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Comparison of Fe–Mn enhanced coagulation and O_3-BAC for removing natural organic matter from source waters: a case study

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ABSTRACT

This plant-scale investigation compared two process improvement strategies for Lianyungang drinking water treatment plant (L-DWTP), a typical plant employing conventional processes to treat source water impacted by seasonal non-point pollution. Hierarchical cluster analysis grouped it into two clusters, i.e. normal period and polluted period. Originally, the L-DWTP exhibited poor organic matter removal efficiency, and 76.7% of the effluent permanganate index (COD_{Mn}) levels exceeded the state regulation requirement (<3 mg/L). In addition, chloroform concentration was observed to exceed the regulation requirement (60 μg/L) by 14.2 and 56.2% in normal and polluted periods. The combined use of $FeCl_3$ and $KMnO_4$ (Fe–Mn enhanced coagulation) increased the COD_{Mn} removal efficiency by 10.6%, and decreased the chloroform formation by 26.4%. It indicates that about 94.5% of effluent COD_{Mn} values and nearly all of chloroform levels may meet the standard in normal period. However, Fe–Mn enhanced coagulation shows limitation in polluted period. The advanced treatment by ozone-biological activated carbon process (O_3-BAC) increases the COD_{Mn} removal efficiency by 29.5%, and decreases the chloroform formation by 43%, indicating that effluent levels may meet the standard both in normal and polluted periods. Cost was also compared, and the extra cost for Fe–Mn enhanced coagulation is only about 20% of that for O_3-BAC. In conclusion, O_3-BAC works well both in normal and polluted periods. Fe–Mn enhanced coagulation only shows good performance in normal period, but is more economical. Therefore, it is proposed to use Fe–Mn enhanced coagulation in normal period, while O_3-BAC during polluted period. These obtained plant-scale data are valuable to optimize the operation of DWTPs with similar challenges.

Keywords: Seasonal non-point pollution; Enhanced coagulation; $FeCl_3$; $KMnO_4$; O_3-BAC

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1. Introduction

The surface waters of lakes, rivers, and reservoirs serve as the main sources for drinking water treatment plants (DWTPs) in China [1]. However, surface water is susceptible to human activities, especially non-point pollution. Non-point pollution mainly includes urban run-off, agricultural run-off, and soil corrosion, which are more difficult to control than that of point pollution such as municipal and industrial wastewater discharge. Different from point pollution, non-point pollution is a seasonal phenomenon, largely affected by climate within the basin [2]. The effects of non-point pollution on water environments have recently received a great attention in China [3]. Non-point pollutants often include high levels of natural organic matter (NOM) and synthetic organic matter (SOM) [4]. SOM was affected by human activity, which may show more complicated characteristics than NOM. Compared with NOM, some SOM are more hydrophilic, with lower molecular weight and lower SUVA value, which makes them more difficult to be removed in the coagulation process [4]. NOM and SOM may cause unfavorable color, taste, and odor, and serve as carbon source for the regrowth of micro-organism in the pipe distribution system [5]. Moreover, NOM and SOM may react with chlorine to form carcinogenic disinfection by product (DBPs) [6].

In China, more than 90% of the DWTPs use the conventional treatment processes, i.e. coagulation, sedimentation, filtration, and disinfection, for the treatment of surface water. These DWTPs were generally designed several decades ago and mainly focused on the removal of turbidity and the control of micro-organisms rather than NOM and SOM [7]. Recently, China has issued the new national drinking water standard with much more stringent requirements [8]. For example, the levels of NH_4^+-N and permanganate index (COD_{Mn}) were not regulated in the former edition. In the new standard, the level of COD_{Mn}, which is the only comprehensive index of OM concentration in Chinese drinking water standard, is required to be below 3 mg/L in normal conditions, and lower than 5 mg/L in case COD_{Mn} level of the source water exceeds 6 mg/L. Furthermore, the effluent level of NH_4^+-N is required to be below 0.5 mg/L. For comparison's sake, 3 mg/L is set as the only achieving goal in this study. The newly issued standard raises technical challenges to many DWTPs such as Lianyungang DWTP (L-DWTP) in China. In L-DWTP, the level of effluents of COD_{Mn} ranged between 2.5 and 5.6 mg/L, with an average value of 3.31 mg/L, which exceeding the regulatory requirement by about 10%. Therefore, it is of crucial importance to implement upgrades of processes to enhance the removal of COD_{Mn} for these DWTPs.

Enhanced coagulation is regarded by United States Environmental Protection Agency (USEPA) as the best available technology for the removal of OM and the control of DBPs formation [9]. In most cases, enhanced coagulation is achieved by significantly increasing the doses of coagulants [9]. However, the overdosed coagulants result in elevated operation cost, remarkable production of sludge, and also increased level of residual metal thereafter [10]. Potassium permanganate ($KMnO_4$) and ferric chloride ($FeCl_3$) may be valuable to aid coagulation [11,12]. $KMnO_4$ can be reduced to *in situ* δMnO_2, which may serve as a coagulant seed to promote the formation of larger flocs [11,13], and act as adsorbents toward OM. These effects benefit the removal of COD_{Mn} by coagulation. However, the negatively charged δMnO_2 may also increase coagulant doses to balance its adverse effect [14]. $FeCl_3$ is reported to be more effective in a wider pH range than alum salts with respect to the removal of OM [12,15], and it can also balance the negative effect of MnO_2 [16]. Moreover, the simultaneous use of alum and iron salts, i.e. dual Al–Fe coagulant, has been reported to exhibit better coagulating ability than using them separately [17]. The precipitants of Al and Fe hydroxide and the *in situ* δMnO_2 exhibit distinct performance toward OM, and the combined use of these species may be highly efficient [16]. In addition, to achieve the same goal, the dose may be much less than that of solo use of Al coagulant, which may ease the problems caused by overdosing of coagulants [18]. However, rare studies have focused on its treatability toward the source water with seasonal non-point pollution.

The advanced treatment by ozone-biological activated carbon process (O_3-BAC) is widely used to treat polluted source water [19]. O_3-BAC is effective at reducing the total organic carbon, controlling taste and odor, and minimizing the formation of DBPs [20,21]. O_3 oxidizes OM to relatively smaller molecular compounds toward which BAC exhibits better absorbability and biodegradability [22]. O_3-BAC also improves the degradation of pesticide, and promotes the removal of NH_4^+-N [23]. However, few studies have compared the treatability and operation costs between Fe–Mn enhanced coagulation and O_3-BAC toward the source water with seasonal non-point pollution, and optimized these two treatment strategies thereafter.

This study compares the treatability and costs of the abovementioned two processes toward the source water with seasonal non-point pollution in normal and polluted periods, and aims to propose feasible and economical technological strategies to optimize the removal of OM in plant scale. These field data may be valuable to enhance the treatment of non-point pollutants for many other DWTPs.

2. Materials and methods

2.1. Materials and reagents

Unless otherwise noted, all the reagents used in jar experiment were of analytical grade, while all the reagents used in plant-scale experiment were of industrial grade. Commercial poly aluminum chloride (PACl) was purchased from a purification reagent company in Jiangsu province, China, and used in the L-DWTP as the coagulant. The ratio of active species was about 10% as Al_2O_3.

2.2. Description of the treatment of L-DWTP

The L-DWTP locates in Jiangsu province, Eastern of China. Xiaoyin River, which is the downstream of Hongze Lake basin, serves as the water source. The location of L-DWTP and the source water is shown in Fig. 1. At the first pump station, raw water was pumped and then entered the plant after about 10 min. Pre-chlorination, pipe mixing, coagulation, laminar sedimentation, quartz sand filtration, and post-chlorination were the main treatment processes. The retention times for coagulation, sedimentation, and filtration were about 21 min, 1.7 h, and 20 min. Filtration rate was 9.7 m/h. Pre-chlorination dose ranged from 1.3 to 1.8 mg/L, and pose-chlorination dose ranged from 2.3 to 7.8 mg/L according to source water condition and plant operation condition. Three-stage tapered mixing was adopted to avoid the breakage of the formed flocs on the basis of adequate mixing, and the velocity in each stage was 0.28, 0.24, and 0.13 m/s, respectively. PACl was used as the coagulant, and the dose was about 30 mg/L. The designed treatment scale was 100,000 m^3/d, and the normal scale ranged from 80,000 to 120,000 m^3/d.

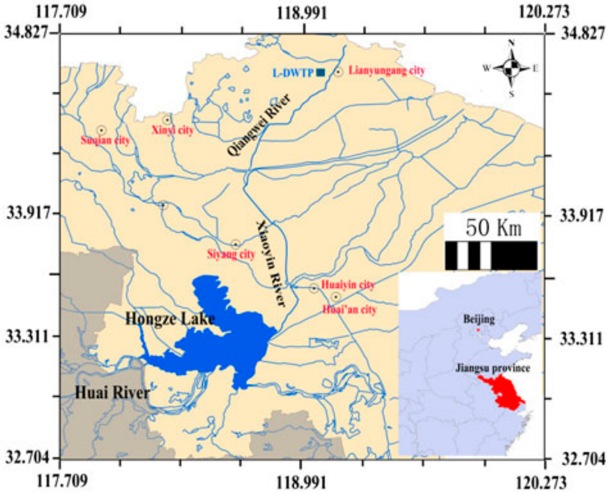

Fig. 1. Location of L LYG DWTP (L-DWTP) and the source water.

2.3. Experimental method

2.3.1. Bench-scale experiment

Batch jar tests were conducted in a ZR3-6 coagulation test mixer. Water samples were rapid-mixed (200 rev/min, 10 s) followed by the dosing of $FeCl_3$ and $KMnO_4$. After that, slow-mixing (40 rev/min, 10 min) was used to simulate the addition of reagents at the first pump station. Then, coagulant of PACl with a dose of 30 mg/L was added, followed by sequential slow-mixing (59 rev/min, 7 min; 50 rev/min, 7 min; and 32 rev/min, 7 min) to simulate the coagulation process. Then, static settling for 10 min was adopted to simulate the sedimentation process. The tapered mixing was to avoid the breakage of the formed flocs on the basis of adequate mixing. The abovementioned operating conditions was set to mimic the full-scale plant.

2.3.2. Plant-scale experiment for Fe–Mn enhanced coagulation

No substantial change in the treatment processes was done, except that $KMnO_4$ was dosed at the suction well of the first pump station, and $FeCl_3$ were dosed together with PACl at the pipe before coagulation and was mixed with water there. PACl dose was 30 mg/L, and the doses of $KMnO_4$ and $FeCl_3$ were 0.4–1.0 mg/L as $KMnO_4$ and 2.5–7.0 mg/L as $FeCl_3$.

2.3.3. O_3-BAC process

O_3-BAC process followed with filtration. The designed treatment scale was 200,000 m^3/d, and the normal scale ranged from 80,000 to 120,000 m^3/d. The capacity was designed double to set aside extra capacity for further upgrade of original processes. A 10-grids shutter filter was used for BAC filtration. The residence time was about 12 min, the filtration rate was about 10.9 m/h, and the empty bed contact was 0.2 h. Double-layer filter mediums of granular activated carbons and sand were used. The depths of granular activated carbon and sand filtration bed were

2.2 m and 0.5 m, respectively. These parameters were set by designers according to standards. DNA was extracted from filter medium to assess the number of microbe. DNA extraction was performed in triplicate for sample. Real-time PCR was used to obtain the quantitative distribution of bacteria, archaea, ammonia oxidation bacteria (AOB), and ammonia oxidation archaea (AOA).

2.4. Analysis methods

The concentration of dissolved organic carbon (DOC) in water sample was measured by a TOC-V_{CPH} total organic carbon analyzer (Shimadzu, Japan). NOM was fractionated using a stirred ultrafiltration cell device (Model 8200, Amicon, Millipore), and the experimental details followed the procedure done by Kitis et al. [24]. Ultraviolet spectra were measured by U-3010 UV–vis spectrophotometer (Hitachi Co., Japan) equipped with 10 mm quartz curettes and pH was measured using Orion 3 Star pH Bench top meter (Thermo Scientific, USA). Fluorescence spectra were measured using an F-4500 fluorescence spectrophotometer (Hitachi, Japan) according to the method established by Chen et al. [25]. Turbidity was measured with a 2100 Turbidity Meter (Hach Co., USA). COD_{Mn}, NH_4^+-N, chromaticity, and chloroform were measured according to standard methods [26]. Hierarchical cluster and *t*-test analysis was done with SPSS 22. DNA was extracted using a PowerWater DNA isolation kit (Mo Bio Laboratories, Inc., Carlsbad, CA, USA), and DNA concentration was measured by TBS-380 Fluorometer (Turner Biosystems, CA, USA). Bacterial and archaeal 16S rRNA or amoA were quantified by an ABI 7300 fast real-time PCR system based on the SYBR Green I method. The experimental details were described previously [27].

3. Results and discussion

3.1. Characterization of source water

Fig. 2(a) presents the influent levels of NH_4^+-N, COD_{Mn}, chromaticity, and turbidity for L-DWTP from 1 January 2008 to 15 December 2010. It was obviously observed that these parameters showed higher levels from June to August each year, indicating the seasonal heavy pollution of the sources. In order to quantitatively compare these two periods, we took half month as minimum calculated unit, and adopted hierarchical clustering by the Ward's method for sample classification. It was reported that hierarchical clustering by the Ward's method possesses a small space distorting effect, uses more information on cluster contents than other methods, and yields the most meaningful clusters [2].

The dendrogram of source water obtained by the Ward's method is shown in Fig. 2(b), and two well-differentiated clusters can be seen. The first group from the bottom is assorted with samples collected in periods from 16 June to 31 August 2008, from 16 June to 31 July 2009, and from 1 July to 15 August 2010. Fig. 2(a) shows that source water characteristics such as COD_{Mn} and NH_4^+-N increased sharply in these periods, and therefore were classified as polluted periods. The second group from the top was thus classified as normal period. In normal period, the average levels for COD_{Mn}, NH_4^+-N, turbidity, and chromaticity were 4.89, 0.45 mg/L, 17.3 NTU, and 18.4, respectively. In the polluted period, COD_{Mn}, NH_4^+-N, turbidity, and chromaticity increased sharply, with average values of 6.39, 1.10 mg/L, 23.9 NTU, and 28.1, respectively.

Source water was collected in different periods, and OM was also characterized. Table 1 shows the main characteristics of water samples collected in normal and polluted periods, respectively. In normal periods, the DOC level was 5.38 mg/L. The SUVA value for raw water was 1.52 L/cm mg, and the species with molecular weights in the range of 3–10 kDa had the highest SUVA level of 2.25 L/cm mg. SUVA value was reported to correlate well with aromatic carbon content and DBPs formation potential [28]. In polluted period, the DOC reached much higher level of 9.11 mg/L, and average SUVA value was as high as 2.29 L/m mg, implying that DBPs formed in this period may be in high levels [6]. Fig. 3(a) presents the molecular distribution of source water. In normal period, the molecular weight distribution was 25.7, 12.4, 15.0, 10.8, and 36.1% for fractions of >100, 30–100, 10–30, 3–10, and <3 kDa, respectively. While in polluted period, the corresponding molecular weight distribution was 22.3, 8.8, 12.8, 23.2, and 32.9%, respectively. The species with molecular weight below 10 kDa constituted 56.1% of the total DOC. This value was higher than that of 46.9% in normal period, and that of 44.2% in our previous study at WeiShan Lake [16]. It was reported that coagulation showed poor removal efficiency toward small MW NOM, e.g. MW < 10 kDa species [29]. It can thus be inferred that OM in this study was more difficult to be removed by coagulation than that in our previous study [16], especially during polluted period.

Fig. 3(b) presents the fluorescence excitation–emission matrix of source water, and the EEM spectra were divided into five regions based on the method established by Chen et al. [25]: region I and II (aromatic protein-like, $\lambda ex < 250$ nm, $\lambda em < 380$ nm),

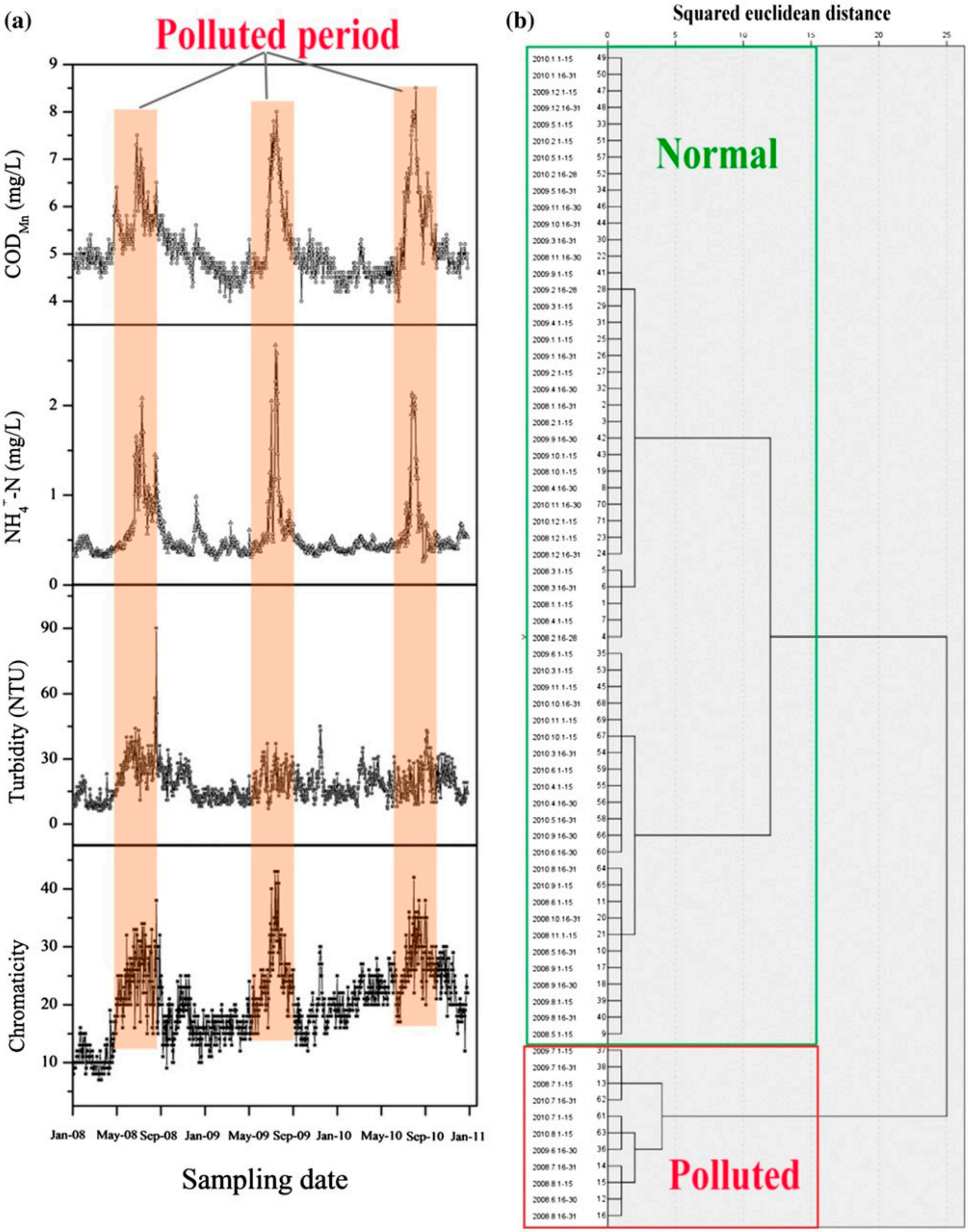

Fig. 2. Seasonal variation of COD$_{Mn}$, NH$_4^+$-N, turbidity, and color in influents of L-DWTP (2008.1.1-2010.12.15): (a) variation of water characteristics; (b) dendrogram based on hierarchical clustering (Ward’s method).

Table 1
Characterization of raw water and NOM fractions of L-DWTP collected in normal and heavily polluted periods

Date	Parameter	Raw water	MW > 100 kDa	30–100 kDa	10–30 kDa	3–10 kDa	<3 kDa
Normal period	DOC (mg/L)	5.38	1.38	0.67	0.80	0.68	1.94
	UV_{254} (cm^{-1})	0.082	0.014	0.012	0.012	0.013	0.012
	SUVA (L/m mg)	1.52	1.01	1.79	1.49	2.25	0.62
Heavily polluted period	DOC (mg/L)	9.11	2.03	0.80	1.17	2.11	3.00
	UV_{254} (cm^{-1})	0.209	0.031	0.022	0.032	0.058	0.074
	SUVA (L/m mg)	2.29	1.53	2.75	2.74	2.75	2.47

Notes: SVUA (specific ultraviolet absorbance) was calculated from ultraviolet absorbance at 254 nm (UV_{254}) divided by the dissolved organic carbon (DOC) concentration (SUVA = 100 × UV/DOC) (L/m mg).

region III (fulvic acid-like, $\lambda ex < 250$ nm, $\lambda em > 380$ nm), region IV (soluble microbial byproduct-like, $\lambda ex > 250$ nm, $\lambda em < 380$ nm), and region V (humic acid-like, $\lambda ex > 250$ nm, $\lambda em > 380$ nm). To quantify the difference between these two periods, the regional integration of the fluorescence spectra beneath each region was conducted by Eq. (1) [25]:

$$\Phi_{i,n} \approx \mathrm{MF}_i \sum\nolimits_{\mathrm{ex}} \sum\nolimits_{\mathrm{em}} I(\lambda_{\mathrm{ex}}\lambda_{\mathrm{em}})\Delta\lambda_{\mathrm{ex}}\Delta\lambda_{\mathrm{em}} (\text{For discrete data}) \tag{1}$$

where $\Phi_{i,n}$ is the normalized EEM volume beneath region "i" of the EEM; MF_i is a multiplication factor for each region. The $\Phi_{i,n}$ of OM during normal and polluted periods is shown in the bottom of Fig. 3(b).

It can be inferred that OM was dominated by aromatic protein and soluble microbial byproduct-like matters in normal period, whereas fulvic acid-like and humic acid-like matters in polluted period. The above results indicate that the source water for L-DWTP was severely impacted by human activities, especially by non-point pollution, such as non-point agricultural run-off, which may vary seasonally [3]. This raises a great challenge to L-DWTP, which is also the situation that quite a few DWTPs in China face [30].

3.2. Operation of DWTP without process upgrade

The effluent levels of COD_{Mn}, NH_4^+-N, turbidity, and chromaticity in normal and polluted periods were shown in Table 2. The average removal efficiencies of turbidity and chromaticity were 96.1 and 58.7%, and the average effluent levels were 0.7 NTU and 7.53, respectively. In most cases, turbidity and chromaticity levels can achieve the regulatory requirements of below 1 NTU and 15, respectively.

Histogram of effluent levels of COD_{Mn} and NH_4^+-N was shown in Fig. 4. The removal efficiency of NH_4^+-N was 68.5%, and effluents level was 0.17 mg/L on average. As is shown in Fig. 4, all of the effluents level of NH_4^+-N was below the regulatory maximum of 0.5 mg/L in normal period. However, in polluted period, 11.4% of the effluents level of NH_4^+-N exceeded the regulatory standard, and had a maximum of 1.6 mg/L. On the other hand, the original processes showed poor removal efficiency toward COD_{Mn}, with an average of 34.7%. The effluents concentration of COD_{Mn} was 3.31 mg/L on average, and the rates of effluent samples exceeding the limit were 74.9 and 98.7% in normal and polluted periods, respectively. High levels of NH_4^+-N and COD_{Mn} may serve as nitrogen and carbon source for the regrowth of micro-organism in the pipe distribution system, which may reduce the stability of water supply [5]. Moreover, OM may react with chlorine to form DBPs [6]. As shown in Table 2, chloroform was observed to exceed the limit by 14.2 and 56.2% in normal period and polluted periods, respectively, which may oppose great threaten toward people health [31].

3.3. Strategies to enhance removal of COD_{Mn} and optimize other relative indexes

3.3.1. Fe–Mn enhanced coagulation

Bench study about Fe–Mn enhanced coagulation was conducted prior to plant-scale study, and the result is presented in Fig. 5. It can be inferred that the addition of $KMnO_4$ may promote the removal of COD_{Mn}. Addition of 0.4–0.8 mg/L of $KMnO_4$ can result in increase in COD_{Mn} removal efficiency by 0.2–2.4%. However, the addition of $KMnO_4$ may also inhibit the removal of turbidity. Introduction of 0.4–0.8 mg/L of $KMnO_4$ may lead to increase in residual turbidity by 0.2–0.4 NTU. This can be explained that reduction of $KMnO_4$ to tiny particulate δMnO_2, which contributes to the increase in turbidity. Addition of $FeCl_3$ may promote the removal of both COD_{Mn} and turbidity. It can be inferred that the

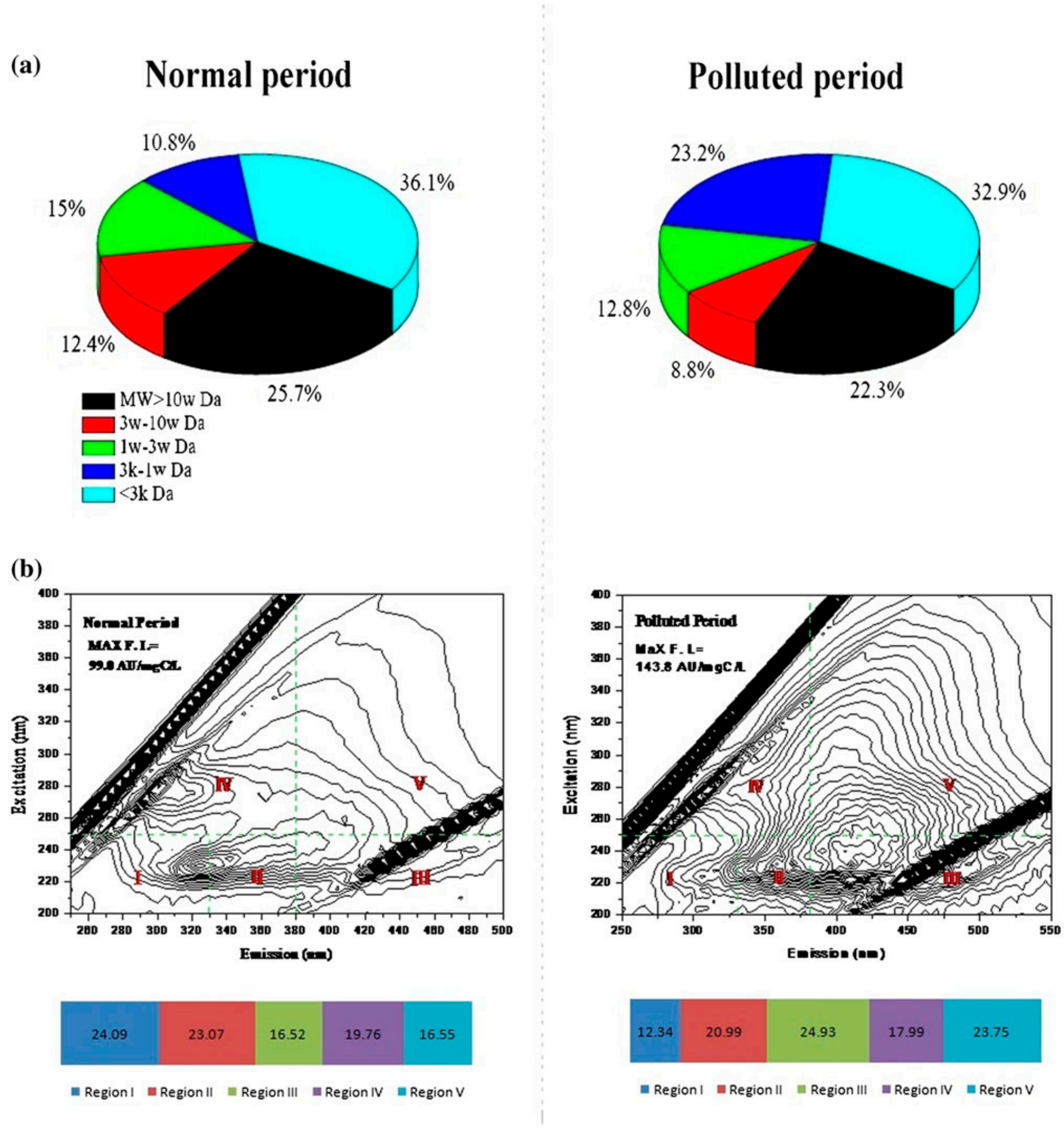

Fig. 3. Characterization of source water in normal period and polluted period: (a) molecular weight distribution; (b) fluorescence excitation–emission matrix.

removal efficiency of COD_{Mn} increased, while the residual turbidity decreased as the increased concentration of $FeCl_3$ at the same $KMnO_4$ concentration. When the concentration of $KMnO_4$ and $FeCl_3$ was 0.8 mg/L as $KMnO_4$ and 1.2 mg/L as Fe, the removal efficiency of COD_{Mn} increased to as high as 35.8% compared with 22.9% when no aiding coagulant was added. This increased removal efficiency of 12.9% indicates that about 97.1% of L-DWTP effluent COD_{Mn} values may meet the regulatory requirement

Table 2
Characterization of effluent water in normal and polluted periods (2008.1.1–2010.4.1)

	COD_{Mn} mg/L	NH_4^+-N mg/L	Turbidity NTU	Chromaticity	Pre-chlorination dose mg/L	Post-chlorination dose mg/L	Residual chlorine mg/L	$CHCl_3$ μg/L
Normal period	3.22	0.12	0.75	7.53	1.6	3.1	1.0	48.5
Polluted period	3.88	0.41	0.75	9.52	5.3	6.4	1.5	83.7
Standards in China	<3.0*	<0.5	<1	<15	/	/	>0.3	<60

*<5.0 if the source water exceeds 6 mg/L.

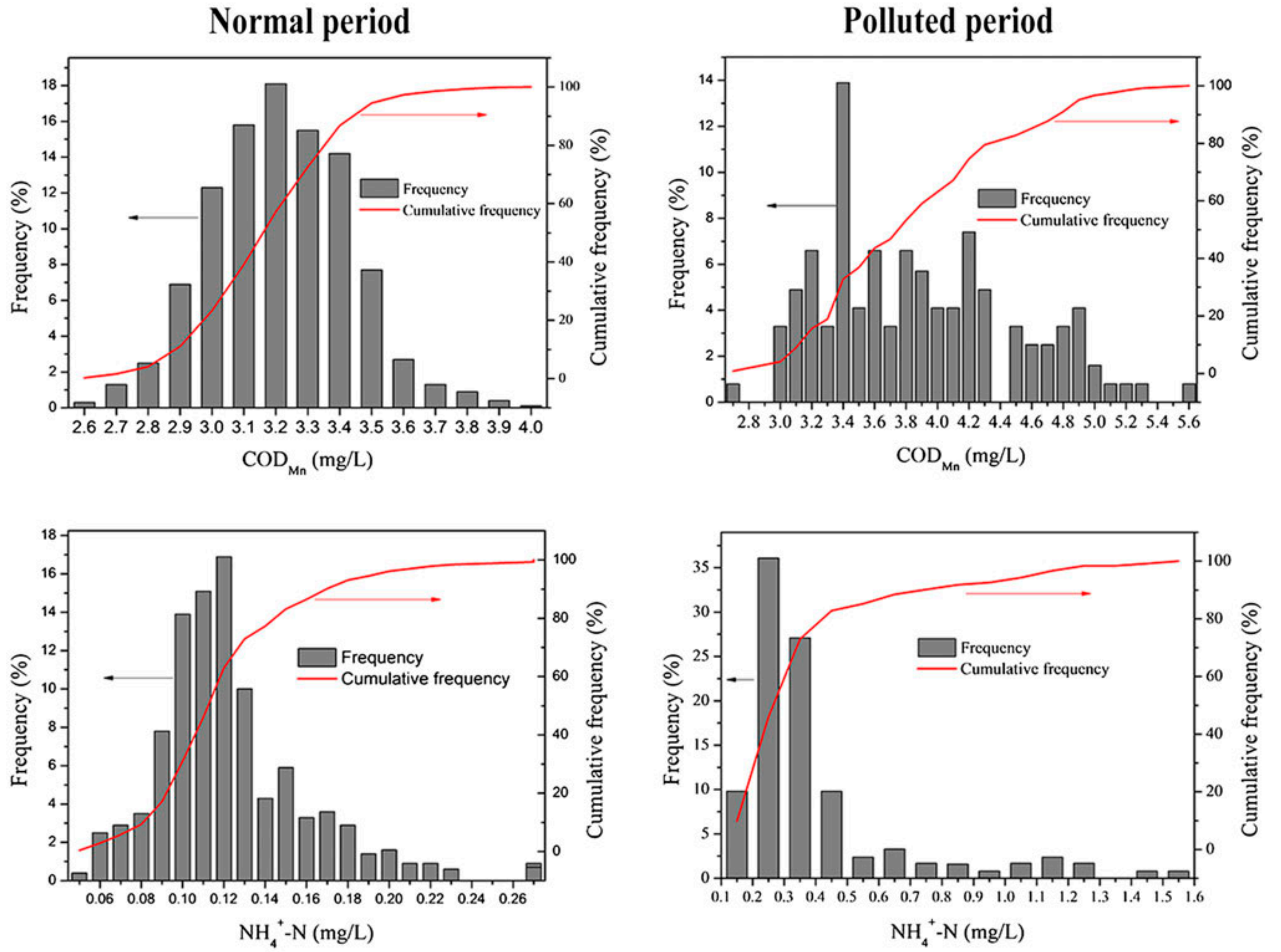

Fig. 4. Histogram of effluent levels of COD_{Mn} and NH_4^+-N for L-DWTP without process upgrade (2008.1.1-2010.4.1).

in normal period, and the corresponding value was 24.1% for polluted period. It can also be observed that when only $KMnO_4$ was added, COD_{Mn} removal efficiency only increased by 2.3% when the concentration of $KMnO_4$ increased from 0.4 to 0.8 mg/L. However, in the presence of 0.2–1.2 mg/L $FeCl_3$, the corresponding increased value was 3.2–10.2% because of the addition of $KMnO_4$. This confirmed the assumption that the addition of $KMnO_4$ and $FeCl_3$ has a synergistic effect with respect to the removal of OM. Further

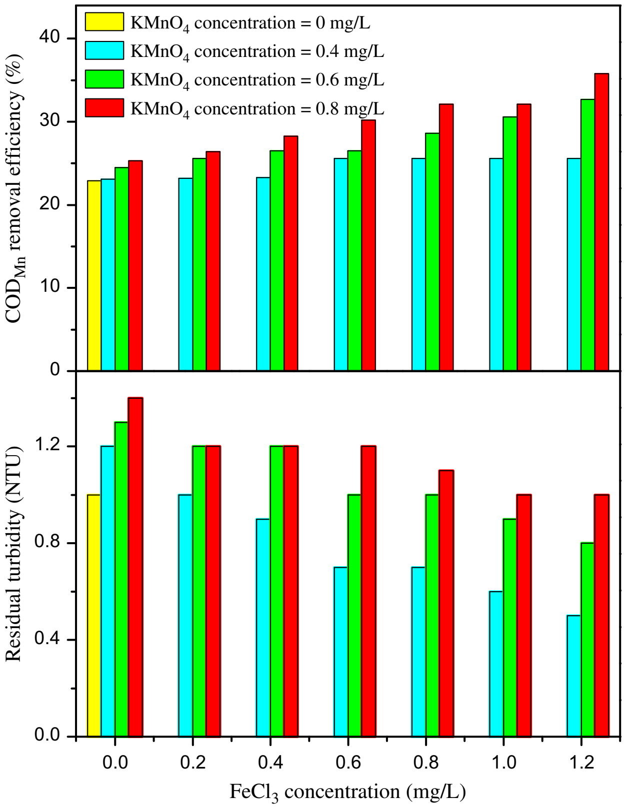

Fig. 5. Effect of different aiding coagulant concentrations on the removal of COD_{Mn} and turbidity (COD_{Mn} = 4.9 mg/L, turbidity = 13 NTU; coagulation condition: 200 r, 10´´ → 150 r, 2´22´´ → 59 r, 7´3´´ → 50 r, 7´4´´ → 32 r, 7´ → 0 r, 10´, and PAC dose = 30mg/L).

evaluation of the $FeCl_3$ and $KMnO_4$ in plant-scale study was to be carried out.

Because emergency measures such as addition of high dose of chlorine and PAC were adopted in polluted period, Fe–Mn enhanced coagulation was not processed in polluted period and only processed in normal period. Group statistics and *t*-test regarding the removal of COD_{Mn}, NH_4^+-N, turbidity, and chromaticity were shown in Tables 3 and 4. Significant difference ($p < 0.05$) was observed with the removal efficiency of COD_{Mn}, turbidity, and chromaticity, which increased by 10.6, 1.8, and 10.3%, respectively. As the average influent level of COD_{Mn} was 4.89 mg/L, it can infer that the removed COD_{Mn} was increased by 0.22 mg/L on average. It can be inferred from Fig. 4 that the effluent COD_{Mn} level achieved the rate increased from 23.3 to 94.5%, which was a great progress. In addition, COD_{Mn}, NH_4^+-N, turbidity, and chromaticity levels in each unit were also recorded in Table 5. It can be inferred that during normal period without process upgrade, coagulation, sedimentation, and filtration accounted for 56.0% of the removed COD_{Mn}, and post-chlorination accounted for 44.0%. While during Fe–Mn coagulation, the abovementioned ratios changed to be 83.8 and 16.2%. Post-chlorination contributed to much less of the total removal of COD_{Mn} and chromaticity. The reason for chlorination removed less COD_{Mn} and chromaticity during Fe–Mn enhanced coagulation was that $KMnO_4$ can be taken as pre-oxidant and less chlorine was used. Moreover, more COD_{Mn} and chromaticity was removed in coagulation process, and less was left to react with chlorine during post-chlorination. In addition, chloroform was also decreased by 26.4% to be 50.4 μg/L, achieving the standard of 60 μg/L. It was in accordance with the previous study that high chlorine contributive ratio may result in high effluents concentration of halogenated byproduct [32].

However, Fe–Mn enhanced coagulation showed obvious limitation during polluted period. It can be inferred from Fig. 4 that the upgrade effluent COD_{Mn} level achieved the rate only increased from 4.1 to 36.9%. In addition, no significant difference ($p < 0.05$) was observed regarding the removal of NH_4^+-N, which may be a serious problem in polluted period. Therefore, other measures should be adopted in polluted period.

3.3.2. Advanced treatment by O_3-BAC

Table 6 presents the plant-scale study after O_3-BAC was adopted in normal and polluted periods, respectively. Compared with conventional process, conventional process coupled with O_3-BAC had optimal removal toward COD_{Mn}, NH_4^+-N, turbidity, and chromaticity. In normal period, the removal efficiencies for COD_{Mn}, NH_4^+-N, turbidity, and chromaticity increased by 29.5, 6.7, 6.2, and 35.3%, respectively. In addition, chloroform was decreased by 50.9% to be 33.6 μg/L. In polluted period, the removal efficiencies for COD_{Mn}, NH_4^+-N, turbidity, and chromaticity increased by 25.5, 32.9, 0.3, and 25.0%, respectively. Moreover, chloroform was decreased by 43.0% to be 53.4 μg/L. The effluent levels of all abovementioned parameters can meet the regulatory standard both in normal and polluted periods.

The age of the BAC was 6 months when the plant-scale experiment was adopted. DNA concentration in filter medium test was 1,533 ng/g, indicating abundant micro-organism was present. Therefore, we assumed that the O_3-BAC system may undergo a period of sorption and biodegradation when the plant-scale experiment was adopted. Real PCR data

Table 3
Group statistics for removal efficiency

	Period	N	Mean	Std. deviation	Std. error mean
COD	1	813	32.513	5.113	0.179
	2	84	43.080	3.640	0.397
NH_4^+-N	1	813	70.590	8.107	0.284
	2	84	72.017	3.745	0.409
Turbidity	1	813	95.060	2.925	0.103
	2	84	96.890	1.908	0.208
Chromaticity	1	813	56.539	13.349	0.468
	2	84	66.829	9.015	0.984

Notes: Period 1: normal period without process upgrade; Period 2: normal period with Fe–Mn enhanced coagulation.

Table 4
Result of t-test for independent samples

		Levene's test for equality of variances		T-test for equality of mean						
									95% confidence interval of the mean difference	
		F	Sig.	T	df	Sig. (two-tailed)	Mean difference	Std error difference	Lower	Upper
COD_{Mn}	Equal variance assumed	14.087	0.000	−7.977	895	0.000	−10.566	0.572	−11.690	−9.443
NH_4^+-N	Equal variance assumed	9.806	0.002	−1.595	895	0.111	−1.427	0.895	−3.183	0.329
Turbidity	Equal variance assumed	15.430	0.000	−5.597	895	0.000	−1.826	0.326	−2.466	−1.186
Chromaticity	Equal variance assumed	15.337	0.000	−6.902	895	0.000	−10.289	1.491	−13.215	−7.363

showed that gene copies in filter medium were 3,213, 609, 253, and 27 mg/g for bacteria, archaea, AOB, and AOA, respectively. Therefore, it can be inferred that bacteria may play the most important role regarding the removal of COD_{Mn} and NH_4^+-N in the BAC system.

3.4. Cost evaluation

Cost evaluation was carried out for the processes upgrading of Fe–Mn enhanced coagulation and O_3-BAC in normal and polluted periods. The treatment scale was set stable as 100,000 m^3/d. Cost in this study was obtained partly according to the operational experience, and partly assumed according to the designed parameters and the current price of used reagents. The average cost during conventional treatment was $33.7/kilostere and this was assumed to remain the same during process improvement periods. Based on optimal doses in Table 7, $FeCl_3$ cost of $578 per ton at 32.7% iron, $KMnO_4$ cost of $2,489 per ton, the costs for $FeCl_3$, and $KMnO_4$ were obtained. Other costs of $0–1.5/kilostere were obtained based on plant-scale experience. The costs for Fe–Mn enhanced coagulation were shown in Table 7.

The costs of O_3-BAC process were considered as the sum of three components: operating costs for ozonation, operating costs for BAC filtration, and other costs such as capital costs and maintenance costs. Operation costs for ozonation were based on oxygen cost of $0.16/kg, production rate of 10% from oxygen to ozone, and electric cost of $1.6/kg ozone, and yielded a figure of $1.6–8.1/kilostere in normal period and $9.6–12.8/kilostere in polluted period. Operating costs for BAC filter were calculated as the costs of first fill and regeneration of BAC. The filled

Table 5
The removal of turbidity, COD_{Mn}, and chromaticity at different unit processes by Fe–Mn enhance coagulation in plant-scale field investigation (PAC doses were 30 mg/L)

			Turbidity		COD_{Mn}		Chromaticity		NH_4^+-N	
	Sampling site	Cl_2 dose (mg/L)		Removal (%)	Concentration (mg/L)	Removal (%)		Removal (%)	Concentration (mg/L)	Removal (%)
Control Period	Influents	Pre:1.74,	8.3	/	5.12	/	18.2	/	0.63	/
	After sed.	Post:6.23	6.7	19.3	4.63	9.6	11.3	37.9	*N.A.*	/
	After Fil.		1.4	79.1	4.11	11.2	11.2	0.9	*N.A.*	/
	Effluents		1.2	14.3	3.2	22.1	6.9	38.4	0.20	68.3
(30 November–5 December 2010)	Total	7.97		85.5		37.5		62.1		68.3
Experiment period	Influents	Pre:1.68,	18.9		4.87	/	23.1	/	0.46	/
	After sed.	Post:2.89	4.8	74.6	3.56	26.9	10.9	52.8	*N.A.*	/
	After Fil.		0.6	87.5	3.20	10.1	7.0	35.8	*N.A.*	/
	Effluents		0.5	16.7	2.86	10.6	5.9	15.7	0.13	71.7
(19 October–29 November 2010)	Total	4.57		97.4		41.3		74.5		71.7

Table 6
The removal of turbidity, COD_{Mn}, chromaticity, and NH_4^+-N at different unit processes after O_3-GAC was adopted in plant-scale field investigation (PAC doses were 30 mg/L)

		Turbidity		COD_{Mn}		Chromaticity		NH_4^+-N	
	Sampling site	Con. (NTU)	Removal (%)	Con. (NTU)	Removal (%)	Con. (N)	Removal (%)	Con. (mg/L)	Removal (%)
Normal period (6 January–2 July 2012)	Influents	19.0		4.74		23.8		0.60	
	After sed.	4.4	76.8	3.9	17.7	16.7	29.8	0.45	25.0
	After Fil.	1.2	72.7	3.3	15.4	11.4	31.7	0.31	31.1
	After GAC	0.4	66.7	1.9	42.4	3.0	73.7	0.27	12.9
	Total		97.9		59.9		87.4		55.0
Polluted period (3–20 July 2012)	Influents	56		9.4		40		3.13	
	After sed.	4.8	91.4	5.8	38.3	25	37.5	2.53	19.2
	After Fil.	0.7	85.4	5.2	10.3	16	36.0	2.13	15.8
	After GAC	0.5	28.6	2.8	46.2	6	62.5	0.93	56.3
	Total		99.1		70.2		85.0		70.3

Table 7
Cost evaluation of Fe–Mn enhanced coagulation and O_3-BAC

Periods		Fe–Mn enhanced coagulation				O_3-BAC			
		$FeCl_3$	$KMnO_4$	Other	Total	O_3[a]	BAC[b]	Other	Total
Normal	Dose (mg/l)	0.2–0.6	0.2–0.6			0.5–2.5	/	/	/
	Cost ($/ML)*	0.4–1.1	0.5–1.5	0–1.5	0.9–4.1	1.6–8.1	6.0–10.0	9.6–16.1	17.1–34.2
Heavily polluted	Dose (mg/L)	0.8–1.2	0.8–1			3–4	/	/	/
	Cost ($/ML)	1.4–2.2	2.0–2.5	0–1.5	3.4–7.2	9.6–12.8	6.0–10.0	9.6–16.1	25.2–38.9

[a] O_3 cost = (oxygen cost/production rate + electric cost) × O_3 dose.

[b] GAC cost = GAC capacity × [(1 − generation rate) × GAC fill cost + generation rate × GAC generation cost]/(life span × DWTP scale).

*The RMB to US dollar exchange rate was 0.1606.

volumes were 1,760 m^3, and therefore 880 ton of BAC with density of 0.5 ton/m^3 was needed. The designed lifespan was estimated at 3–5 years both in normal period and polluted period, and then 50% of the BAC was replaced and 50% was regenerated. Based on the BAC cost of $1,600 per ton and generation cost of $800 per ton, the operation costs for BAC were obtained as $6.0–10.0/kilostere both in normal and polluted periods. Other costs shown in Table 7 were obtained based on plant-scale experience.

It can be inferred that Fe–Mn enhanced coagulation is more economical in all cases. Freese et'al. assessed the cost of enhanced coagulation and advanced treatment, and concluded that enhanced coagulation was less economic attractive than advanced treatment processes in the case of treating polluted waters at large works [10]. It was ascribed to that enhanced coagulation was achieved by increasing the coagulant by more than seven times in polluted condition compared with clean condition in that study. While in this study, PACl coagulant remained stable and only small extra doses of $FeCl_3$ and $KMnO_4$ were added.

4. Conclusion

It is a great challenge for many DWTPs in China to achieve the newly issued drinking water standards, i.e. COD_{Mn}, especially for those use source water with seriously polluted non-point pollution. This plant-scale investigation indicates that the traditional processes can hardly meet the regulatory standard for parameters such as COD_{Mn}. The source water condition exhibited two different periods of normal and polluted periods. The original processes showed poor removal efficiency toward COD_{Mn}, with an average of 34.7%. The concentration of effluents of COD_{Mn} was 3.31 mg/L on average, and the rates of effluent samples over the limit were 74.9 and 98.7% in normal and polluted periods, respectively. In addition, 11.4% of the effluents level of NH_4^+-N exceeded the regulatory standard in polluted period. Moreover, chloroform was observed to exceed the limit by 14.2 and 56.2% in normal period and polluted period, respectively. The combined use of $FeCl_3$ and $KMnO_4$ (Fe–Mn enhanced coagulation) increased the COD_{Mn} removal efficiency by 10.7%, and the rate of effluent COD_{Mn} levels exceeding the state regulation requirement, decreased to be 5.5% in normal period. In addition, chloroform was also decreased by 26.4% to achieve the required standard. Unfortunately, Fe–Mn enhanced coagulation cannot achieve the regulatory standard in polluted period. In this case, O_3-BAC worked well and effluent COD_{Mn}, NH_4^+-N and chloroform levels may all meet the regulatory requirement both in normal and polluted periods. Bacterial was observed to play a key role in the BAC system. Cost was also evaluated and compared between abovementioned two technologies. The average cost during conventional treatment was $33.7/kilostere and this would remain the same during process improvement periods. The extra costs during Fe–Mn enhanced coagulation were $0.9–4.1/kilostere and $3.4–7.2 in normal and polluted periods, respectively, while the corresponding values were $17.1–34.2/kilostere and $25.2–38.9/kilostere for O_3-BAC. Comparatively, the average cost of Fe–Mn enhanced coagulation was only about 8.6 and 11.2% of that for O_3-BAC in normal and polluted periods, respectively. Based on abovementioned economic and feasible considerations, it is proposed to use Fe–Mn enhanced coagulation in normal period and to implement O_3-BAC during polluted period. These obtained plant-scale data are valuable to optimize the operation of DWTPs with similar challenges.

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