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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 (ClO_3^-) in the water. The results show that 100 mL 3.06 mg/L of ClO_3^- in ascorbic acid and ClO_3^- quality ratio 7.19, pH =6.2,35℃, the reaction time of for 15 min, the removal rate was 100%. And ferrous reduction method to remove 100mL 3.06 mg/L of ClO_3^- in pH = 6.2, Fe^{2+} and ClO_3^- quality ratio 1.79, 30℃ 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 ClO_3^- disinfection by-products. ClO_3^- 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 $ClO_3^- \leqq 0.7$ mg/L [6]. This article uses the method of chemical reduction of water ClO_3^- 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.

*Address correspondence to this author at School of Civil Engineer and Architecture, East China Jiaotong University, Nanchang, 330013, China; Tel:＋8613970936091; E-mail: 149862562@qq.com

2.2. The Experimental Steps

2.2.1. The Configuration of the Water

According to take 0.2551g $NaClO_3$ in a small amount of water, and then constant volume in 1000mL volumetric flask and with the concentration of 200mg/L reservior fluid simulation ClO_3^- water. Experiment used different concentration of ClO_3^- 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 ClO_3^- 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 ClO_3^- 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 ClO_3^- by iodine volume method [7,8]. The experimental results the ClO_3^- concentration, the removal rate of ClO_3^- to characterization.

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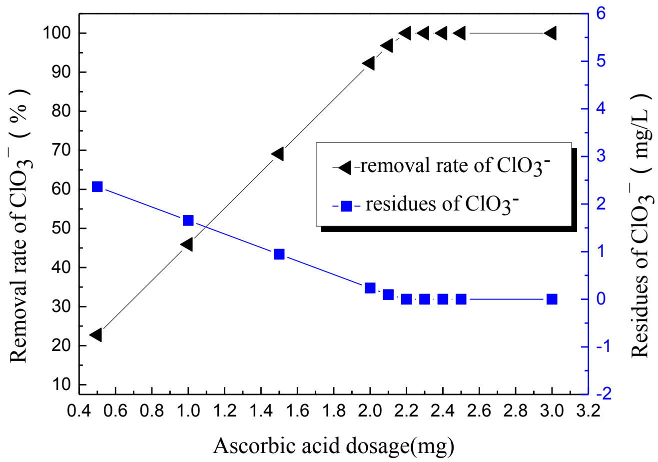

Fig. (1). Influence of dosage on removal rate.

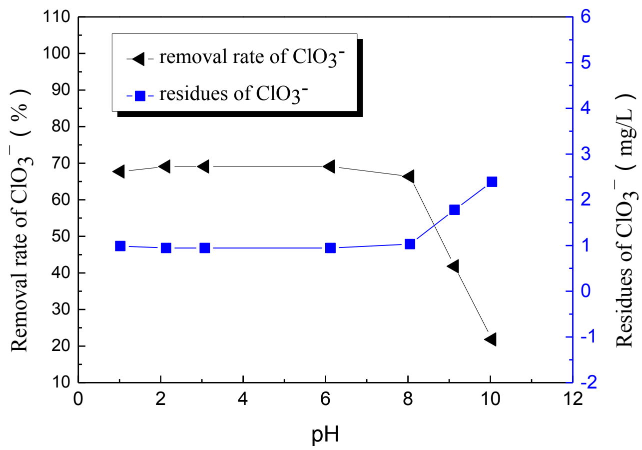

Fig. (2). Influence of pH on removal rate.

Removal rate: $D\%=\frac{C_{01}\times C_{e1}}{C_{01}}\times 100\%$

Concentration: $C=\frac{V_1\times C_1}{V}\times\frac{1}{4}\times 83.46\times 1000$

Among, C_0 and C_e are respectively before and after the reaction of 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 ClO_3^- is 83.46.

3. EXPERIMENTAL RESULTS ANALYSIS

3.1. Ascorbic Acid on ClO_3^- Removal Process Research

3.1.1. The removal Effect of Quantity

Take 100mL concentration is 3.06mg/L 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 ClO_3^- concentration in the solution, removing effect as shown in Fig. (**1**).

Fig. (**1**) shows, with the increase of ascorbic acid dosing quantity, and the removal rate of 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 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 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 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 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 ClO_3^- concentration in the solution. Remove the effect as shown in Fig. (**2**).

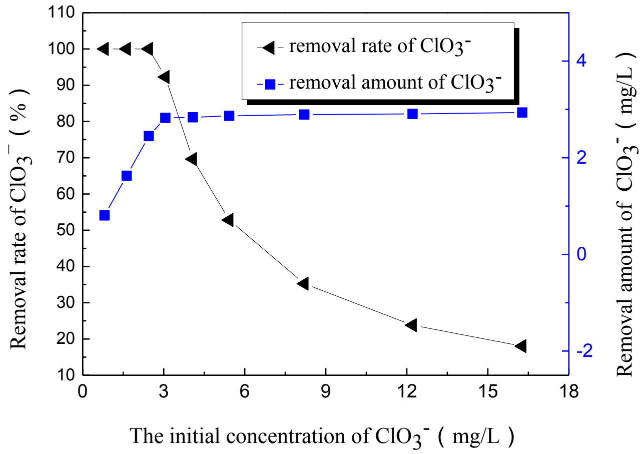

Fig. (3). Influence of initial concentration on removal rate.

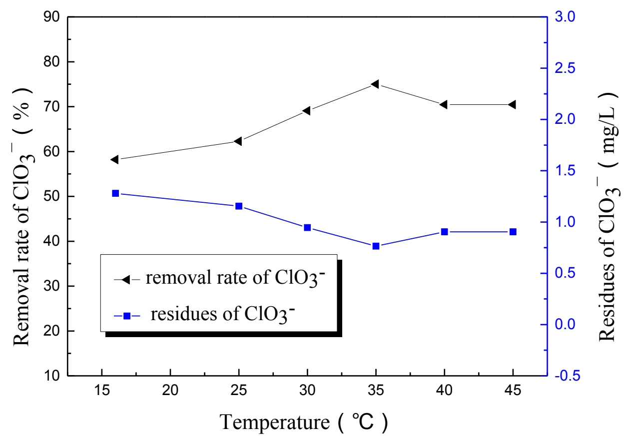

Fig. (4). Influence of temperature on removal rate.

Fig. (**2**) shows, under the condition of acid, pH value against bad blood acid removal ClO_3^- little impact. But when the pH 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 has 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 $C_0 \geq 3$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°C and 45°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**).

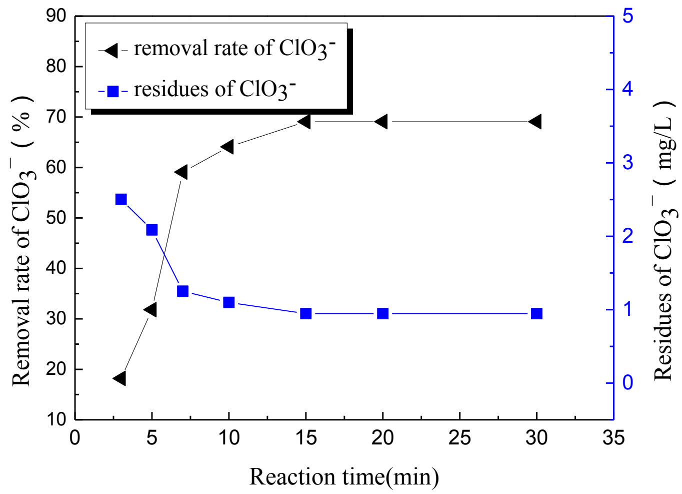

Fig. (5). Influence of response time on removal rate.

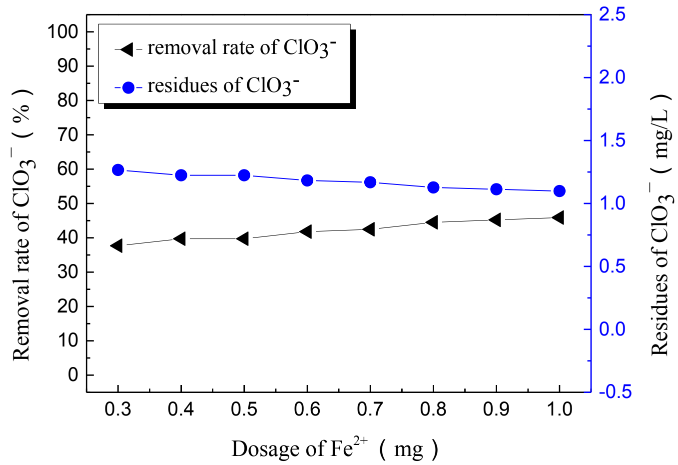

Fig. (6). Influence of dosage on removal rate.

Can be seen from the Fig. (**4**), temperature against bad blood acid removing ClO_3^- there is a greater impact. When temperature above 35°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°C at best.

3.1.5. The Removal Effect of the Reaction Time

Take the initial concentration of 3.06mg/L ClO_3^- 100mL to 250mL volumetric flask of iodine solution, add 1.5mg ascorbic acid, reaction temperature for 28°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℃ 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,

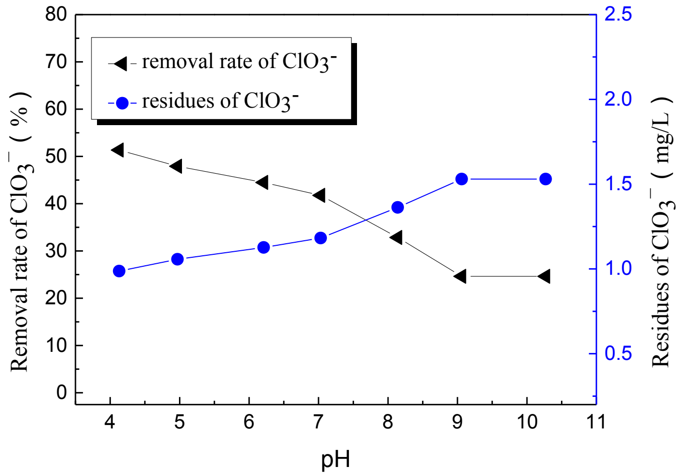

Fig. (7). Influence of pH on removal rate.

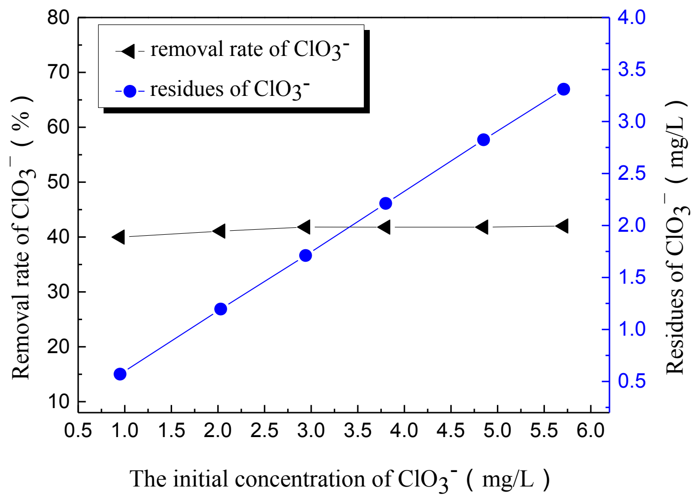

Fig. (8). Influence of initial concentration on removal rate.

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

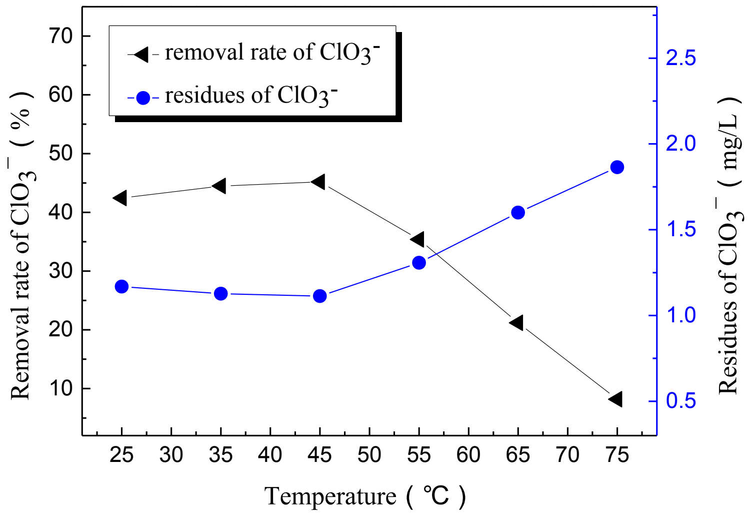

Fig. (9). Influence of temperature on removal rate.

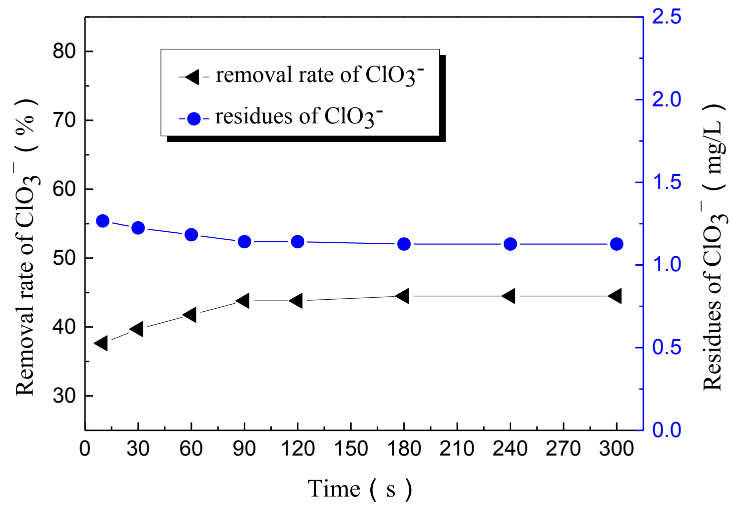

Fig. (10). Influence of response time on removal rate.

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℃,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℃,Fe^{2+} hydrolysis happens to generate Fe $(OH)_3$.So,in the actual process of reaction,the temperature control in best is 30℃.

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℃, 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℃~35℃ 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℃~45℃ 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.

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