated effect follows the independent effect. The integrated effect of Al^{3+} and $HCOO^-$ follows the addition effect.

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1. Introduction

Advanced oxidation processes are a new means of objective pollutant-removal for drinking water and wastewater [1], which generally can generate the hydroxyl radicals, and thus they are of efficiency. Therefore, ozone/hydrogen peroxide (O_3/H_2O_2) process is considered to have a strong ability to generate hydroxyl radical (OH^\bullet), and have a strong effect on pollutant-removal. Consequently, the process has a great priority over others in the large-scale water treatment plant [2,3]. Therefore, many researches have been conducted for the efficacy of O_3/H_2O_2 to purify water [4–8], and several ions found have a potential to affect the efficacy. HCO_3^- and CO_3^{2-} react with OH^\bullet , and consume OH^\bullet to decrease the efficacy of O_3/H_2O_2 [5,9], and thus have inhibitions. But humic substances with low concentration and $HCOO^-$ have enhancement [7,9]. The effects of these ions are from the studies with one component in drinking water treatment [10,11], and most of them are model micro-polluted water, but few are with wastewater treatment. In fact, a treated water is

of multi-components, which may also influence the generation or (and) lifetime of OH^\bullet , and even have interactions among these components, so multi-components may also affect the efficacy of O_3/H_2O_2 process and their mechanisms may be more complex. The effects of other ions of the treated water, especially the coexistence of multi-components on the pollutant-removal by O_3/H_2O_2 , attract more and more attention, because these are helpful to the study on O_3/H_2O_2 in future, and even to its practice in water treatment.

In this work, TNT in the explosive-wastewater is used as an objective pollutant and its removal rates and their reaction rate constants are employed to judge the efficacy of O_3/H_2O_2 process. Carbonate is a common chemical component in wastewater, and its concentration increases with organic substance removal generally. The water environment is anaerobic wholly or partly for low concentration of dissolved oxygen caused by the transferring and consumption of oxygen, and some organic substances are transformed into simple organic acid substances here [12]. On other hand, during the producing and manufacturing processes for the blasting powder, some simple organic acid matters and metal ions (such as Cu^{2+} and Al^{3+}) are also released into wastewater. Thus, carbonate is present in a certain content, $HCOO^-$ also exists in explosive-wastewater absolutely.

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According to the relation between pH and carbonate in water [13], the most form of carbonate is HCO_3^- in the TNT model wastewater under pH 7.9. Based on these, HCO_3^- , HCOO^- , Cu^{2+} and Al^{3+} are selected to investigate their integrated effect on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$.

2. Experimental methods

2.1. Reagent

A series of chemicals were purchased from Xi'an chemical reagents company, Xi'an city, Shaanxi province, PR China. Their commercial and chemical names are listed in the following: 2,4,6-trinitrotoluene (TNT), NaHCO_3 , $\text{Al}_2(\text{SO}_4)_3$, HCOOH , CuSO_4 and H_2SO_4 (density 1.84). All of these are of analytical grade.

2.2. Model TNT wastewater

Under 25 °C, the analytical pure TNT is dissolved in tap water to make model wastewater for testing. In the study, the initial mass concentration (C_0) is about 30 mg/L, and pH 7.9.

2.3. Apparatus, equipment and experiment process

2.3.1. Apparatus and equipments

XFZ-5BI type ozone generator (manufactured by Tsinghua University, China), Gas flow counter (manufactured by Xi'an Institute of Thermal Engineering, Shaanxi Province, China), D100B-type peristaltic pump (manufactured by Huxi instruments company, Shanghai, China) and pH-3C type pH analyzer (manufactured by Leici Instrumental Factory, Shanghai, China).

2.3.2. Experiment process

The reactor is a 1000 mL jar. O_3 producer works firstly, and then moderates its amperage and oxygen gas intake pressure, until the concentration of O_3 is stabilized in the out-take gas. The out-take gas is mixed with the model wastewater in a reactor through an air-distributor, and H_2O_2 input by the peristaltic pump into the reactor and blended with model wastewater simultaneously. During the test process, the surplus out-take gas is mixed with $\text{Na}_2\text{S}_2\text{O}_3$ solution to decompose O_3 . A sample about 20 mL is taken every 8 min, and analyzed immediately for TNT and other components concentrations. Before analysis, we have adjusted pH of samples to 2 or so by H_2SO_4 (density 1.84) to reduce the effect of metal ions. In this paper, the mass concentration of ozone is 2.3566 mg/L and its flux is 0.05 m^3/h , and $\text{O}_3/\text{H}_2\text{O}_2$ molecular ratio is kept at 2:1, unless particular declaration.

2.4. Analytical methods

The concentration of TNT is determined by the spectrometer method [14](GB/T 13903-95, China), O_3 concentration in the liquid is determined by the Karman-Indigo method [15]. pH is recorded by pH-3C analyzer.

Kinetics of TNT-removal is determined from a plot of the natural logarithm of the TNT concentration as a function of time. Pseudo-first-order rate constants (k) are determined by regression analysis.

3. Results and discussion

3.1. Integrated effect of HCO_3^- and HCOO^-

To research the integrated effect of HCO_3^- and HCOO^- on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$, four reactors filled with 800 mL model wastewater are prepared firstly, and then on the test design, HCO_3^- is added to one, HCOO^- to one, HCO_3^- and HCOO^- to another one, and the other one is controlled as blank test. The results of these tests are shown in Fig. 1.

Compared with the control test, the presence of HCO_3^- or HCOO^- in the wastewater is of no good to TNT-removal, and decreased TNT-removal rates in certain degree respectively (Fig. 1). Thus, both of HCO_3^- and HCOO^- inhibited TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$. Compared the two anions, HCOO^- inhibited TNT-removal more strongly than HCO_3^- . HCO_3^- had a small inhibition, which was coincided with results of the studies by [5,6]. When the two anions coexisted, TNT-removal rate descended much more than either one. When the tests lasts for 24 min, compared with the control test, TNT-removal rate decreases about 23.2% by the two components coexistence. The decrease is greater than each of HCO_3^- (1.3%) and HCOO^- (13.6%) respectively, and also greater than the sum of the decreases of HCO_3^- and HCOO^- (1.3 + 13.6 = 14.9%). Obviously, the integrated effect of HCO_3^- and HCOO^- coexistence on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$, was not a simple addition of the two effects of HCO_3^- and HCOO^- , but synergistic effect.

The contaminant-removal by $\text{O}_3/\text{H}_2\text{O}_2$ is caused from OH^\bullet in fact and OH^\bullet is produced from the reaction between O_3 and H_2O_2 [3]:

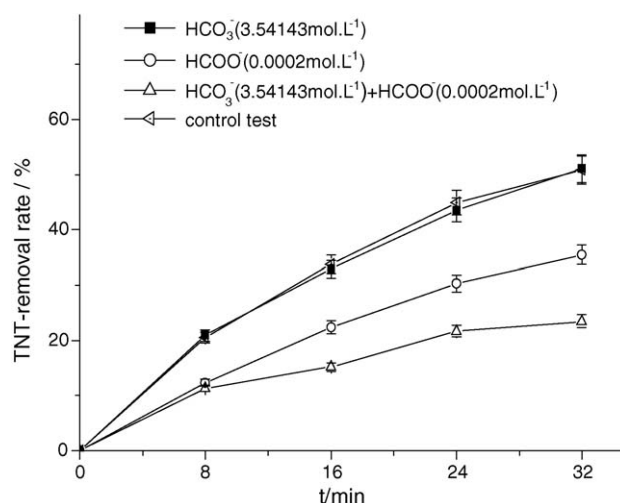
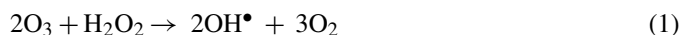


Fig. 1. Integrated effect of HCO_3^- (3.54143 mol/L) and HCOO^- (0.0002 mol/L) on TNT-removal.

Table 1
Pseudo-first-order rate constants (k) of TNT-removal by O_3/H_2O_2 under conditions with several wastewater qualities

Ions added to the wastewater	K (s^{-1})	R (%)
Blank test (control test)	0.02366	0.9873
$HCOO^-$ (0.0002 mol/L)	0.01448	0.9910
HCO_3^- (3.54143 mol/L)	0.02338	0.9920
$HCOO^-$ (0.0002 mol/L) + HCO_3^- (3.54143 mol/L)	0.00941	0.9478
$HCOO^-$ (0.0001 mol/L)	0.02105	0.9924
$HCOO^-$ (0.0001 mol/L) + HCO_3^- (3.54143 mol/L)	0.01326	0.9892
HCO_3^- (1.19048 mol/L)	0.02359	0.9874
$HCOO^-$ (0.0002 mol/L) + HCO_3^- (1.19048 mol/L)	0.01137	0.9635
Cu^{2+} (0.03125 mol/L)	0.00636	0.9876
Cu^{2+} (0.00313 mol/L)	0.00117	0.9737
$HCOO^-$ (0.0002 mol/L) + Cu^{2+} (0.03125 mol/L)	0.00450	0.9897
$HCOO^-$ (0.0001 mol/L) + Cu^{2+} (0.00313 mol/L)	0.00923	0.9968
Al^{3+} (0.002016 mol/L)	0.02393	0.9850
$HCOO^-$ (0.0002 mol/L) + Al^{3+} (0.002016 mol/L)	0.01598	0.9584
$HCOO^-$ (0.0001 mol/L) + Al^{3+} (0.002016 mol/L)	0.01925	0.9698
Al^{3+} (0.00806 mol/L)	0.02422	0.9894
$HCOO^-$ (0.0002 mol/L) + Al^{3+} (0.00806 mol/L)	0.01440	0.9896

When O_3 and H_2O_2 are supplied constantly, and their concentrations are unvarying. Thus, OH^\bullet concentration is also stable in the reactor. Under the study conditions, the contaminant degradation process followed pseudo-first-order dynamics [16–18], and the inhibition or promotion ability of each component can be measured by the decrease of pollutant-removal reaction rate constant. Kinetics of TNT-loss were determined from a plot of the natural logarithm of the TNT concentration as a function of time. Pseudo-first-order rate constants (k) were determined by regression analysis, and the results were shown in Table 1. Pseudo-first-order rate constant for TNT-removal in control test was $0.02366 s^{-1}$ (K_{14}), and in tests with $HCOO^-$ or HCO_3^- were $0.02338 s^{-1}$ (K_{13}) or $0.01448 s^{-1}$ (K_{12}), respectively, and in test with both is $0.0094 s^{-1}$ (K_{11}). Obviously, $(K_{14} - K_{11}) > ((K_{14} - K_{12}) + (K_{14} - K_{13})) > (K_{14} - K_{13})$. Therefore, whether $HCOO^-$ and HCO_3^- are individual or coexistent, both of them have the inhibition influence on TNT-removal by O_3/H_2O_2 . And the inhibition of $HCOO^-$ and HCO_3^- coexisted was greater than one of both, and also greater than the sum of their single potentials. The TNT-removal rates and their reaction rate constants of the tests under other

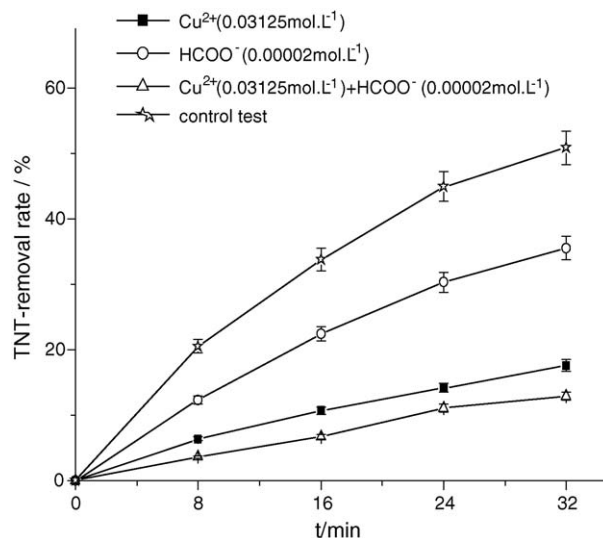


Fig. 3. Integrated effect of Cu^{2+} (0.03125 mol/L) and $HCOO^-$ (0.00002 mol/L) on TNT-removal.

concentrations of $HCOO^-$ and HCO_3^- are shown in Fig. 2 and Table 1, respectively. Analyzed these data, the same regularities were drawn. Therefore, the integrated effect of these two components on TNT-removal by O_3/H_2O_2 is not a simple addition of their single effects, but obeyed synergistic effect.

3.2. Integrated effect of Cu^{2+} and $HCOO^-$

The preparation is described in Section 3.1 mostly to study the integrated effect of Cu^{2+} and $HCOO^-$ on TNT-removal by O_3/H_2O_2 , and Cu^{2+} is used instead of HCO_3^- . The results of these tests are shown in Fig. 3.

In this test study, though the concentrations of Cu^{2+} and $HCOO^-$ were only 0.03125 and 0.00002 mol/L, respectively, compared with the control test, both of them also depressed TNT-removal in certain degree. For instance, when the test is being done for 24 min, TNT-removal rate is 44.9% in the control test, 14.2 and 30.3% in the test with Cu^{2+} and $HCOO^-$, respectively, and 11.1% in the test with Cu^{2+} and $HCOO^-$ coexisted. Compared with the control test, TNT-removal rates decrease about 30.7 and 14.6% by the presence of Cu^{2+} or $HCOO^-$ respectively,

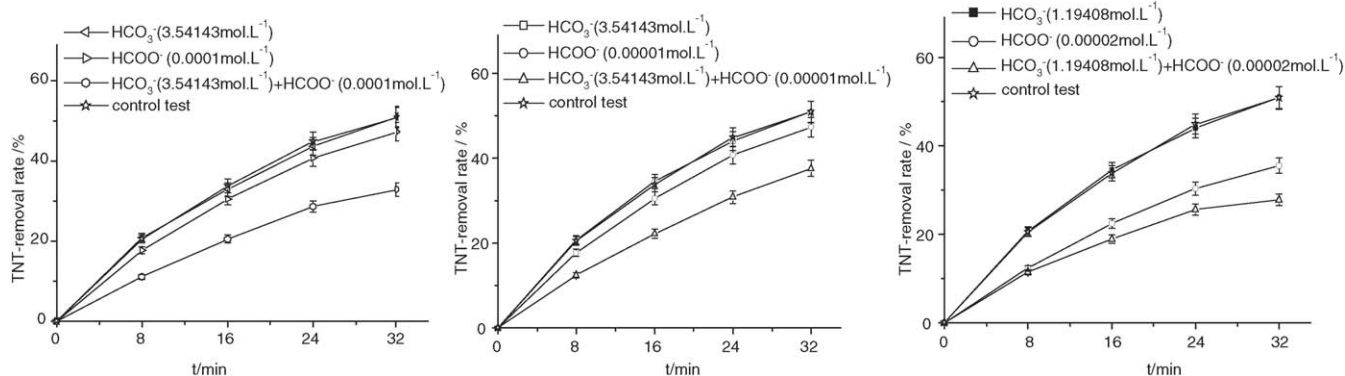


Fig. 2. Integrated effect of HCO_3^- and $HCOO^-$ on TNT-removal under the more concentrations.

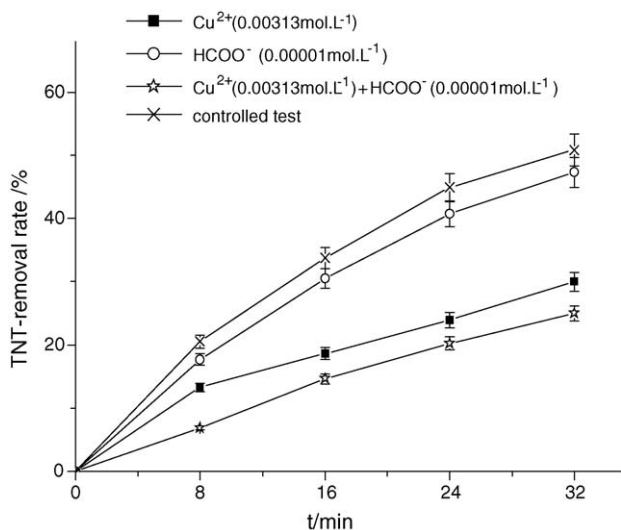


Fig. 4. Integrated effect of Cu^{2+} (0.00313 mol/L) and HCOO^- (0.00001 mol/L) on TNT-removal.

and depress about 33.8% by the presence of Cu^{2+} . Obviously, Cu^{2+} also inhibited TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$, and the inhibition is much stronger than that of HCOO^- or HCO_3^- . The integrated effect of Cu^{2+} and HCOO^- inhibited TNT-removal as the one of HCO_3^- and HCOO^- , and their integrated inhibition was between one of both and the sum of both inhibitions.

Pseudo-first-order rate constants are determined for the TNT-loss reactions in Fig. 3 by regression analysis, and shown in Table 1 too. Under the study conditions, pollutant-removal reaction rate constant of the control test is 0.02366 s^{-1} , the constants of the tests with Cu^{2+} or HCOO^- existed individually are 0.02366 and 0.01448 s^{-1} respectively, and the constant of the tests with their coexistence is 0.0045 s^{-1} . Compared with the constant of the control test, the constant lowered about 0.01730 s^{-1} for Cu^{2+} , 0.00918 s^{-1} for HCOO^- , and 0.01916 s^{-1} for their coexistence. In view of the pollutant-removal rate constant, whether HCOO^- and Cu^{2+} exist alone or coexisted, they always inhibited TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$. And their integrated inhibition is between one of both and the sum of both inhibitions. So did to the two ions with other concentrations (Fig. 4 and Table 1). The conclusion obtained in view of the constants is same as that obtained in view of the TNT-removal rates. Therefore, the integrated effect of Cu^{2+} and HCOO^- is as independent effect. That differ from the integrated effect of HCO_3^- and HCOO^- . These lighted that the integrated effects of two different ions were diverse and their mechanisms may be complex.

3.3. Integrated effect of HCOO^- and Al^{3+}

To study the integrated effect of HCOO^- and Al^{3+} on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$, the preparation of the study is described in Section 3.1 mostly, and Al^{3+} is used instead of HCO_3^- . The results of the tests are shown in Fig. 5.

Under the study conditions, compared with control test, in view of TNT-removal rate, the followings are obtained: (1) Al^{3+} here is found to exert enhanced effect on TNT-removal, and

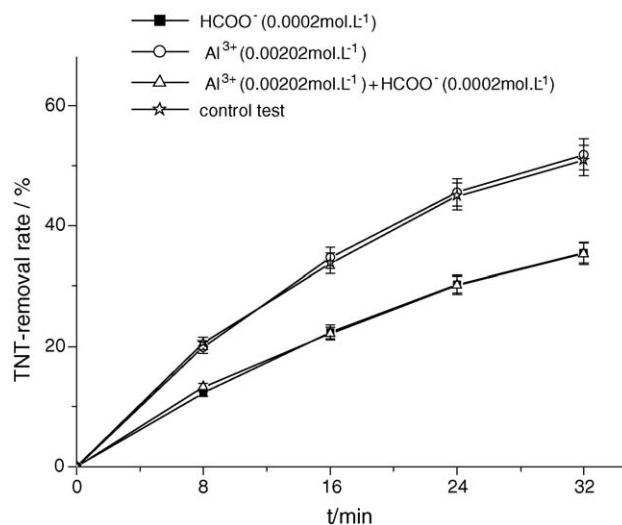


Fig. 5. Integrated effect of Al^{3+} (0.02667 mol/L) and HCOO^- (0.00002 mol/L) on TNT-removal.

against not only the effect of the selected metal ion, Cu^{2+} , but also the other selected anions, HCO_3^- and HCOO^- . These maybe suggest that one selected ion has its own effect on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$. (2) TNT-removal rate in the test with selected ions Al^{3+} and HCOO^- coexisted, is smaller than that in control test, likewise smaller than that in the test with Al^{3+} solely, but greater than that in the test with HCOO^- solely. For instance, when the tests last for 32 min, the TNT-removal rate was 50.8% in control test, 51.8 and 35.3% in the tests with Al^{3+} and HCOO^- solely respectively, 35.5% in the test with Al^{3+} and HCOO^- coexisted. Obviously, Al^{3+} accelerated the efficacy of $\text{O}_3/\text{H}_2\text{O}_2$ and diminished the inhibition of HCOO^- , thus the removal rate in the test with Al^{3+} and HCOO^- coexisted is greater than that for HCOO^- existed.

Pseudo-first-order rate constants for the TNT-loss reaction in Fig. 5 determined by regression analysis are shown in Table 1 too. The TNT-removal reaction rate constant is 0.02366 s^{-1} (K_{34}) for TNT-loss in control test, and 0.02393 s^{-1} (K_{33}) and 0.01448 s^{-1} (K_{32}) are in the tests with HCOO^- and HCO_3^- alone respectively, and 0.01598 s^{-1} (K_{31}) in the test with HCOO^- and HCO_3^- coexisted. Obviously, $(K_{34} - K_{33}) > 0$, the present of Al^{3+} is useful to TNT-removal, and enhanced the efficacy of $\text{O}_3/\text{H}_2\text{O}_2$. $(K_{34} - K_{31}) < (K_{34} - K_{32}) < 0$, and $(K_{34} - K_{31}) \approx (K_{34} - K_{32}) - 2(K_{34} - K_{33})$, exposed that their coexistence had a potential to inhibit TNT-removal. The integrated effect was smaller than that for HCOO^- , and mostly equal to HCOO^- inhibition subtracted two times of the acceleration of Al^{3+} . Therefore, the integrated effect of Al^{3+} and HCOO^- on TNT-removal by $\text{O}_3/\text{H}_2\text{O}_2$ is approximately considered as sum of their single effects, and is called the addition effect. The integrated effect was different from that for HCO_3^- and HCOO^- coexisted and Cu^{2+} and HCOO^- coexisted. These also exposed that multi-components had complicated effect on pollutant-removal by $\text{O}_3/\text{H}_2\text{O}_2$, and their mechanisms were complex.

The tests on the integrated effect of HCOO^- and Al^{3+} with other concentrations were conducted, the TNT-removal rates and reaction rate constants were shown in Fig. 6 and

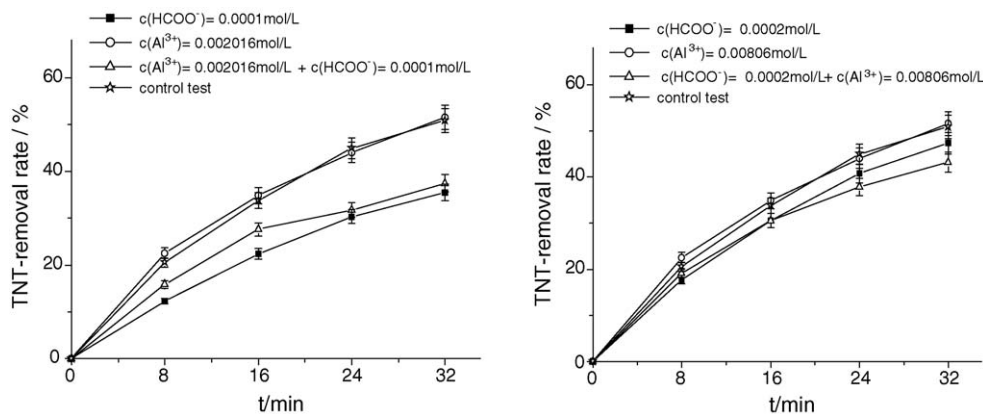


Fig. 6. Integrated effect of Al^{3+} and HCOO^- on TNT-removal under the more concentrations.

Table 1. Analyzed these data, and the same conclusions were drawn.

From all the tests above, it is found that different type of ions have different effect, and the integrated effects of the selected ions coexisted are also different. Why these phenomena are caused needs to be studied in the future.

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