# Study on polluted raw water by pre-oxidation of chloramine

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**Abstract:** Considering that contaminated raw water mostly contain high Ammonia - N and a majority of water treatment plants use prechlorination process in China, efficiency of chloramine as a coagulant aid in enhancing coagulation was investigated by Jar stirring, using raw water sample of A city which was containing high concentration of NOM and bromide in winter. The results showed that, compared with no preoxidation, preformed chloramine apparently decreased the turbidity of settled and filtered water with low dosage (2.0 mg/L), and the aid-coagulation efficiency was further enhanced with the increase of chlorine ($Cl_2$) to Ammonia-N (N) ratio.

**Key words:** preoxidation; chloramines; turbidity; water treatment

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# 预氯胺化处理受污染水源水的试验

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**摘 要**:对于高氨氮的受污染水源水的预处理国内大部分水厂通常采用预氯化工艺. 以某市受污染水源水为研究对象,通过烧杯试验探讨了氯胺的预氧化助凝效能。结果表明,同无预氯胺化相比,氯胺在低投加量(2.0 mg/L)时,可明显降低水样的滤后浊度和沉后浊度,并且氯胺的助凝效能随氯、氮比率的增加而增强.

**关键词**:预氧化;氯胺;浊度;水处理

## 1 Introduction

Effective removal of cryptosporidium oocysts and Giardia by water treatment processes mostly rely on efficient chemical coagulation to entrap oocysts in coagulant floc articles, followed by removal of the floc solids by sediment, flotation, or filtration, so now improving the particle removal efficiency is also an important objective as improving NOM removal by enhanced coagulation process[1~4]. But recent investigations showed that[5,6], natural organic matters (NOM) could significantly heighten stabilization of inorganicparticulates in water, which caused high par-

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ticle counts and turbidity in finished water due to poor coagulation effectiveness, especially for low temperature and low turbidity raw water. Preoxidation has been one of principle means for improving the coagulation process, which is generally aimed at destroying the organic coating on the surface of particle and improving particles removal efficiency[7,8]. Traditionally, chorine was predominant oxidant widely utilized in water treatment plant, However, when water is chlorinated, chlorine reacts readily with a wide variety of organics to form disinfection by-products, such as the well-known trihalomethanes and haloacetic acids[9~11]. These DBPs have been identified as cancer - causing reagents in the last three decades[12], so prechlorination was progressively restricted in most countries[13].

Many investigations were conducted to evaluate the efficiency of enhancing particle separation processes by different alternative oxidants, such as ozone, chlorine dioxide, potassium permanganate, hydrogen peroxide, or ferrate[14, 15]. Ozone was reported to have significant positive aid - coagulation effectiveness on particle removal at low dosages, especially in organic rich raw water[16, 17], but in some cases preozonation would hinder the removal of turbidity and increase the concentration of residual coagulant metals at low coagulant doses[18], furthermore, for raw water containing high bromide, an amount of bromate would be formed during ozonation process suspected of being more hazardous to human health[19]. Permanganate preoxidation obviously enhanced the coagulation of several kinds of surface waters, with substantial reduction in the settled turbidity[20, 21], but its disinfection efficiency was rather weak.

Now chloramine was the most favorable disinfectant due to its low DBPs yields during application and low cost. But little attention was paid to its oxidation efficiency of enhancing coagulation of polluted surface water, partly because of its perceived relative inferior oxidation strength to other alternative chemicals, but at preoxidation unit its disinfection effect was better than ozone or permanganate at usual dosage due to its high combined residual chlorine concentration and long inactivation duration ability.

In china, seriously contaminated raw water generally contains high concentrations of NOM and Ammonia—N, and many water treatment facilities still apply breakpoint prechlorination process for low cost reasons. Considering the resource water quality characteristics and water treatment processes traits, chloramine preoxidation was mentioned. In comparison to other alternative oxidants such as ozone, chlorine dioxide, chloramine preoxidation has the advantages of low cost, easy operation and maintenance. It may be an economic method to enhance the conventional water treatment process on occasions with limited funds for capital investment in some countries.

In this paper, using the significantly contaminated raw water of A city containing high bromide and NOM as sample, the efficiency of chloramine preoxidation in improving the coagulation of surface waters (indicated as turbidity and particle counts) was investigated by laboratory-scale in low temperature and low turbidity periods.

## 2 Materials and Methods

### 2.1 Raw water quality characteristics

All of the experiments were performed in winter, and the representative characteristics of raw water quality are low temperature, low turbidity, rich in humic matters, and high bromide concentration. Humic matter and bromide are the main precursors of disinfection by-products. Typical raw water quality parameters are showed in Table 1.

**Table 1 typical raw water quality parameters**

| Parameters | Turbidity /ntu | Abs at 254 nm (Abs/cm) | TOC/ (mg · L$^{-1}$) | Alkalinity /(mg · L$^{-1}$) | $NH_3$—N/ (mg · L$^{-1}$) |
|---|---|---|---|---|---|
| Values | 5.2～9.6 | 0.096～0.134 | 4.3～5.2 | 190～230 | 0.08～0.14 |
| Parameters | Colour /CU | Mn (mg · L$^{-1}$) | Total hardness ($CaCO_3$ · L$^{-1}$) | Temperature /℃ | pH value |
| Values | 15～25 | <0.1 | 80～100 | 1～3 | 7.6～7.9 |

2.2 **Preformed chloramine preparation for Jar tests**

In all cases, reagent grade chemicals were used without further purification. Stock chlorine solutions were prepared by diluting sodium hypochlorite into chlorine-demand-free water to a concentration of about 2.00 g/L, and then standardized by iodometric method. Ammonia chloride solutions were prepared by dissolving ammonia chloride powder which was baked for 2 h at 100 ℃ in chlorine-demand-free water to a concentration of 1.00 g/L (calculated as N). Chlorine solution mixes with ammonia solution at a certain proportion at pH 8.0 and stirred with magnetic stirrer for 20 min to form monochloramine. Then mixture is tested by DPD - FAS titration method to distinguish the monochloramine and dichloramine. If there is little or no dichloramine, the mixture is preformed chloramine. All solutions were mixed with distilled deionized water produced on a Milli - Q filter apparatus. Preformed chloramine solutions were mixed immediately before use and were discarded after use.

2.3 **Jar - tests studies**

The effects of variable concentrations and $Cl_2$ :N ratio of monochloramine on Ferric Chloride coagulation were studied through jar - test experiments using the raw water containing above water quality characters. All the studies were conducted in a series of 6 glass beakers with a six-unit stirrer apparatus. 1.5 L water sample and a certain dosage of monochloramine were mixed at a speed of 200 r/min for a period of time. Then, all of the water sample were subjected to coagulation with the addition of specific dosage of Ferric Chloride, at 200 r/min for 1 min. subsequently, the sample were slowly stirred with the coagulant at 80 r/min for 18 min, and settled for 30 min. Sample of supernatant after sedimentation were siphoned, and filtered with a filter paper (1～2 μm pore size). The residual turbidity of settled and filtered water was analyzed using a turbidity meter.

# 3 Results and Discussion

Residual turbidity was used as the principle indicator for the evaluation of the efficiency of monochloramine preoxidation in enhancing coagulation of the experimental raw water. The low temperature and low turbidity water is rather difficult to coagulation due to the slower rate of hydrolysis of coagulants and the difficulty in flocculation because of the low concentration of particles in the water.

Figure 1 shows a typical comparison of a series of coagulation tests with different coagulant or monochloramine dosage. It is shown that, the addition of Ferric dosage without preoxidation caused a limit reduction

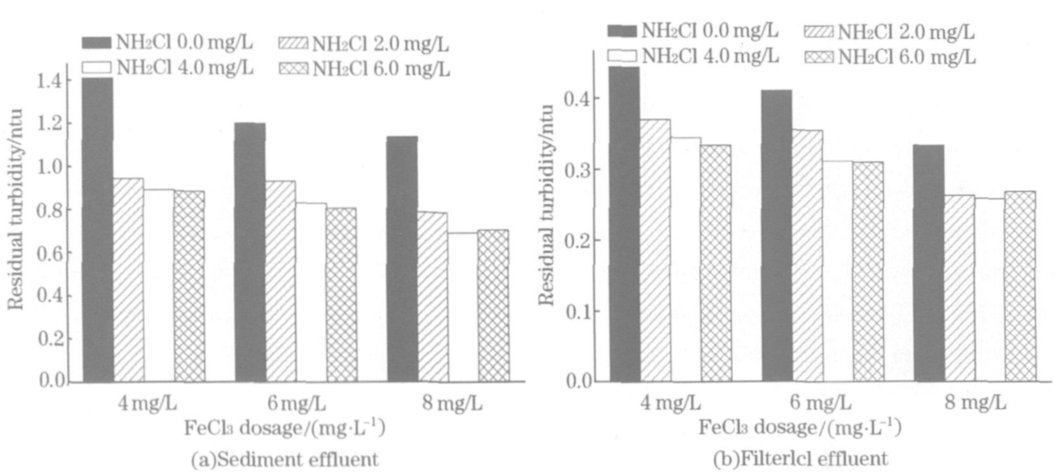


**Figure 1 Settled and filtered water residual turbidity as a function of monochloramine concentration and Ferric chloride dosage in jar-test studies**

of turbidity in settled water, whilst the low dosage of monochloramine could obviously decrease the turbidity of settled water. For example, when Ferric dosage was at 4.0 mg/L and 8.0 mg/L, the residual turbidity of settled water was respectively 1.41 ntu and 1.14 ntu, and the turbidity of sediment water at 4.0 mg/L Ferric dosage was reduced to 0.891 ntu by the addition of 2.0 mg/L monochloramine. It is noted that higher dose of monochloramine did not achieve further apparently reduction in turbidity, and the optimum monochloramine dosage range was among 2.0～4.0mg/L. In the case of filtered water, there was also a great reduction in turbidity of filtered water (filtered by 1～2 μm pore size filter papers) with low monochloramine dosage (< 2.0 mg/L), and further increasing chloramine dosage up to 6.0 mg/L achieved slightly additional reduction in turbidity, especially at high ferric dosage (8.0 mg/L) the extent of reduction is very limited. The filtration results indicated that the floc particle size in the process of coagulation with monochloramine is larger than the case without preoxidation.

The effect of $Cl_2$ ∶N ratios on the settled and filtered residual turbidity during chloramine preoxidation is shown in Figure 2. It shows that there was a substantial reduction in turbidity of both settled and filtered

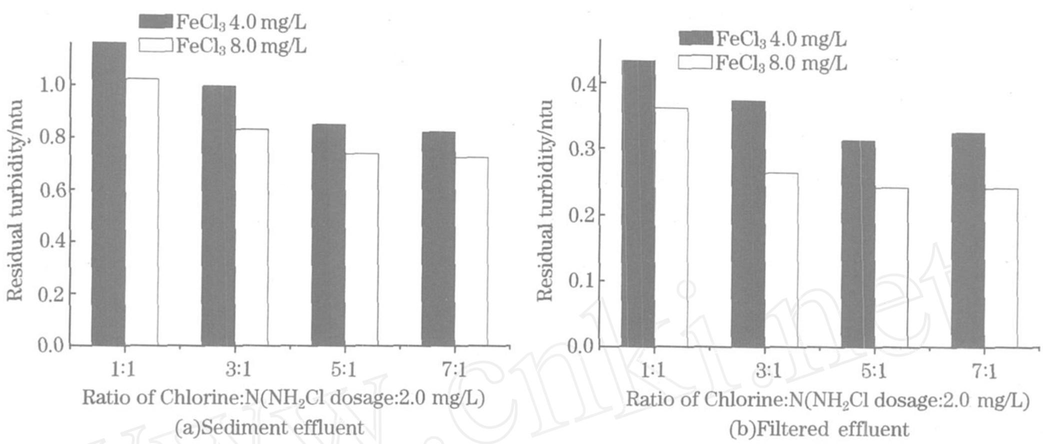


**Figure 2 Settled and filtered water residual turbidity as a function of $Cl_2$ ∶N ratio and Ferric chloride dosage in jar-test studies (monochloramine dosage: 2.0mg/L, as effective free chlorine):**

water with the increase of $Cl_2$ ∶N ratio of monochloramine, And the extent of reduction in turbidity was more slight with higher Ferric dosage and higher $Cl_2$ ∶N ratio of monochloramine, especially for filtered water.

## 4 Conclusions

Laboratory experiments were conducted for enhancing the coagulation of stabilized surface water by chloramine preoxidation. Jar-test studies indicated that the turbidity removal of settled water and filtered water was remarkably improved by small amount of preformed chloramine preoxidation, increasing $Cl_2$ ∶N ratio further enhanced the coagulation during prechloramination. Therefore, chloramine is an effective oxidant for enhancing the coagulation of surface water.

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