

## Kinetics of Chlorine Dioxide Oxidation of Benzidine in Wastewater

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(Received: 13 December 2011;

Accepted: 2 August 2012)

AJC-11908

Reaction kinetics of benzidine oxidation with  $\text{ClO}_2$  in the wastewater were investigated systematically by detecting concentrations of benzidine with HPLC at regular intervals. The results showed that the reaction was first-order with respect to both  $\text{ClO}_2$  and benzidine and the entire reaction was of second-order. Under condition of pH 6.5 and water temperature 298 K, the second-order reaction rate constant  $k$  was  $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$ . The reaction activation energy was  $51.1 \text{ kJ mol}^{-1}$ , revealing that the reaction could take place under usual water treatment conditions. The rate constants increased with the reaction pH increasing, then decreased. Hydrazobenzene, azobenzene and *para*-benzoquinone were detected by GC-MS as intermediates of the free benzidine- $\text{ClO}_2$  reaction.

**Key Words:** Chlorine dioxide, Benzidine, Kinetics, Intermediates.

### INTRODUCTION

Benzidine derivatives, is a kind of non-natural organic pollutant, could be generated from tannery wastewaters containing large amounts of dyes and pigments after illumination, heating or biological treatment. The compounds are highly toxic, carcinogenic, mutagenic, teratogenic, stable in water, almost non-biodegradable and irremovable with conventional water treatment technology, thus internationally recognized as priority pollutants<sup>1</sup>. It is essential that benzidines in tannery wastewater are removed. Therefore, it is of importance to investigate how to better remove benzidines from wastewater to protect human health and the environment. There are only some preliminary research works of benzidine derivatives treatment technology by far and the reaction kinetics still remained unclear.

Chlorine dioxide ( $\text{ClO}_2$ ) is a strong oxidant that exhibit good performance in both organic and inorganic pollutant removal. Furthermore, it hardly forms any harmful organic halide such as trihalomethanes (THMs) while reacting with organic compounds in water<sup>2</sup>. Thus,  $\text{ClO}_2$  is widely used in drinking water and industrial wastewater oxidation treatments. Chlorine dioxide oxidation method is currently accepted as the most prominent technology for water treatment. However, the reports about benzidine treatment with the method are limited. In this work,  $\text{ClO}_2$  oxidation method was applied to clarify the oxidation kinetics of benzidine removal in water.

### EXPERIMENTAL

Benzidine (AR), diluted from solution of benzidine dissolved in methanol with dichloromethane; chlorine dioxide, generated from  $\text{NaClO}_2/\text{K}_2\text{S}_2\text{O}_8$  in 10 %  $\text{H}_2\text{SO}_4$ .  $\text{ClO}_2$  of above 99.8 % purity was degassed before resolved in cold water and restored in sealed brown bottle and dark place as stock solution. The  $\text{ClO}_2$  solution was calibrated and serially diluted before use.

1100 Series HPLC (Agilent Co., USA); 6890-5973 GC-MS (Agilent Co., USA); HJ-6 heating magnetic stirrer (Hongkai Instrument Co., Jiangsu, China); ZD-2 potentiometric titrimeter (Shanghai Leici Analytical Instrument Co., Shanghai, China).

**Methods:** pH value and temperature of the system were kept constant during the reaction procedure. pH value was controlled by a pH-stat apparatus (consists of 3, 4 and 5 in Fig. 1). Briefly, pH sensor was used to adjust the added acid and base solution volume (diluted  $\text{H}_2\text{SO}_4$  and NaOH solution) during reaction to maintain the pH value, heating system of the magnetic stirrer was used to control the temperature within  $\pm 0.1 \text{ }^\circ\text{C}$ .

The reaction was carried out in dark and constant temperature. pH values of  $\text{ClO}_2$  solution, benzidine solution and  $\text{Na}_2\text{S}_2\text{O}_3$  solution were adjusted with diluted  $\text{H}_2\text{SO}_4$  (HCl will cause  $\text{Cl}^-$  contamination) before the experiments. Appropriate volume of  $\text{ClO}_2$  was added to benzidine solution for oxidation reaction before turn-on the magnetic stirrer.  $0.05 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  was used as terminating reagent after reaction.

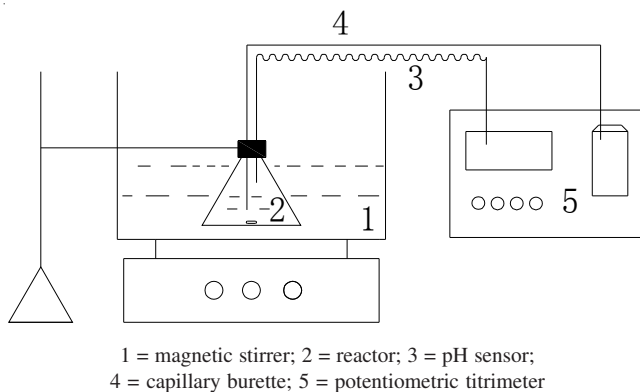


Fig. 1. Experimental equipment chat on benzidine oxidized by  $\text{ClO}_2$

### Analytical methods

**Determination of  $\text{ClO}_2$  concentration:** Concentration of  $\text{ClO}_2$  was determined by successive iodimetric technique<sup>3</sup>.

**Benzidine determination with HPLC:** The reacted solution was transferred to 100 mL separating funnel, extracted by 5 mL dichloromethane for three times. The extract was dehydrated and concentrated before filtrated with 0.45  $\mu\text{m}$  filter membrane. A mini-injector was served for sampling and the concentration of the residual benzidine was determined by means of HPLC. HPLC parameters: methanol:water (85:15 v/v); Hypersil ODS column, 250 mm long, 4.6 mm diameter; flow rate: 1.0  $\text{mL min}^{-1}$ ; sample volume: 5  $\mu\text{L}$ ; column pressure: 5.00 MPa; G1314A ultraviolet detector wavelength: 254 nm.

**Reaction intermediates identification with GC-MS:** The reacted solution after colour interferences removal was transferred to 100 mL separating funnel, extracted by 5 mL dichloromethane for three times. The extract was dehydrated and concentrated to 1 mL, then subjected to GC-MS determination. GC-MS parameters: GC silica capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ); temperature program: 323 K (3 min)  $\rightarrow$  5 K  $\text{min}^{-1}$   $\rightarrow$  473 K (2 min)  $\rightarrow$  10 K  $\text{min}^{-1}$   $\rightarrow$  553 K (5 min); carrier gas: high purity helium; MS electron ionization (EI): 70 eV; scanning range: 35-400; detector voltage: 220 V.

## RESULTS AND DISCUSSION

### Kinetics of the reaction between $\text{ClO}_2$ and benzidine

**Reaction order of benzidine:** With benzidine (BD) initial concentration ( $[\text{BD}]_0$ ) of 0.25  $\text{mmol L}^{-1}$ , 298 K and pH 6.5, plot of  $-\ln(C_t/C_0)$  ( $C_t$  - the concentration of benzidine at the time  $t$ ,  $C_0$  - the initial concentration of benzidine) vs.  $t$  (time) was obtained and shown in Fig. 2. A good linearity was obtained between  $-\ln(C_t/C_0)$  and  $t$ , illustrating that the reaction was the first-order with respect to benzidine.

**Reaction order of  $\text{ClO}_2$ :** The slope in Fig. 2 was the apparent rate constant  $k'$  of the reaction. A linear equation of  $y = -3.3457 + 0.9788x$  ( $R = 0.9788$ ) was obtained between  $\ln k'$  and  $\ln[\text{ClO}_2]_0$  as shown in Fig. 3 and the slope was the order of  $\text{ClO}_2$  in the reaction, namely, approximate first order.

**Determination of the second order reaction rate constant  $k$ :** Based on the above experimental results, oxidation reaction of benzidine with  $\text{ClO}_2$  could be characterized as follows:

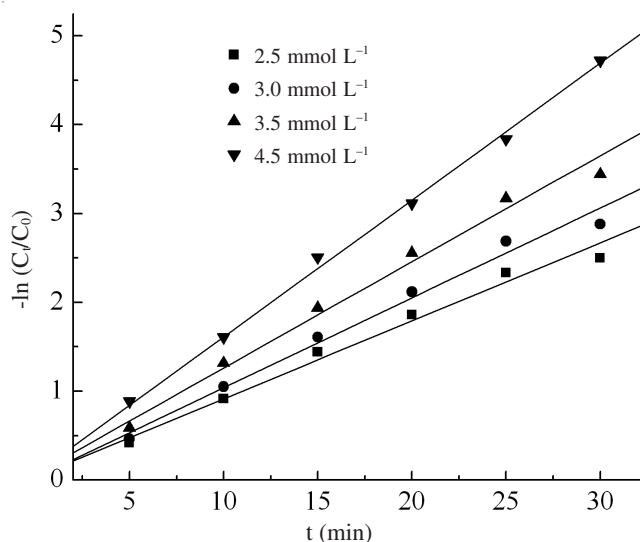


Fig. 2. Relation between  $-\ln(C_t/C_0)$  and time 298 K; pH: 6.5;  $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$ ;  $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$  (■), 3.0  $\text{mmol L}^{-1}$  (●), 3.5  $\text{mmol L}^{-1}$  (▲), 4.5  $\text{mmol L}^{-1}$  (▼)

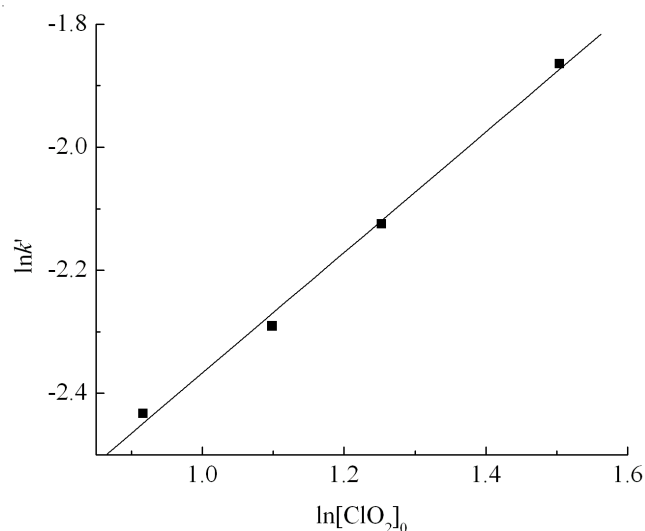


Fig. 3. Relation between  $\ln k'$  and  $\ln[\text{ClO}_2]_0$

$$-\frac{d[\text{BD}]}{dt} = k[\text{BD}][\text{ClO}_2] \quad (\text{where BD is benzidine}) \quad (1)$$

With respect to the initial condition,  $t = 0$ ,  $[\text{BD}] = [\text{BD}]_0$ , it can be integrated as:

$$\ln \frac{[\text{BD}]_0}{[\text{BD}]} = k \int_0^t [\text{ClO}_2] dt \quad (2)$$

$[\text{ClO}_2]_0 \gg [\text{BD}]_0$ , so the  $\text{ClO}_2$  concentration could be treat as a constant, i.e.:

$$\ln \frac{[\text{BD}]_0}{[\text{BD}]} = k[\text{ClO}_2]t \quad (3)$$

$$k = k' / [\text{ClO}_2]_0 \quad (4)$$

where  $k'$  is apparent rate constant,  $k$  is second order reaction rate constant.

Under condition of 298 K and pH 6.5, second order rate constant  $k$  of reaction was calculated as an average value of  $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$  from eqn. 4.

**Effect of temperature on reaction rate constant:** Under condition of  $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$ ,  $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$  and pH 6.5, second order reaction rate constants  $k$  were  $2.833 \times 10^{-4}$ ,  $3.883 \times 10^{-4}$ ,  $5.850 \times 10^{-4}$  and  $7.817 \times 10^{-4} \text{ L (mmol s)}^{-1}$  with water temperature  $T = 288, 293, 298$  and  $303 \text{ K}$ , respectively. As shown in Fig. 4, a linear equation of  $\ln k = 17.245 - 6146.6 (1/T)$  ( $R^2 = 0.9902$ ) was obtained, which means the relation between reaction rate constant  $k$  and absolute temperature is in good accordance with Arrhenius empirical equation. The slope of the equation is  $-E_a/R$  and intercept is  $\ln A$ . The reaction activation energy was calculated as  $E_a = 51102.8 \text{ J mol}^{-1} \approx 51.1 \text{ kJ mol}^{-1}$ ,  $A = 5.143 \times 10^5 \text{ L (mmol s)}^{-1}$ . Apparently,  $\text{ClO}_2$  oxidation of benzidine could proceed under common water treatment conditions.

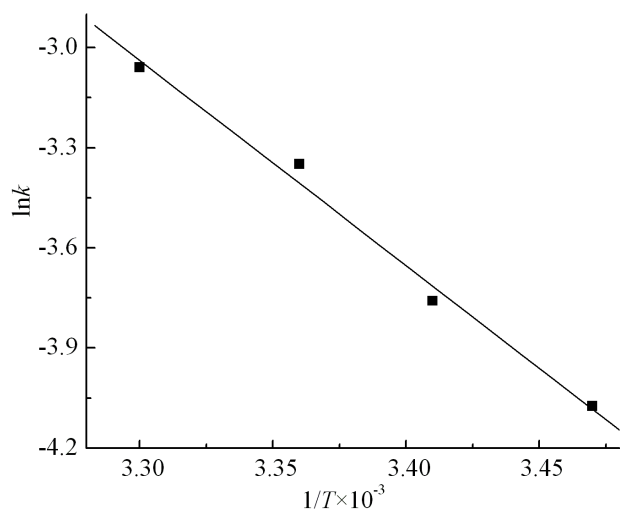


Fig. 4. Relation between rate constant and temperature. pH: 6.5;  $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$ ;  $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$ ; Temp. 288 K, 293 K, 298 K, 303 K

**Effect of pH value on reaction rate constant:** The solution pH changes not only the oxidation potential of  $\text{ClO}_2$ , but also presence state of benzidine in water as well. Thus, pH is a key factor affecting reaction rate. Under condition of  $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$ ,  $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$  and 298 K, second order reaction rate constants  $k$  were  $1.383 \times 10^{-4}$ ,  $3.667 \times 10^{-4}$ ,  $5.850 \times 10^{-4}$ ,  $5.167 \times 10^{-4}$  and  $3.283 \times 10^{-4} \text{ L (mmol s)}^{-1}$  with pH value of 3.0, 4.66, 6.5, 8.0 and 9.5, respectively.

As shown in Fig. 5, second order reaction rate constant  $k$  was increased with the increase of pH value to pH 9.5 and then decreased down. The reaction rate constant  $k$  was affected by oxidation potential of  $\text{ClO}_2$  as well as presence state of benzidine. The oxidation potential of  $\text{ClO}_2$  was the predominant factor affecting the reaction rate constant  $k$  while presence state of benzidine remained unchanged. With pH value higher than 9, oxidation potential was decreased due to disproportionation reaction of  $\text{ClO}_2^4$ .

**Reaction intermediates identification of  $\text{ClO}_2$  oxidation of benzidine:** The colourless benzidine solution turned to light red gradually, then pale yellow slowly and almost colourless finally during the oxidation reaction at pH 6.5, which meant a series coloured intermediates generated during the oxidation reaction<sup>5,6</sup>.

Since it was found that the reaction proceeded quickly and finished in about 60 min, some sampling time, such as

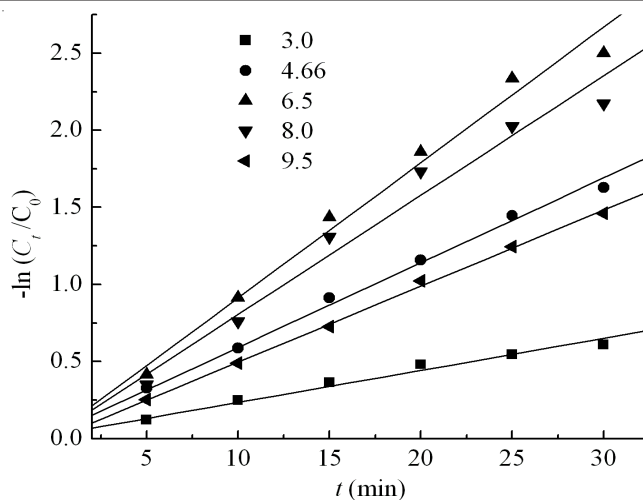


Fig. 5. Relation between  $-\ln(C_t/C_0)$  and time under different reaction pH; 298K;  $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$ ;  $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$ ; pH = 3.0 (■), 4.66 (●), 6.5 (▲), 8.0 (▼), 9.5 (◄)

0, 5, 18 and 60 min, were chosen to reveal the intermediates. Typical GC patterns of the reaction solution intermediates at different time, containing the residual benzidine and products formed, are provided as Fig. 6(a) to (d), respectively, where compounds related to the starting pollutant show retention time in the range from 6.27 to 21.98 min. Prior to the commencement of oxidation, the first GC chromatogram of the benzidine solution was collected [Fig. 6(a)]. This shows a clear trace at the retention time of 21.21 min. After reacted with  $\text{ClO}_2$  for 5 min [Fig. 6(b)], the GC analysis revealed that the concentration of benzidine in the solution decreased dramatically and two new peaks appeared with retention time at 9.14 and 12.45 min, respectively. At 18 min of the reaction proceeded [Fig. 6(c)], The peak of the benzidine further decreased and the peak of the product at 9.14 min increased with the decrease at 12.45 min. At the termination of the procedure, 60 min, the peak of benzidine decreased continuously with time, while another new strong peak appeared with retention time at 6.42 min, but there were no other peaks that appeared [Fig. 6(d)].

It is evident that there are three intermediates mainly formed during the reaction and they were identified by EI mass spectra through above 95 % match with the NIST 02L MS library. The results reveals that the three intermediates are hydrazobenzene, azobenzene and *para*-benzoquinone. Furthermore, the identification of the products were established from a comparison of the GC-MS data with that of an authentic sample.

## Conclusion

The reaction between  $\text{ClO}_2$  and benzidine was first-order with respect to both  $\text{ClO}_2$  and benzidine and the entire reaction was of second-order. Under condition of pH 6.5 and 298 K, the second-order reaction rate constant  $k$  was  $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$ . The rate constant  $k$  had the same change with the reaction temperature. The reaction activation energy was 51.1  $\text{kJ mol}^{-1}$ , revealing that the reaction could take place under usual water treatment conditions. The rate constant  $k$  increased with the reaction pH increasing, then decreased. Sequences

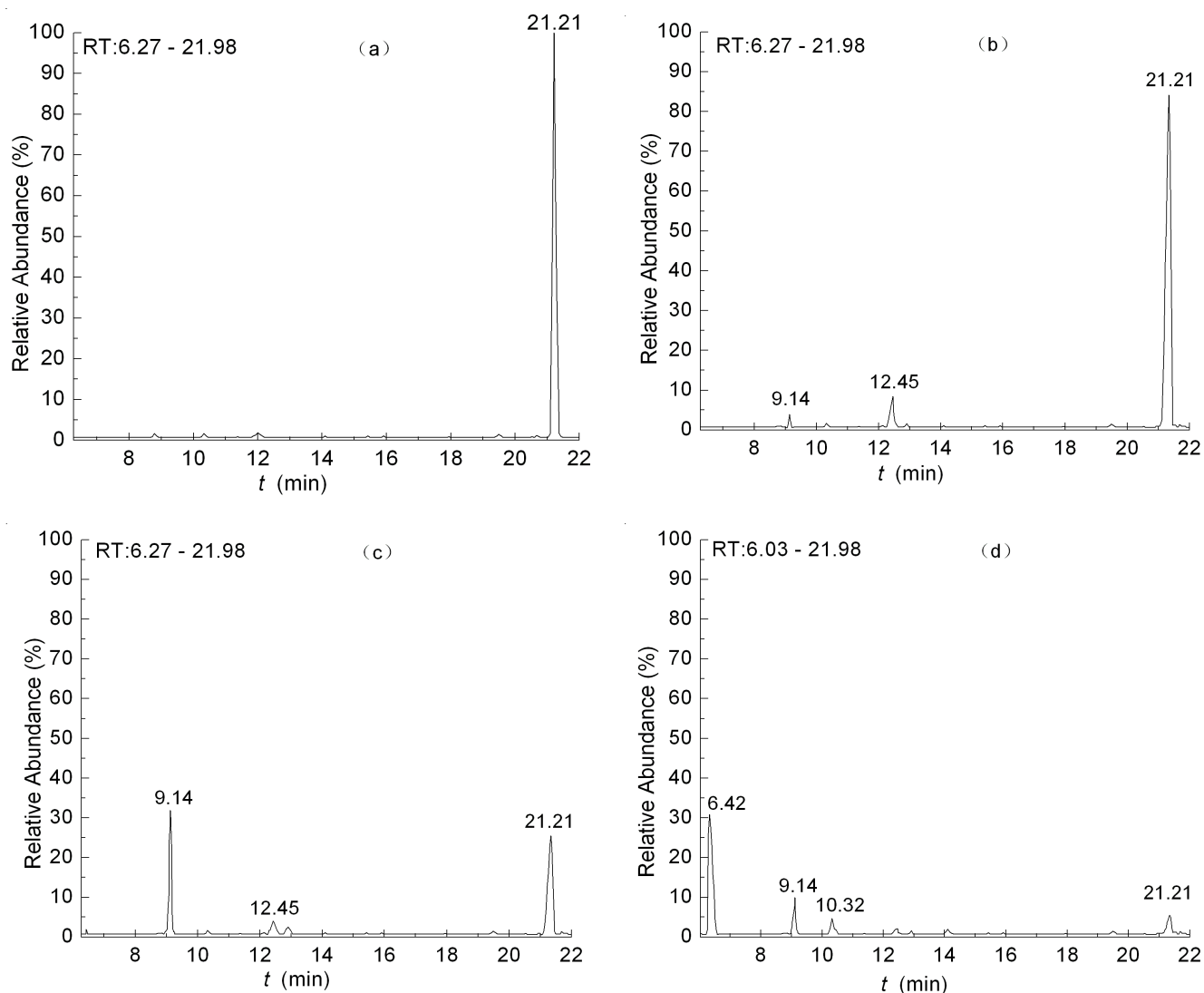


Fig. 6. Ion current chromatogram of benzidine reacted with  $\text{ClO}_2$  under different time at pH 6.5; Reaction time: (a) 0 min; (b) 5 min; (c) 18 min; (d) 60 min

of the main intermediates of the free benzidine- $\text{ClO}_2$  reaction were hydrazobenzene, azobenzene and *para*-benzoquinone by GC-MS technique.

#### ACKNOWLEDGEMENTS

This research work was financially supported by the Foundation for University Key Teacher of Heilongjiang Province of China (Item No. 1252G071) and Youth Foundation of Qiqihar University (Item No. 2010K-Z09).

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