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REACTION KINETICS AND THIOUREA REMOVAL BY OZONE OXIDATION

Thiourea is a toxicant which will bring some adverse effects to the public health. In the study, thiourea was degraded via ozonation process. The results show that the ozonation is an effective method to remove thiourea from wastewaters. When the ozone flow rate was $600 \text{ cm}^3 \cdot \text{min}^{-1}$, pH was 7.3, the temperature was $20 \text{ }^\circ\text{C}$, 93.97% of thiourea (200 cm^3 solution of $3 \text{ g} \cdot \text{dm}^{-3}$) could be degraded after 9 min of reaction. The reaction order of ozonation of thiourea n was 0.11, and the reaction rate constant $k = 0.4898 \text{ g}^{0.89} \cdot (\text{dm}^3)^{-0.89} \cdot \text{min}^{-1}$.

1. INTRODUCTION

Thiourea (NH_2CSNH_2), a sulfur-containing organic compound, has many industrial applications [1]. It can be used as bleach or a dye to prevent oxidation in textile industry [2]. In the pharmaceutical industry, thiourea is used for manufacturing thiourea dioxide, norsulfazole, flurouracil, niridazole, methylthiouracil, propylthiouracil, antiradon. Thiourea has also been greatly used in the agrochemistry, for producing insecticides, bactericides, herbicides, phytohormones etc. In acidic solutions, thiourea reacts with gold and silver forming soluble complexes [3]. Thiourea has always been used for selective leaching of gold and silver from printed circuit board scrap. Thiourea can act as metal rust preventer and corrosion inhibitor in clean industry, which has both sides of promoting cleaning ability and repressing erosion, it is mainly used for cleaning of high pressure boilers and tower machine equipment [4]. Thiourea and its oxides are also greatly used in sulfur chemistry [5].

Some thioureas are well known toxins. Thiourea caused liver and thyroid tumors in rats [6]. Thiourea intaken by humans may bring serious health hazard such as repressing thyroid gland and the function of blood organ, arousing central nervous sys-

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tem to paralyze or lower the breathing, even caused death. Because of its potential toxicity, thiourea must be removed from wastewater.

The removal of thiourea in nature is slow, but it is sensitive to the strong oxidizer. The common oxidants used for degradation thiourea are hydrogen peroxide, manganese dioxide, potassium permanganate, tetraethyl lead, etc., but these oxidants may have secondary pollution after the oxidation-reduction reaction with thiourea.

Recently, various authors try to use some green oxidants, for instance, Virender. Sharma studied the rates of thiourea oxidation with Fe(VI) [1], Rainer [7] et al. studied thiourea oxidation with potassium monopersulfate and Qingyu examined decomposition and oxidation kinetics of thiourea dioxide and thiourea trioxide [8]. But these experiments show some shortcomings of the processes studied such as low removal efficiency, long reaction time and complicated responding condition.

Comparing with the other thiourea treatment technologies, ozone oxidation treatment seems to be simpler, greener and more efficient. However, little work has been done on thiourea ozonation. Ozone is a strong and green oxidizer, its oxidation potential in acid solutions reaches up to 2.07 eV [9]. It can react with organic matter in water without bringing secondary pollution. Decomposition and oxidation of ozone in water is very complex, currently model of ozone decomposition proposed by Staehelin [10] is that it may produce hydroxyl radical (OH^{\bullet}) in the oxidation process. The hydroxyl radical (OH^{\bullet}) is known as one of the most active oxidants which can react with a wide variety of organic pollutants in water. Among all known oxidants, only fluorine has a higher oxidation potential than the hydroxyl radical [11]. Several kinds of technologies based on the ozone reaction have been applied to the treatment of many toxic or non-biodegradable organics in wastewater and soil. But there are few reports about the ozonation of thiourea.

In this paper, studies of thiourea in wastewater oxidation with ozone were carried out, and the best responding conditions model of thiourea ozonation was established. The main influential factors of thiourea removal by ozone oxidation was found, the kinetic model was established, the reaction order and reaction rate constant of thiourea oxidation with ozone was calculated, thus theoretical guidance could be supplied for practical application of thiourea oxidation with ozone.

2. MATERIALS AND METHODS

Chemicals. Thiourea (99.0%) was obtained from the Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. All the solutions were prepared in de-ionized water. Methanol (99.8%) was obtained from the Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other chemicals used in this experiment were A.R. grade and used as received.

Ozonation experiments. Ozonation experiments were carried out by using an ozone generator (QRC21, Institute of Plasma Physics and Chemistry of Dalian Haishi University, Dalian, China), the provided gas was pure oxygen (99.5%).

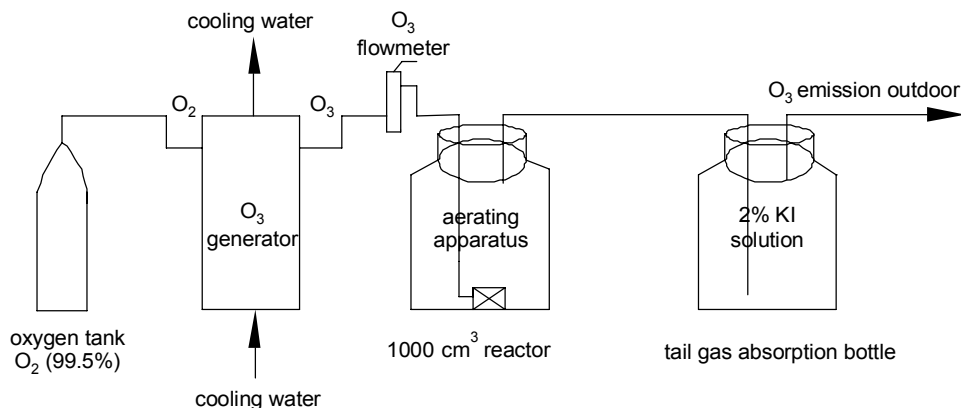


Fig. 1. Scheme of process for thiourea treatment with ozone

Batch ozonation experiments were conducted in a glass container (1000 cm³) as shown in Fig. 1. The ozone flow discharge was monitored with a flowmeter (150–1500 cm³·min⁻¹). The ozone concentrations of the solution were monitored by iodimetry [12]. Ozone was introduced into the reactor through a gas diffuser from the bottom after the reactor was filled with 200 cm³ of the thiourea solution. The mass ratio of ozone in the gas mixture at the inlet of the reactor was 4–5 wt. %, and 0.1–1.1 wt. % at the outlet of the reactor at various flow rates and reaction times.

When the ozonation processes are starting, first, turn on the O₃ generator, wait 10 min until the production of ozone is stable. Turn on the gas valve, then the ozone can go through the flowmeter into the 1000 cm³ reactor. In the reactor, there is a gas diffuser which can break the ozone gas to small bubbles. Part of the ozone reacts with the reactants, the unreacted ozone comes into the tail gas absorption bottle and will be absorbed by KI solution.

Analysis of samples. The chromatographic system used in this study was Shimadzu LC-2010 AHT HPLC, the separation was performed at 30 °C in a shim-pak·C18 column (4 μm, 416 nm × 25 nm), 40% methanol in water as mobile phase. A UV-VIS detector was used to detect thiourea at 242 nm. The injection volume of each sample extract was 10 μl, the appearance time of thiourea was about in 3.2 min (Fig. 2).

The measure of ozone concentration in pure water is used according to e People's Republic of China Urban Construction Industry Standard, CJ/T 3028.2-94. Ozone reacting with KI (20%) can free iodine out, acid treatment is used after sampling, then Na₂S₂O₃ (0.1000 mol·dm⁻³), a standard solution for titrant, and starch solution is used

for indicator. The amount of ozone in water can be calculated according to the consumption of $\text{Na}_2\text{S}_2\text{O}_3$ ($0.1000 \text{ mol}\cdot\text{dm}^{-3}$) standard solution.

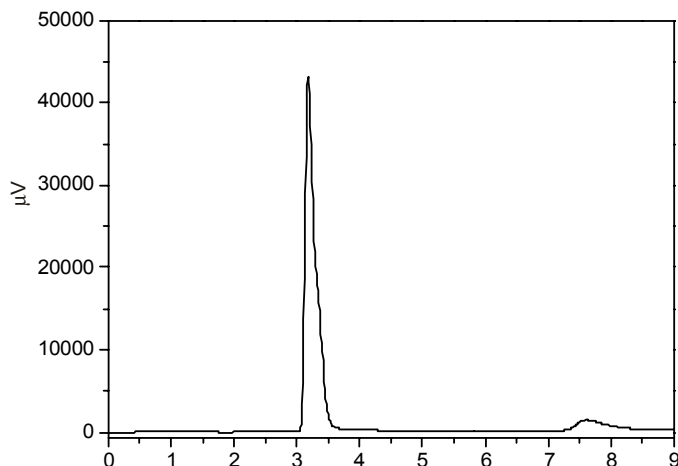
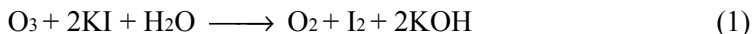


Fig. 2. The HPLC chromatogram map of thiourea standard solution

The reaction equations and computational formula are as follows:



$$c_{\text{O}_3} = \frac{2400AB}{V_0} \quad [\text{mg}/\text{dm}^{-3}] \quad (3)$$

where V_0 is the volume of water sample (1000 cm^3), A – the consumption of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution (cm^3), B – the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution ($0.1000 \text{ mol}\cdot\text{dm}^{-3}$) c_{O_3} – ozone concentration ($\text{mg}\cdot\text{dm}^{-3}$).

Process parameters. The reaction time, ozone flow rate, pH, temperature were examined at the concentration of thiourea solution of $3 \text{ g}\cdot\text{dm}^{-3}$. In each experiment, a single factor was studied, while other factors were kept constant. Its most appropriate value was determined after one experiment. The reaction times were 1, 2, 3, 6, 9, 12 and 15 min. The ozone flow rate was $600 \text{ cm}^3\cdot\text{min}^{-1}$, the reaction pH corresponded to initial pH of the thiourea solution and the temperature was $20 \text{ }^\circ\text{C}$. Ozone flow rates were 300, 450, 600, 750 and $900 \text{ cm}^3\cdot\text{min}^{-1}$. The initial pH of the solutions were 4.12, 6.04, 8.02, 10.11 and 12.09. The temperatures were 10, 20, 30, 40 and $50 \text{ }^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. EFFECTS OF REACTION TIME

The effect of the treatment time on thiourea removal with ozone oxidation was studied. Figure 3 shows the effect of reaction time on the thiourea removal by ozone oxidation. It is evident that the removal rate of thiourea increased as the treatment time increased. As the reaction time increased, the amount of ozone increased as well but the amount of thiourea was constant; thus the longer the time, the higher removal rate of the thiourea. When the ozonation time increased from 1 min to 12 min, thiourea removal rates were 5.34%, 26.32%, 53.12%, 82.87%, 93.97% and eventually 97.84%. The removal rate changed little when the reaction time increased more than 9 min. When most of thiourea was removed, the accumulating intermediate products could consume some ozone, that maybe due the removal curve turned smoothly. When the ozonation time reached up to 15 min, the thiourea matter could not be detected by HPLC.

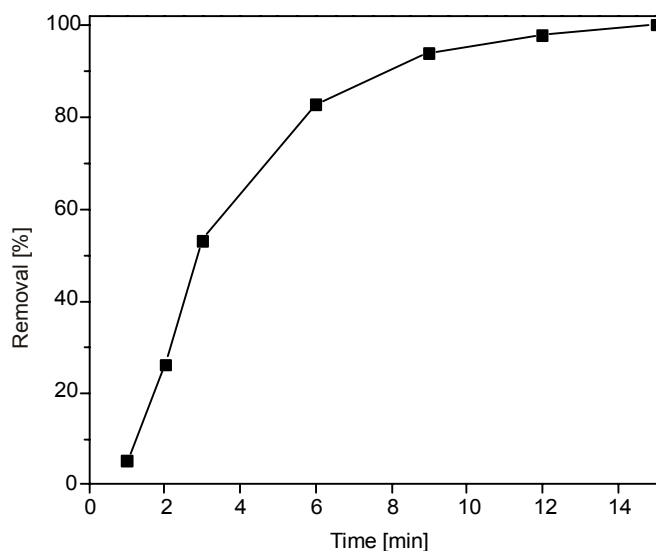


Fig. 3. The removal values of thiourea with O_3 oxidation at various reaction times

With different reaction times, the quantities of reacted thiourea were 0.032, 0.158, 0.319, 0.497, 0.564, 0.587, 0.599 g, and the ratio of ozone dose with the removal of thiourea were 1.34, 0.54, 0.40, 0.52, 0.69, 0.88, and 1.67 g/g. When the reaction times were 2, 3 and 6 min, the ozone oxidation efficiency was high but the thiourea removal rate was relatively low. When the thiourea removal rate was higher than 90% in 9 min, the ozone oxidation efficiency was the best, comparing the removal rate factor and economic factor, the best reaction time was 9 min.

3.2. EFFECTS OF OZONE FLOW RATE

The flow rate of ozone is an important operating factor of thiourea oxidation. Figure 4 shows the effect of ozone flow rate on thiourea reductions. The removal rate of thiourea increased as the ozone flow rate increased. At the initial stage, when the ozone flow rate changed from $300 \text{ cm}^3 \cdot \text{min}^{-1}$ to $600 \text{ cm}^3 \cdot \text{min}^{-1}$, the curve increased abruptly, then along with the ozone flow rate increase, the thiourea removal trend became smoother.

When the flow rates were $300, 450, 600, 750$ and $900 \text{ cm}^3 \cdot \text{min}^{-1}$, the ozone concentrations at the outlet of the reactor were $3.86, 4.90, 5.84, 6.03$ and $6.68 \text{ mg} \cdot \text{dm}^{-3}$, respectively. When the ozone flow rate was $600 \text{ cm}^3 \cdot \text{min}^{-1}$, the removal rate of thiourea reached to 93.97% . Keeping on increasing the ozone flow rate, the removal rate changed little, the removal rates were 94.76% and 96.98% when the ozone flow rates were $750 \text{ cm}^3 \cdot \text{min}^{-1}$ and $900 \text{ cm}^3 \cdot \text{min}^{-1}$, respectively. There may be three reasons for this phenomenon. First, thiourea acts as an electron donor and is oxidized with ozone directly, which causes its rapid removal when the ozone flow increases in the beginning. Secondly, the increase in ozone flow rate above $600 \text{ cm}^3 \cdot \text{min}^{-1}$ did not increase much the concentrations of ozone in solution. Thirdly, the more thiourea reacts with ozone, the more intermediate products are created, thus, part of ozone is consumed by the intermediate products, which makes the curve more smooth after the ozone flow rate raised up to $600 \text{ cm}^3 \cdot \text{min}^{-1}$. Comparing the removal factor and economic factor, the best ozone flow rate is $600 \text{ cm}^3 \cdot \text{min}^{-1}$.

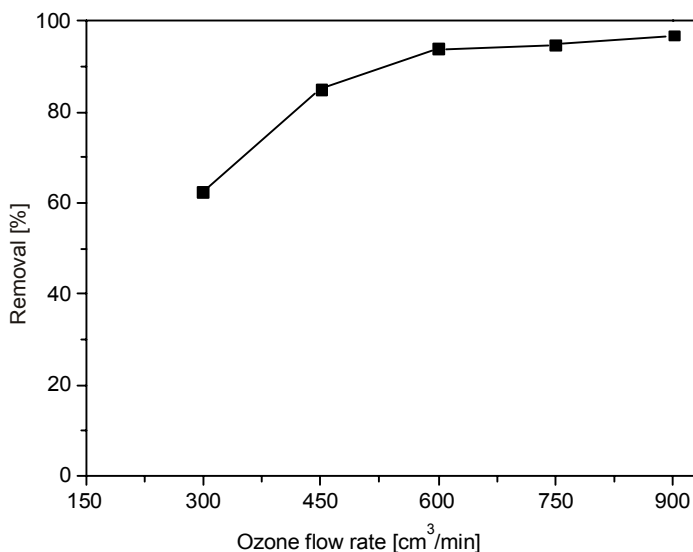


Fig. 4. The removal values of thiourea with O_3 oxidation at various O_3 flow rates

3.3. EFFECTS OF INITIAL pH OF THE SOLUTION

1 M HCl and 1 M NaOH were used to adjust pH of the solutions. Figure 5 shows the removal rates of thiourea oxidized with O_3 at various pH. For pH changes from 4 to 12, the removal rates of thiourea are at similar, which shows that thiourea ozonation roughly depends on pH. Ozone reacts with organics in water directly and in indirect reaction through hydroxyl radicals which are produced by ozone [13]. Under the usual conditions, the direct reaction is selective with organic pollutant, but the indirect reaction is non-selective. For the oxidation-reduction potential of HO^\bullet radical up to 2.80 V, its reaction rate constant with the overwhelming majority of organics is 10^8 – 10^{10} $dm^3 \cdot (mol \cdot s)^{-1}$ [14]. At low pH, ozone exclusively reacts with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic or dipolar addition (i.e., direct pathway) [15]. On the other hand, at standard conditions, ozone decomposes hydroxyl radicals, which are highly oxidizing species [16] reacting in a non-selective way with a wide range of organic and inorganic compounds in water (i.e. indirect ozonation) [17]. Normally, under acidic conditions (pH < 4) the direct ozonation dominates, in the range of pH 4–9 both are present, and indirect reaction prevails when pH > 9 [18].

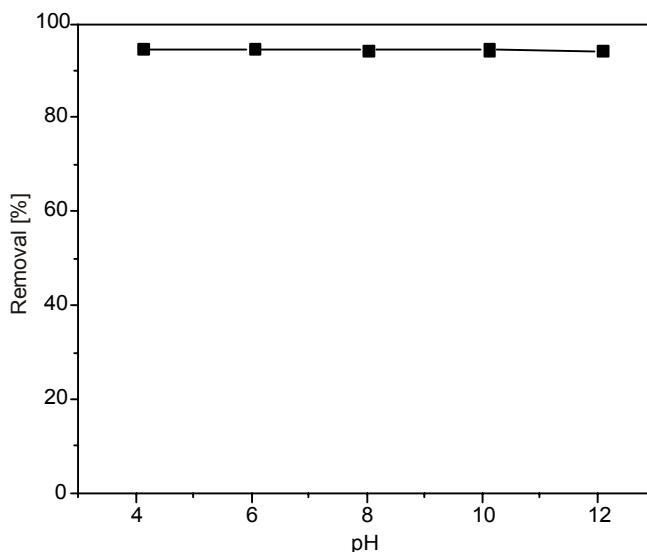


Fig. 5. The removal rates of thiourea with O_3 oxidation at various pH

Thiourea has specific functional groups which can react exclusively with ozone, thus, at low pH, ozone selectively oxidizes thiourea. OH^- groups can accelerate decaying of ozone to form HO^\bullet radicals, which can react with thiourea non-selectively and immediately ($k = 10^8$ – 10^{11} $M^{-1} \cdot s^{-1}$) [18]. pH of thiourea standard solution with various

concentrations are about the same, ca. 7.3. After oxidation, pH ranged from 3.2 to 3.9, pointing to the fact that some acids are produced in the process. These acids may consume OH^- ions in the solution. Moreover, CO_2 as the removal product dissolves in the solution producing CO_3^{2-} and HCO_3^- , and the two anions can eliminate hydroxyl radicals [19]. Maybe due to the above reasons, the initial pH has little influence in the process of thiourea ozonation. In practice, the best pH value is initial pH of the solution.

3.4. EFFECTS OF TEMPERATURE OF THE SOLUTION

Figure 6 shows the results of thiourea oxidation with ozone at various temperatures. It indicates that temperature, similarly as pH, roughly influenced thiourea ozonation.

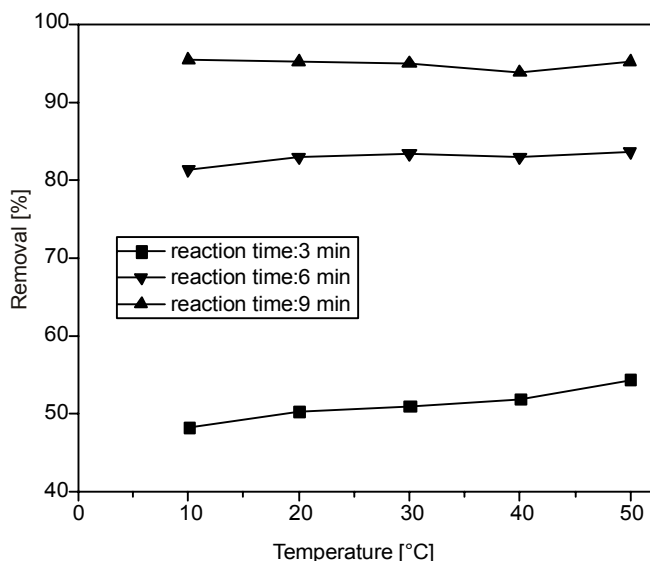


Fig. 6. The removal values of thiourea oxidized with O_3 at various times and temperatures

When the reaction time was 3 min, the effect of temperature in thiourea removal was little more visible than for 6 and 9 min, but still slight. As the pH factor has no influence on thiourea ozonation, it shows that the ozonation of thiourea is a main direct reaction. Although increase in the temperature can increase the reaction rate constant and the percent of the activated molecules, it also increases Henry's constant. Ozone easily escapes from the solution and its concentration in liquid phase decreases which causes decrease in the reaction rate. Due to these two conflicting factors, the influence of temperature on thiourea ozonation is ambiguous. However, increase in

temperature can also accelerate the attenuation of free hydroxyl radicals [20]. In practice, taking the normal temperature in thiourea ozonation process is economical.

3.5. REACTION KINETICS OF THIOUREA OXIDATION WITH OZONE

The half-life method is used to calculate the reaction order n and the reaction rate constant k [21]. In general, the reaction of ozone oxidation is a second order reaction, with respect to the oxidant (ozone or HO \cdot) and the infectant M are it is of the first order [22, 23]. For $n \neq 1$, we have:

$$t_{\theta} = \frac{1}{(n-1)k} \left[\frac{1}{\theta^{n-1}} - 1 \right] \frac{1}{c_0^{n-1}} \quad (1)$$

where θ is the rate of the reaction times, c_0 is the initial concentration of thiourea. Assuming that I is

$$I = \frac{1}{(n-1)k} \left[\frac{1}{\theta^{n-1}} - 1 \right] \quad (2)$$

we obtain

$$t_{\theta} = I \frac{1}{c_0^{n-1}} \quad (3)$$

and

$$\ln t_{\theta} = \ln I + (1-n) \ln c_0 \quad (4)$$

From the dependence of $\ln t_{\theta}$ on c_0 , the reaction order n can be calculated. According to the half-life method, if $\theta = 1/2$,

$$I = \frac{2^{n-1} - 1}{(n-1)k} \quad (5)$$

from the intercept of the $\ln t_{\theta} - \ln c_0$ fitting, the reaction rate constant k can be calculated.

The conditions of the experiment were as follows: initial pH of the solution was 7.3, temperature was 20 °C, the ozone flow rate was 600 cm 3 .min $^{-1}$, the initial concentrations of thiourea solution were 1, 2, 3, 4 and 5 g.dm $^{-3}$ the reaction times were 1,

2, 3, 4 and 5 min. After further processing the experimental data, the dependence of $-\ln(c/c_0)$ on O_3 oxidation time t at various initial thiourea concentrations can be obtained (Fig. 7).

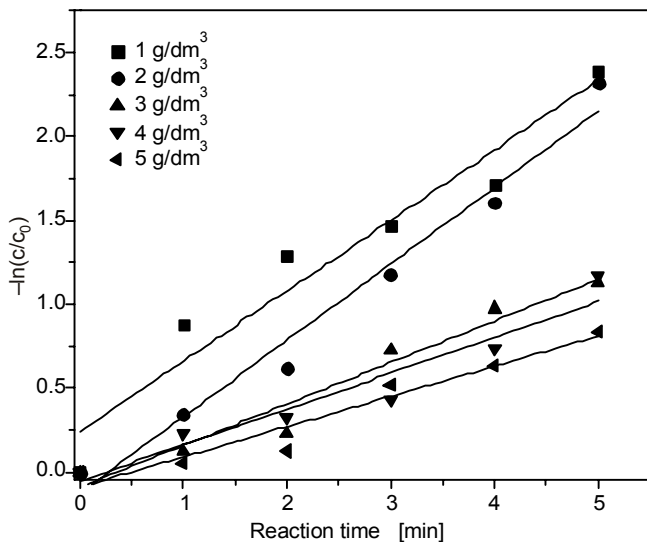


Fig. 7. Dependences of $-\ln(c/c_0)$ on O_3 oxidation time at various initial thiourea concentrations

Figure 7 shows that the slope of the linear dependences decreases as the concentrations of thiourea increases. In Table 1, the data on the reaction kinetics of thiourea ozonation has been collected

Table.1. Data on reaction kinetics of O_3 oxidation with thiourea

c_0 [g·dm ⁻³]	Fitting the equation of $-\ln(c/c_0)$ and t	Correlation coefficient (R^2)	$t_{1/2}$ [min]	$\ln t_{1/2}$	$\ln c_0$
1	$y = 0.4182x + 0.2455$	0.9404	1.0704	0.0680	0
2	$y = 0.4555x - 0.1263$	0.9777	1.7987	0.5871	0.6931
3	$y = 0.2472x - 0.0892$	0.9550	3.1642	1.1519	1.0986
4	$y = 0.2139x - 0.0553$	0.9254	3.4984	1.2523	1.3863
5	$y = 0.1801x - 0.0905$	0.9400	4.3503	1.4702	1.6094

It is evident from Eq. (4) that $\ln c_0$ has a positive correlation with $\ln t_{1/2}$. According to Table 1, dependence of $\ln t_{1/2}$ on $\ln c_0$ has been plotted (Fig. 8), the equation of the fitting line is $y = 0.89x + 0.0538$, and the correlation coefficient R^2 is 0.9822. From Equations (4), (5), $n = 0.11$ and $k = 0.4898 \text{ g}^{0.89} \cdot (\text{dm}^3)^{-0.89} \cdot \text{min}^{-1}$ have been calculated. The results obtained indicate that with increasing concentration of thiourea reaction rate increases and the reaction rate of thiourea with ozone oxidation is very fast.

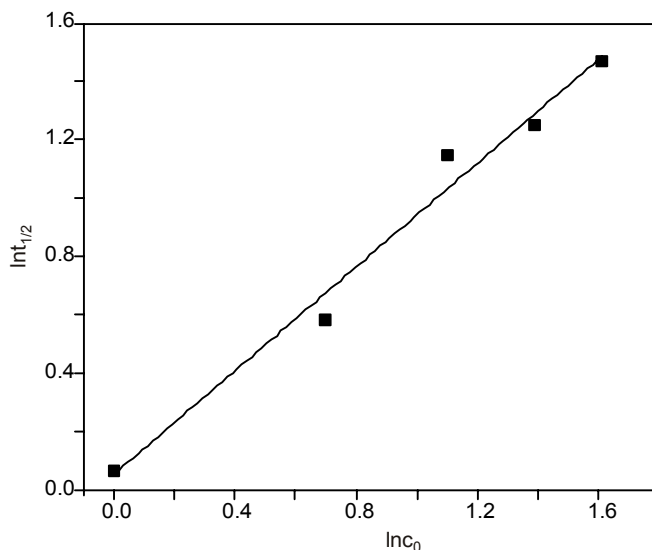


Fig. 8. Relationship of $\ln t_{1/2}$ on $\ln c_0$

4. CONCLUSIONS

- Ozone has a remarkable influence on the removal of thiourea. When the flow rate of ozone is $600 \text{ cm}^3 \cdot \text{min}^{-1}$, pH = 7.3, the reaction temperature = $20 \text{ }^\circ\text{C}$, the reaction time = 6 min, the removal rate is 82.91%, if the oxidization time is 9 min, the removal rate could reach 93.97%.

- The increase of reaction time and ozone concentration can increase the removal of thiourea. The removal of thiourea with ozone is roughly independent of pH and temperature.

- The reaction order of thiourea ozonation n is 0.11 and the reaction rate constant k is $0.4898 \text{ g}^{0.89} \cdot (\text{dm}^3)^{-0.89} \cdot \text{min}^{-1}$, which indicates that ozone has a great effect on the removal of thiourea.

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