Experimental Study on Chemical Reduction Method to Remove the Chlorate Ions in the Water

Xiuguo Lu*, Jianju Duan and Yue Deng

School of Civil Engineer and Architecture, East China Jiaotong University, Nanchang, 330013, China

Abstract: Study on using ascorbic acid and ferrous reduction method to removal the chlorate ions (ClO₃⁻) in the water. The results show that 100 mL 3.06 mg/L of ClO₃⁻ in ascorbic acid and ClO₃⁻ quality ratio 7.19, pH =6.2,35°C, the reaction time of for 15 min, the removal rate was 100%. And ferrous reduction method to remove 100mL 3.06 mg/L of ClO₃⁻ in pH = 6.2, Fe²⁺ and ClO₃⁻ quality ratio 1.79, 30°C for 30min, the removal rate was 51%.

Keywords: Ascorbic acid, ferrous ion, chlorate ions.

1. INTRODUCTION

Since found that the traditional liquid chlorine disinfection has "three to" function will produce organic halogen content, chlorine dioxide was elected the drinking water disinfection substitutes [1, 2], chlorine dioxide is a kind of strong oxidizer, sterilization effect is good, almost don’t produce in the process of disinfection has "three" effect of halogenated organic content [3]. But recent studies have found that chlorine dioxide disinfection produces ClO₃⁻ disinfection by-products. ClO₃⁻ toxicological effect is bigger, it can cause hemolytic anemia, and denaturation of hemoglobin for animal blood, may inhibit the role of serum thyroxine, cause fetal cerebellum weight descent, neurobehavioral function slowly or cell number; Will also cause the loss of infant brain weight side effects, etc [4, 5]. Our country "drinking water health standards" GB5749-2006 regulation in drinking water ClO₃⁻ ≤0.7 mg/L [6]. This article uses the method of chemical reduction of water ClO₃⁻ remove the experiments.

2. INTRODUCTION OF THE EXPERIMENT

2.1. Instruments and Reagents

Instrument: Electronic analytical balance; HACH ultraviolet spectrophotometer; Color dish; PH meter (PHS-3C); Digital display temperature table; Magnetic stirrer etc.

Reagent: Ascorbic acid; Ammonium ferrous sulfate; Potassium iodide; Sodium hydroxide; Sodium chlorate etc, the above reagents are for AR.

2.2. The Experimental Steps

2.2.1. The Configuration of the Water

According to take 0.2551g NaClO₃ in a small amount of water, and then constant volume in 1000mL volumetric flask and with the concentration of 200mg/L reservoir fluid simulation ClO₃⁻ water. Experiment used different concentration of ClO₃⁻ on the basis of the dilute solution.

2.2.2. The Experimental Steps

(1) The method of ascorbic acid

Take a certain concentration of 100mL ClO₃⁻ in the middle of 250mL conical flask, add a certain amount of ascorbic acid chemical reduction experiments, using the single factor variable method, investigate ascorbic acid dosing quantity, pH, initial concentration, reaction temperature and reaction time on the removal rate and the effect of choosing the best processing parameters and experimental mechanism preliminarily.

(2) The method of ferrous salt

Take a certain concentration of 100mL ClO₃⁻ in the middle of 250mL conical flask, add a certain amount of ferrous, static chemical oxidation reduction experiments, using the single factor variable method to investigate ferrous dosing quantity, pH, initial concentration, temperature and reaction time on the removal rate and the effect of preliminary experiment mechanism is discussed in this paper.

2.2.3. Experimental Results Represent

Determination of ClO₃⁻ by iodine volume method [7,8]. The experimental results the ClO₃⁻ concentration, the removal rate of ClO₃⁻ to characterization.
Removal rate: \[ D\% = \frac{C_0 - C_e}{C_0} \times 100\% \]

Concentration: \[ C = \frac{V \times C_1}{V} \times \frac{1}{4} \times 83.46 \times 1000 \]

Among, \( C_0 \) and \( C_e \) are respectively before and after the reaction of \( \text{ClO}_3^- \) concentration (mg/L); \( V \) is the volume of water (mL); \( V_1 \) is consumed by titration sodium thiosulfate standard titration fluid volume (mL); \( C_1 \) is the concentration of sodium thiosulfate standard titration solution, mol/L; The relative molecular weight of \( \text{ClO}_3^- \) is 83.46.

3. EXPERIMENTAL RESULTS ANALYSIS

3.1. Ascorbic Acid on \( \text{ClO}_3^- \) Removal Process Research

3.1.1. The removal Effect of Quantity

Take 100mL concentration is 3.06mg/L \( \text{ClO}_3^- \) solution in the middle of 250mL volumetric flask of iodine, added 0.5mg, 1.0mg, 1.5mg, 2.0mg, 2.0mg, 2.2mg, 2.3mg, 2.4mg, 2.5mg, 3.0mg ascorbic acid, mixing, waiting for response after 20min determines \( \text{ClO}_3^- \) concentration in the solution, removing effect as shown in Fig. (1).

Fig. (1). Influence of dosage on removal rate.

Fig. (2). Influence of pH on removal rate.

Fig. (1) shows, with the increase of ascorbic acid dosing quantity, and the removal rate of \( \text{ClO}_3^- \) the trend of increasing, when the additive amount of ascorbic acid 2.2mg or less, because of the insufficient amount of ascorbic acid, the reaction is incomplete, there is still residual \( \text{ClO}_3^- \) at this time. When the additive amount of ascorbic acid 2.2mg, removal rate was stable, and reached 100%, the mass of ascorbic acid and \( \text{ClO}_3^- \) ratio 7.19, reaction completely. So, in the actual process of reaction, in order to achieve the best removal rate, ascorbic acid dosing amount should be controlled in ascorbic acid and \( \text{ClO}_3^- \) the extent of the mass ratio of 7.19 or higher.

3.1.2. The Removal Effect of pH

Take 100mL of initial concentration of 3.06mg/L \( \text{ClO}_3^- \) solution in the middle of 250mL volumetric flask of iodine, adjust the water of the initial pH value were 1.02, 2.13, 3.07, 6.12, 8.05, 9.13, 10.04, add 1.5mg ascorbic acid, fast mixing, stay reaction after 20min to determine residual \( \text{ClO}_3^- \) concentration in the solution. Remove the effect as shown in Fig. (2).
The initial concentration of ClO$_3^-$ against the removal rate of ClO$_3^-$ shows little impact. But when the pH is 8.0 or higher, the removal rate of ClO$_3^-$ fell sharply. This is because the pH of ClO$_3^-$ and the REDOX potential of ascorbic acid have a great influence. When pH 8.0 or higher, alkaline, ClO$_3^-$ oxidizing and reducing of ascorbic acid is reduced, the inhibition of ascorbic acid and ClO$_3^-$ reaction, so the removal rate decreased. Experimental results comprehensively, select pH=6.2 remove ClO$_3^-$ best effect.

3.1.3. The Removal Effect of the Initial Concentration

Respectively take 100mL initial concentration of 0.81, 1.63, 2.45, 3.06, 4.08, 5.42, 8.21, 12.21, 16.27 mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine, adjusting the solution pH=6.2, add 2mg ascorbic acid, mixed evenly, quickly to reaction after 20min to determine residual ClO$_3^-$ concentration in the solution. Under the condition of different initial concentration of ascorbic acid removal ClO$_3^-$ effect as shown in Fig. (3).

From the change trend of removal rate in Fig (3), ascorbic acid dosing quantity must, initial concentration in 1 to 3mg/L, high removal rate is mainly due to excessive, ascorbic acid at this time are the main factors affecting the ascorbic acid dosing quantity.

Dropped from the figure 3 volume change curve, the higher the initial concentration, ClO$_3^-$ remove the more quantity and curve slope is more and more big, the equilibrium moves to the right, the reaction is more and more fully, when $C_0\geq3$mg/L or more, removal amount of ClO$_3^-$ reached a maximum of 2.9mg/L. Because the reactant concentration increasing, the activation number of molecules per unit volume increased, per unit time effective collision number increase, the reaction rate is accelerated, can promote balance moves to the right.

3.1.4. The Removal Effect of the Temperature

Take 100mL concentration is 3.06mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine, add 1.5mg ascorbic acid, fast mixing, controlling different reaction temperature (16,25,30,35,40$^\circ$C and 45$^\circ$C),stay reaction after 20min to determine residual ClO$_3^-$ concentration in the solution. Ascorbic acid at different temperatures to remove ClO$_3^-$ the effect of the changes as shown in Fig. (4).
Can be seen from the Fig. (4), temperature against blood acid removing ClO$_3^-$ there is a greater impact. When temperature above 35$^\circ$C, with the rapid removal rate of the rise of temperature, this may be due to decomposition of ascorbic acid in the solution. So, in the actual process of reaction, the temperature control in 25~35$^\circ$C at best.

### 3.1.5 The Removal Effect of the Reaction Time

Take the initial concentration of 3.06mg/L ClO$_3^-$ to 250mL volumetric flask of iodine solution, add 1.5mg ascorbic acid, reaction temperature for 28$^\circ$C, rapid mixing, controlling different reaction time (3, 5, 7, 10, 15, 20, 30min), the determination of residual ClO$_3^-$ in the final solution concentration. Ascorbic acid removal ClO$_3^-$ the time effect function is shown in Fig. (5).

Can be seen from the Fig. (5), with the increase of reaction time, removal rate is higher and higher, the residual ClO$_3^-$ less and less, when the reaction to 15min removal rate reached 70%, the removal rate and residual are leveled off, completely basic reaction. So in the actual operation process, the general selection of the optimum reaction time for 15min.

### 3.2 Ferrous Salt on ClO$_3^-$ Removal Process Research

#### 3.2.1 The Removal Effect of Quantity

Take 100 mL of initial concentration of 2.03mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine, added 0.3mg, 0.4mg, 0.5mg, 0.6mg, 0.7mg, 0.8mg, 0.9mg, 1.0 mg Fe$^{2+}$, in the 200r/min, the reaction under 30$^\circ$C for 30min after the determination of residual ClO$_3^-$ concentration in the solution. Under the different Fe$^{2+}$ dosing quantity ClO$_3^-$ removal effect as shown in Fig. (6).

By Fig. (6), you can see that with the increase of Fe$^{2+}$ dosing quantity, the removal rate of ClO$_3^-$ the trend of increasing, when the additive amount of Fe$^{2+}$ was 0.8mg, the removal rate was stable, the mass of Fe$^{2+}$ and ClO$_3^-$ 1.79. So, in the actual process of reaction, in order to achieve the best removal rate, Fe$^{2+}$ dosing amount should be controlled in Fe$^{2+}$ and ClO$_3^-$ mass ratio of 1.79 or higher.

#### 3.2.2 The Removal Effect of pH

Take 100mL of initial concentration of 2.03mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine,
adjust the water of the initial pH value were 4.13, 4.97, 6.21, 7.03, 8.14, 9.06 and 10.27, joined 0.8mg Fe$^{2+}$, in 200r/min, the summer temperature under 30° for 30min after the determination of residual ClO$_3^-$ concentration in the solution. Under different pH conditions Fe$^{2+}$ removal ClO$_3^-$ effect as shown in Fig. (7).

As can be seen from the Fig. (7), the pH of the influence of Fe$^{2+}$ removal ClO$_3^-$ is bigger. The smaller the pH, the better the results of the removal of ClO$_3^-$. This is mainly because under acid condition, Fe$^{2+}$ has the strong reducibility, promoted the Fe$^{2+}$ and ClO$_3^-$ reaction. At the same time, with the increase of pH of Fe$^{2+}$ and ClO$_3^-$ quality ratio was between 1.53~1.66, and the greater the pH mass ratio is larger, also this is mainly because the greater the pH in decreasing the reducibility of Fe$^{2+}$. Experimental results comprehensively, selecting pH=6.2 remove ClO$_3^-$ the best comprehensive effect.

### 3.2.3. The Removal Effect of the Initial Concentration

Respectively take 100mL initial concentration of 0.95, 2.03, 3.80, 4.85, 5.71mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine, press Fe$^{2+}$/ClO$_3^-$ =3 quality than adding the Fe$^{2+}$, in the 200r/min, the summer temperature under 30° for 30min after the determination of residual ClO$_3^-$ concentration in the solution. Under the condition of different initial concentration of Fe$^{2+}$ removal ClO$_3^-$ effect as shown in Fig. (8).

From Fig. (8) removal rate change trend, Fe$^{2+}$/ClO$_3^-$ = 3, initial concentration in 1~6 mg/L, the initial concentration effect on the removal rate is very weak, the experimental results show that in low concentration, as long as the control quality of Fe$^{2+}$ and ClO$_3^-$ and all other things being equal, ClO$_3^-$ removal rate is almost not affected by initial concentration.

### 3.2.4. The Removal Effect of the Temperature

Take 100mL of initial concentration of 2.03mg/L ClO$_3^-$ solution in the middle of 250mL volumetric flask of iodine, add 0.8 mg Fe$^{2+}$, mixing, controlling different reaction temperature (25°, 35°, 45° and 55°, 65°, 75°), reaction under 200r/min 30min after the determination of residual
ClO$_3^-$ concentration in the solution. Different temperatures of Fe$^{2+}$ removal ClO$_3^-$ effect as shown in Fig. (9).

Can be seen from the Fig. (9), the temperature of Fe$^{2+}$ removal ClO$_3^-$ is a greater impact. ClO$_3^-$ removal rate increased with the increasing of temperature slowly, but when the temperature reaches 45°C, with removal rate and rapid the rise of temperature, this is due to the reaction of Fe$^{2+}$ and ClO$_3^-$ belongs to the endothermic reaction, in a certain temperature range, the rise of temperature of reaction. But when the temperature is above 45°C, Fe$^{2+}$ hydrolysis happens to generate Fe(OH)$_3$. So, in the actual process of reaction, the temperature control in best is 30°C.

### 3.2.5. The Removal Effect of the Reaction Time

Take the initial concentration of 2.03mg/L ClO$_3^-$ 100mL to 250mL volumetric flask of iodine solution, add 0.8mg Fe$^{2+}$, reaction temperature of 30°C, rapid mixing. Controlling different reaction time (10s, 30s, 60s, 90s, 120s, 180s, 240s and 300s), the determination of residual ClO$_3^-$ in the final solution concentration. Fe$^{2+}$ removal ClO$_3^-$ the time effect function is shown in Fig. (10).

As can be seen from the figure 10, the reaction of Fe$^{2+}$ and ClO$_3^-$ in a few minutes to seconds can completely basic reaction. So in the process of actual operation can save time, generally choose the optimum reaction time for 2min.

### CONCLUSION

(1) Ascorbic acid removal ClO$_3^-$ experiments show that the reaction of ascorbic acid and ClO$_3^-$ speed slow, at the time of 15min to basic response completely; Ascorbic acid removal effect of ClO$_3^-$ as ascorbic acid dosing quantity increases, when the ascorbic acid and ClO$_3^-$ 7.19 removal rate was 100%, while the quality of response completely; And relationship with the pH of the water body will decrease,
pH=6.2 remove ClO$_3^-$ the best effect; With the increase of temperature ClO$_3^-$ remove immediately after the first rise is reduced, the temperature control in 25°C~35°C best; The higher the initial concentration, fully some reaction, but ClO$_3^-$ bad blood acid removal ClO$_3^-$ influenced by initial concentration are faint.

(2) Fe$^{2+}$ removal ClO$_3^-$ experiments show that the reaction of Fe$^{2+}$ and ClO$_3^-$ quickly and completely in 2min to the basic reaction;Fe$^{2+}$ of ClO$_3^-$ removal effect with ascorbic acid dosing quantity increases, and relationship with the water samples of pH value will decrease, pH=6.2 remove ClO$_3^-$ the best effect; With the increase of temperature ClO$_3^-$ remove immediately after the first rise is reduced, the temperature control in 25°C~45°C best; The higher the initial concentration, fully some reaction, but ClO$_3^-$ bad blood acid removal ClO$_3^-$ influenced by initial concentration are faint.

(3) According to the experimental results compared the removal effect of ascorbic acid and Fe$^{2+}$, ascorbic acid of ClO$_3^-$ removing effect is better, can be used as a reductant preference.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

This work is supported by the national natural science and technology fund, China (No.51168013) and national science and technology support project, China (No.2014BAC04B03).

REFERENCES


Received: September 16, 2014 Revised: December 23, 2014 Accepted: December 31, 2014 © Lu et al.; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.