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Using chloramine as a coagulant aid in enhancing coagulation of Yellow River water in China*

YANG Wei†[1,2], CHEN Jie[3], LI Xing[4], LIANG Heng[2], HE Wen-jie[5], LI Gui-bai[2]

(*[1]Department of Environmental Engineering, Harbin University of Commerce, Harbin 150076, China*)

(*[2]School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China*)

(*[3]Suzhou Litree Ultra-filtration Membrane Technology Co., Ltd., Suzhou 215152, China*)

(*[4]College of Civil Engineering and Architecture, Beijing University of Technology, Beijing 100023, China*)

(*[5]Tianjin Waterworks Group Company Ltd., Tianjin 300040, China*)

†E-mail: yangweiyuyang@163.com

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Abstract: Considering that contaminated raw water mostly contains high Ammonia-N and a majority of water treatment plants use prechlorination process in China, efficiency of chloramines as a coagulant aid in enhancing coagulation was investigated by Jar stirring and pilot-scale tests, using Yellow River water containing high concentration of natural organic matters (NOM) and bromide in winter. The jar tests 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. Pilot-scale studies indicated that, in comparison to the case without preoxidation, the turbidity removal efficiency of flotation and filtration effluent water was significantly improved, the particle counts of filtered water were decreased 63.4%, the average rate of filter head loss was reduced 18.2%, and filter run time was prolonged 15.7%. Therefore, chloramine preoxidation may substantially enhance the particle separation efficiency.

Key words: Preoxidation, Chloramine, Pilot plant, Turbidity, Particle counts, Filter run time
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INTRODUCTION

Effective removal of cryptosporidium oocysts and Giardia by water treatment processes mostly relies on efficient chemical coagulation to entrap oocysts in coagulant floc particles, 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 natural organic matters (NOM) removal by enhanced coagulation process (LeChevallier and Norton, 1992; Betancourt and Rose, 2004; Dugan *et al.*, 2001; Hall and Croll, 1997). But recent investigations (Gibbs, 1983; Jekel, 1986) showed that NOM could significantly enhance stabilization of inorganic particulates in water, which caused high particle counts and turbidity in treated water due to poor coagulation effectiveness, especially of low temperature and low turbidity raw water. Preoxidation has been a principal for improving the coagulation process, which is generally aimed at destroying the organic coating on the surface of particle and improving particles removal efficiency (Jekel, 1998; 1991). Traditionally, chorine is the 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 (DBPs), such as the well-known trihalomethanes and haloacetic acids (Edward *et al.*, 1992; Singer, 1994; Stevens *et al.*, 1989). These DBPs have been identified in the last

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three decades as cancer-causing reagents (Bull and Kopfler, 1991), so prechlorination is progressively restricted in most countries (USEPA, 1998).

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 (Ma and Liu, 2002a; 2002b). Ozone was reported to have significant positive aid-coagulation effectiveness on particle removal at low dosages, especially in organic rich raw water (Reckhow *et al*., 1986; Edwards and Benjamin, 1992), but in some cases preozonation hinders the removal of turbidity and increases the concentration of residual coagulant metals at low coagulant doses (Edwards *et al*., 1994), furthermore, in raw water containing high bromide, an amount of bromate that would be formed during ozonation process is suspected of being more hazardous to human health (von Gunten and Hoigné, 1994). Permanganate preoxidation obviously enhances the coagulation of several kinds of surface waters, with substantial reduction in the settled turbidity (Ma and Li, 1993; Ma *et al*., 1996), but its disinfection efficiency is rather weak.

Chloramine is now the most favored disinfectant due to its low DBPs yields during application and low cost (Qi *et al*., 2004). Numerous investigations of chloramine were focused on disinfection issues, such as disinfection efficiency, effect on distribution system water quality, new DBPs formation, etc. (Goel and Bouwer, 2004; Norton and LeChevallier, 1997; Diehl *et al*., 2000; Mitch *et al*., 2003), little attention was paid to its oxidation efficiency of enhancing coagulation of polluted surface water, partly because of its perceived relatively inferior oxidation strength compared to other alternative chemicals.

In China, seriously contaminated raw water generally contains high concentrations of NOM and Ammonia-N, with many water treatment facilities still applying breakpoint prechlorination process for low cost reasons (Lin, 2004; Xu and Xu, 2000). Considering the resource water quality characteristics and water treatment processes traits, chloramine preoxidation was mentioned. In comparison to other alternative oxidants such as ozone and chlorine dioxide, chloramine preoxidation has the advantages of low cost maintenance and easy operation. It may be an economic method in some countries to enhance the conventional water treatment process on occasions with limited funds for capital investment.

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

MATERIALS AND METHODS

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, high content of humic matters, and high bromide concentration. Humic matter and bromide are the main precursors of DBPs. Typical raw water quality parameters are showed in Table 1.

Table 1 Typical raw water quality parameters

Parameters	Values
Turbidity (NTU)	5.2~9.6
Abs at 254 nm (Abs/cm)	0.096~0.134
TOC (mg/L)	4.3~5.2
Alkalinity (mg/L)	190~230
NH_3-N (mg/L)	0.08~0.14
Colour (Co)	15~25
Mn (mg/L)	<0.1
Total hardness (mg $CaCO_3$/L)	80~100
Temperature (°C)	1~3
pH	7.6~7.9

Preformed chloramine 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 °C 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 the mixture is tested by DPD-FAS titration method to distinguish the monochloramine and dichloramine (Greenberg *et al.*, 1998). 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 discarded after use.

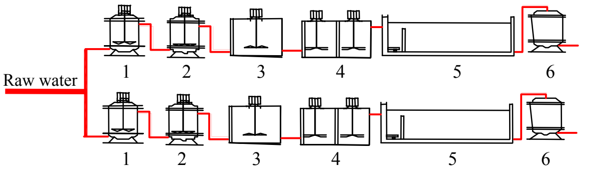
Jar-test studies

The effects of variable concentrations and Cl_2:N ratio of monochloramine on Ferric Chloride coagulation were studied through Jar-test experiments using raw water containing the 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 samples were subjected to coagulation with the addition of specific dosage of Ferric Chloride, at 200 r/min for 1 min. Subsequently, the samples were slowly stirred with the coagulant at 80 r/min for 18 min, and settled for 30 min. Samples of supernatant after sedimentation were siphoned off, and filtered with filter paper (1~2 μm pore size). The residual turbidity of settled and filtered water was analyzed using a turbidity meter (2100 A, HACH Chemical Company, Loveland, USA).

Pilot-scale studies

In order to further assess the aid coagulation efficiency of chloramine preoxidation, short duration pilot experiments were conducted using the permanent pilot plant at the Jieyuan Water Treatment Plant operated by Tianjin Waterworks Ltd. The pilot plant is built up with two parallel systems with a design flow of 240 m^3/d for both units combined, composed of two preoxidation reactors with detention time of 10 min each, a mechanical mixer with detention time of 1 min, a two stage mechanical flocculating tank with total detention time of 18 min, and a DAF tank with detention time of 15 min and reflux ratio of 7%, and a dual media filter with filter velocity of 8 m/h. Fig.1 shows the two parallel systems composed of two preoxidation reactors.

During experimental period, the parameters of the two systems were kept the same, and the coagulant used was Ferric Chloride at dosage of 11.2 mg/L at the mixer inlet. One of the systems was dosed with 0.32 mg/L ammonia followed by 2.0 mg/L chlorine while the other was only dosed 2.0 mg/L chlorine at the inlet of the preoxidation reactor. Ammonia stock solution was made by diluting aqua ammonia in tap water and calibrated before use. Chlorine stock solution was prepared by dissolving chlorine gas in tap water and calibrating by iodometric method before use. All of the chemical agents used in the pilot plant were dosed by peristaltic pump. After a stable time of a few days, turbidity, residual chlorine and trihalomethane were sampled at the outlet of the preoxidation tank, DAF and filter, and followed by the above analysis. Two in-line particle counters were used to monitor the particle counts and size distribution of filtered water (Inter Basic Resources Company, USA).



1, 2: preoxidation reactor; 3: mixing tank; 4: flocculation tank; 5: flotation tank; 6: filter

Fig.1 The two parallel systems with a design flow of 240 m^3/d composed of two preoxidation reactors

RESULTS AND DISCUSSION

Jar-test results

Residual turbidity was used as the principal indicator for evaluating 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.

Fig.2 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 limited reduction of turbidity in settled water, while the low dosage of monochloramine could obviously decrease the turbidity of settled water. For example, when Ferric dosage was 4.0 mg/L and 8.0 mg/L, the residual turbidity of settled water was respectively 1.41 NTU and 1.14 NTU without chloramines, and when Ferric dosage was 4.0 mg/L, the turbidity of sediment water 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 apparent reduction in turbidity, and that the optimum monochloramine dosage range was 2.0~4.0 mg/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 paper) with low monochloramine dosage (<2.0 mg/L), and further increasing chloramine dosage up to 6.0 mg/L yielded slightly additional reduction in turbidity, especially at high Ferric dosage (8.0 mg/L) when the extent of reduction is very limited. The filtration results indicated that the particle counts in the process of coagulation with monochloramine are less than the case without preoxidation.

The effect of Cl_2:N ratios on the settled and filtered residual turbidity during chloramines preoxidation is shown in Fig.3. It shows that there was a substantial reduction in turbidity of both settled and filtered 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.

Pilot-scale experimental results

The pilot-scale study was further conducted to investigate the aid-coagulation effectiveness of chloramine preoxidation for low turbidity and low temperature surface water used as Jar tests. With this study, mainly three aspects are evaluated: (1) effect of chloramine preoxidation on the turbidity of flotation and filtration effluent water, (2) effect of chloramine preoxidation on particle counts and particle size distribution of filtered water, and (3) effect of chloramine preoxidation on filter run period and filter head loss.

Turbidity values at points following flotation and filtration are shown in Fig.4. The residual turbidity of

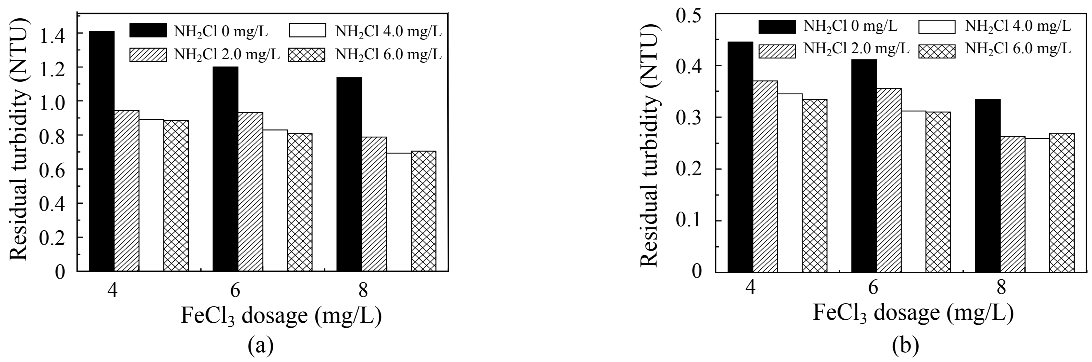


Fig.2 Settled and filtered water residual turbidity as a function of monochloramine concentration and Ferric chloride dosage in Jar-test studies. (a) Sediment effluent water; (b) Filtered effluent water

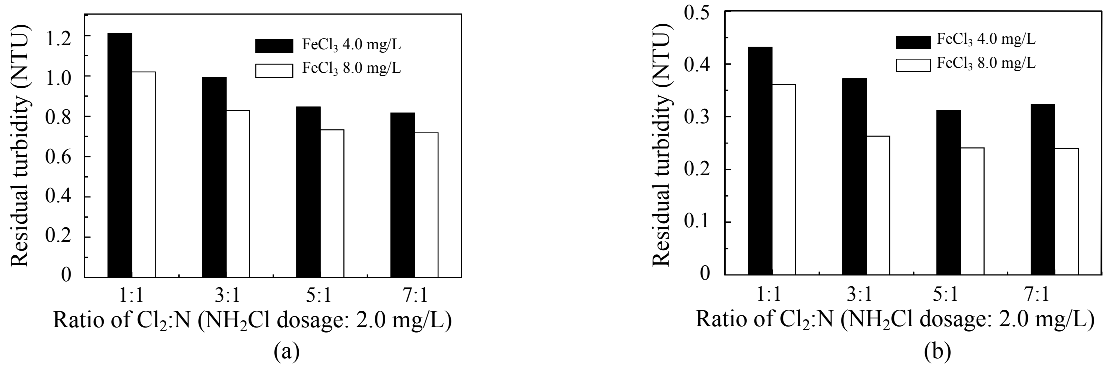


Fig.3 Settled and filtered water residual turbidity as a function of Cl_2:N ratio and Ferric chloride dosage in jar-test studies (monochloramine dosage: 2.0 mg/L, as effective free chlorine). (a) Sediment effluent water; (b) Filtered effluent water

the flotation and filter effluent water with chloramine preoxidation process was obviously lower than that without preoxidation. After the feed of chloramine (0.32 mg/L Ammonia-N and 2.0 mg/L chlorine) at the inlet of the preoxidation tank, the settled turbidity was decreased from ≥1.2 NTU to ≤1.0 NTU, the average value was decreased 0.36 NTU (37.8%). A similar trend was observed for filtered water turbidity, and the average turbidity value was reduced to 0.283 NTU (34.2%).

Fig.5 shows particle counts of filtered water with/without preoxidation. It can be clearly seen that the filtered particle counts were substantially decreased after preoxidation process. Due to the poor coagulation efficiency, the particles of filtered water were rather high for conventional treatment process, with the average value in 18 h running time being 3405 per ml. Then particle counts immediately decreased after the feed of chloramine, and at last became stable at about 1100 per ml. The average filtered particle count was reduced 64.3%.

Fig.6 shows the particle size distribution of filtered water. It is clearly seen that with preoxidation or without preoxidation, small-size particles were predominant in filter effluent water. Compared with no preoxidation process, the 2~7 μm particles were reduced 61.7%, 7~15 μm particles were reduced 68.1%, and 15 μm particles were reduced 82.4%.

Those results further indicated that chloramine enhanced the coagulation of surface water in the experimental period, and that the filter efficiency was distinctly improved. It was reported that particle counts of filtered water have much more obvious relationship than turbidity with some typical waterborne pathogens such as giardia, cryptosporidium, etc., so the substantial reduction of particles counts means that the probability of existence of those pathogens in filter effluent water was greatly reduced. Furthermore, the microorganism safety of filtered water was also improved by chloramine preoxidation.

Fig.7 shows three groups of filter run times with or without chloramine preoxidation. Filters were

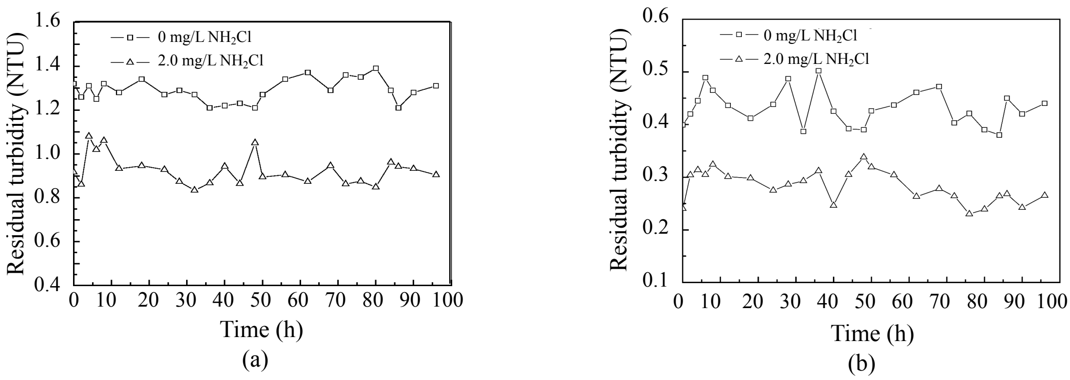


Fig.4 Comparison on the residual turbidity of floatation and filtration effluent water between prechloramination and no preoxidation process for the pilot-plant study. (a) Flotation effluent; (b) Filtration effluent

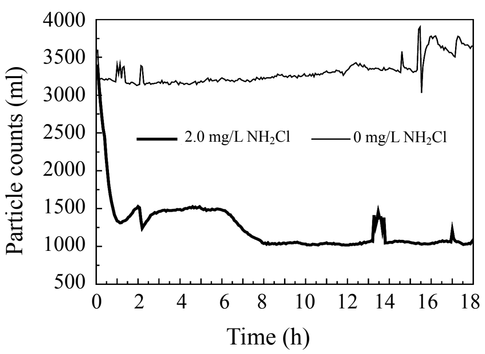


Fig.5 Comparison of total particle counts of filtered water between prechloramination and no preoxidation process for the pilot-plant study

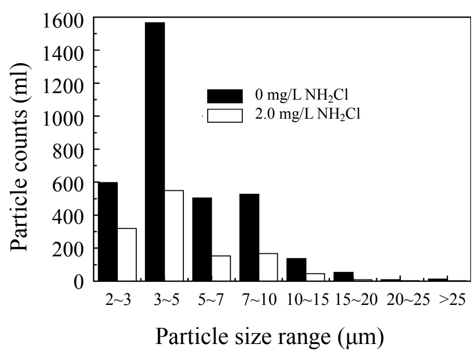


Fig.6 Comparison of particle size distribution of filtered water between prechloramination and no preoxidation process for the pilot-plant study

generally backwashed when the head loss exceeded about 2.2 m. The average run time was prolonged from 22.9 h to 26.5 h (the filter run time was prolonged 15.7%). As noted previously, the decreased turbidity of the flotation effluent turbidity resulted in lower particle loading to the filter; otherwise, the residual chloramine in flotation effluent water may change the characteristics of filter materials with improving the absorbance and interception ability of the filter. Analysis of the head loss data from the filters (Fig.8) showed that the head loss over the filters during no chloramine feed conditions exceeded that during chloramine preoxidation process. The rate of head loss was 8 cm/h with chloramine preoxidation, while it was 9.78 cm/h without preoxidation process.

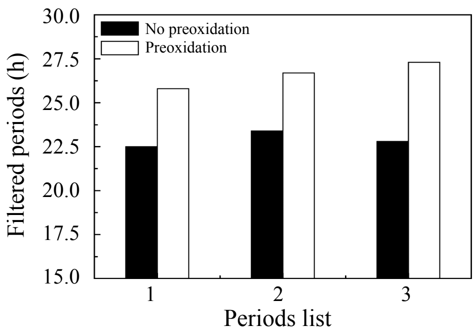


Fig.7 Comparison on filter run time between prechloramination and no preoxidation process for the pilot-plant study

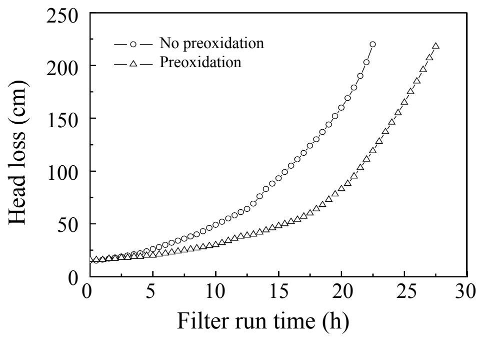


Fig.8 Filter head loss development as a function of filter run time for the prechloramination pilot-plant study

CONCLUSION

Laboratory and pilot-scale 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. Pilot-scale studies showed that, the turbidity of both flotation and filtration effluent water was obviously reduced, the particle counts of filtered water were substantially decreased, and the filter run time was prolonged. Therefore, chloramine is an effective oxidant for enhancing the coagulation of surface water.

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