Removal natural organic matter by coagulation–adsorption and evaluating the serial effect through a chlorine decay model

Xiao Zhan, Baoyu Gao*, Qinyan Yue, Bin Liu, Xing Xu, Qian Li

Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Ji'nan 250100, China

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ABSTRACT

The removal of natural organic matter (NOM) by coagulation and adsorption on modified wheat straw (MWS) was investigated. Two types of inorganic polymer coagulants, polyferric chloride (PFC) and polyaluminum chloride (PAC), were used during experiments. The removal efficiency of NOM in terms of UV_{254}, DOC and COD_{Mn} increased with the dosage of coagulants and adsorbent increasing. Combined coagulation and adsorption showed better UV_{254} and turbidity removal efficiency (61.8% and 95.8% respectively for PFC–MWS, and 61.5% and 94.2% respectively for PAC–MWS) than individual treatment. The effects of combination sequences on DOC fractionation and residual chlorine decay were analyzed and the chlorine data were fitted using a chlorine decay model. In general, the higher the molecular weight of NOM was, the better removal efficiency the combined treatment can achieve. MWS can enhance the removal of NOM with higher molecular weight. The disinfection by-products (DBPs) formation potential in the effluents from coagulation and subsequent adsorption was greater than that in the effluents from adsorption and subsequent coagulation.

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1. Introduction

Natural organic matter (NOM) is a major concern in water treatment, because it can lead to taste, odor and color problems in potable water, and bacterial regrowth in distribution systems [1]. More importantly, NOM serves as a precursor for the formation of disinfection by-products (DBPs) [2–4] if it is insufficiently removed. Therefore, the removal of NOM has become increasingly important issues in drinking water treatment [5].

Drinking water treatment processes mainly consist of coagulation, sedimentation, and gravity filtration, and coagulation is an essential process for the removal of various particulates and organic matter [6,7]. Nevertheless, there are some organic compounds, which cannot be removed at all in a coagulation step. Moreover, conventional treatment processes are periodically faced with challenging water conditions whereby NOM removal can be compromised [8]. In such cases, other processes are needed.

Enhanced coagulation has been proposed as one of the best technology for NOM removal [1], but it increases chemical addition and the production of sludge [9]. Activated carbon is an effective method to remove NOM and has been widely used [10,11], but the running costs are expensive. Further development of adsorbents has been investigated, which are made from agricultural residues (AR). Many researchers have used the materials such as sugarcane bagasse [12], peanut hull [13], apple pomace [14], wheat straw [14], sawdust [15], coconut husk [16], orange peel [17], banana pith [18] and pine bark [19] as adsorbents to remove dyes, heavy metals, nitrate, etc. Wheat straw (WS) is one of the major AR in China and is low-cost and availability [20]. Modified wheat straw (MWS) showed high adsorption capacity. For example, the adsorption capacity is 100–200 mg/g for NO_3^-, 50–85 mg/g for PO_4^{3-}, 200–600 mg/g for Cr^{6+} and 400–5000 mg/g for different organic acid dyes. MWS as an adsorbent is an attractive alternative in water treatment, of which the industry potential is now being reconsidered [19]. However, there is no available literature on NOM removal by MWS.

In this paper, MWS and two types of inorganic polymer coagulants, polyferric chloride (PFC) and polyaluminum chloride (PAC), were used to treat the Yellow River water, which is an important source for drinking water in northern part of China. NOM removal efficiency by individual coagulation and adsorption with MWS as well as the combination treatment was investigated. The fractions of dissolved organic matter (DOM) were analyzed in different combination treatment sequences of coagulation and adsorption. Moreover, the chlorine decay experiments were conducted to estimate the fast and slow reacting nitrogenous as well as organic/inorganic compounds using a chlorine decay model. The formation of DBPs was estimated by the model in order to evaluate the treated water quality.

* Corresponding author. Tel.: +86 531 88364832; fax: +86 531 88364513.
E-mail addresses: zhxiao2007@126.com (X. Zhan), bygao@sdu.edu.cn
(B. Gao), qyyue@sdu.edu.cn (Q. Yue), liubin19860607@126.com (B. Liu), xuxing1984@mail.sdu.edu.cn (X. Xu), liqian@mail.sdu.edu.cn (Q. Li).

Table 1
Characteristics of coagulants.

Coagulant	B	W (Fe_2O_3 or Al_2O_3)/%	Species of Fe or Al (%)			pH
			Fe_a/Al_a	Fe_b/Al_b	Fe_c/Al_c	
PFC	0.5	10.0	17.4	29.8	52.8	0.70 ± 0.10
PAC	2.0	4.5	14.8	32.1	53.1	2.85 ± 0.10
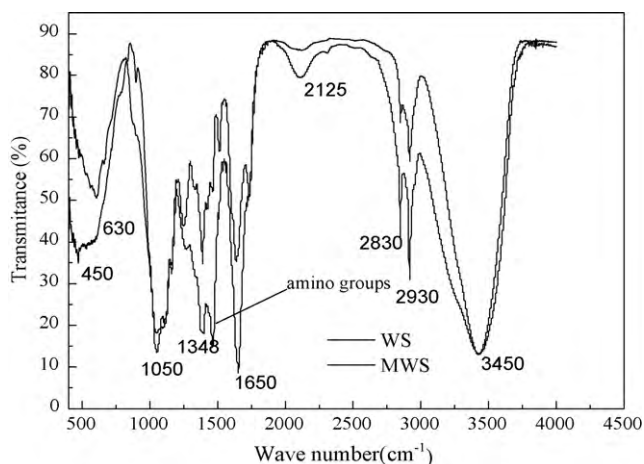
Fig. 1. The IR analysis of MWS and WS.

2. Materials and methods

2.1. Preparation of PAC, PFC and MWS

PAC and PFC used in this study were prepared by dissolving a certain concentration of $AlCl_3 \cdot 6H_2O$ (A.R.) or $FeCl_3 \cdot 6H_2O$ (A.R.) in distilled water, then slowly mixing with Na_2CO_3 powder to obtain the desired basicity value (B, [OH]/[Al] or [OH]/[Fe] ratio) [21,22]. The temperature for the preparation of PAC was kept at 80 °C. The solution of PFC was stirred at room temperature until foam disappeared and became transparent, then, Na_2HPO_4 (A.R.) was added to the solution as a stabilizer ($[Na_2HPO_4]/[Fe] = 0.08$). The characteristics of the coagulants are presented in Table 1.

MWS was prepared from WS, which was obtained from Liao Cheng, Shandong, China. WS was washed with water, dried at 60 °C for 6 h and sieved into particles with diameters 100–250 μm. Then, 2 g of WS were added in a 250 mL three-neck round bottom flask with 20 mL of epichlorohydrin and 25 mL of N,N-dimethylformamide for 1 h. 4 mL of ethylenediamine was added and the solution was stirred for 1 h, followed by adding 20 mL of 99% triethylamine (w/w) and the mixture was stirred for 3 h. The whole process was kept at 85 °C. The product was washed with distilled water to remove residual chemicals, dried at 60 °C for 12 h and then used in all the adsorption experiments. Zeta potential of MWS was determined by electro-kinetic analyzer (JS94H Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) and was +37 mV. The surface area of MWS was 5.7–8.5 m²/g. IR spectra of MWS and WS were recorded on a PerkinElmer "Spectrum BX" spectrometer in the 4000–400 cm⁻¹ region and the results are shown in Fig. 1. As shown in Fig. 1, ketone groups were observed by the band intensity at 2930 cm⁻¹, and the band at 1650 cm⁻¹ was associated with the special vibration of aromatic cyclic groups. The intense

vibration at 1348 cm⁻¹ further indicated that a large number of amino groups have been grafted into the MWS structure.

2.2. Test water

The test water was collected from Jinan (Shandong, China) section of the Yellow River and settled for 24 h to remove silt. The characteristics of the water samples after settlement are shown in Table 2. All the experiments were conducted under the raw water condition.

2.3. Batch tests

2.3.1. Coagulation jar-test experiments

Standard jar tests were conducted on a program-controlled jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at room temperature. 1000 mL of test water was transferred into a beaker and involved a 1 min rapid mix at 200 rpm, a 15 min 40 rpm flocculation stage, and 25 min settlement period for PAC and 15 min for PFC. Then a sample was collected from 2 cm below the surface for measurements and subsequent tests.

2.3.2. Batch adsorption tests

Adsorption experiment was carried out by agitating MWS with test water at the room temperature in a stirrer operating at 150 rpm for 120 min. Subsequently, MWS was removed by filtration through a sand core funnel (G2). A sample was collected for the measurement.

2.3.3. Combined coagulation and adsorption tests

Coagulation and adsorption were combined in the following sequences: (i) coagulation and subsequent adsorption (PFC–MWS/PAC–MWS), (ii) adsorption and subsequent coagulation (MWS–PFC/MWS–PAC). Coagulation and subsequent adsorption tests were conducted by adding various doses of MWS in test water which was collected from 2 cm below the water surface after sedimentation in the coagulation test. Adsorption and subsequent coagulation tests were carried out in the beakers by adding the MWS in stirrers operating at 150 rpm for 120 min and subsequently adding varying dosage of coagulants under the same mixing conditions as coagulation jar-tests. After settling, a sample was collected from 2 cm below the surface for the measurement.

2.4. DOM isolation

The water samples were firstly passed through 0.45 μm membranes to remove particulate matter, and then filtered through ultra filtration membranes (Shanghai Mosu Science Equipment Co. Ltd., China) to be divided into 6 size fractions: >100, 100–30, 30–10, 10–5, 5–1 and <1k Da. DOC was analyzed for each size fraction of

Table 2
Physicochemical characteristics of test water.

T/°C	Turbidity/NTU	pH	DOC/mg L⁻¹	UV_{254}	COD_{Mn}/mg L⁻¹	Hardness/mg $CaCO_3$ L⁻¹	Alkalinity/mg $CaCO_3$ L⁻¹
15–20	10.1–15.6	8.07–8.42	2.058–2.979	0.058–0.071	2.30–2.85	260–300	200–230

DOM. The percentages of DOC, in each size range were calculated as follows:

$$\% < 1k\ Dalton\ (Da) = \frac{C_{1kpermeate}}{C_{raw}} \times 100\% \tag{1}$$

$$\%5k\text{--}1k\ Da = \frac{C_{5kpermeate} - C_{1kpermeate}}{C_{raw}} \times 100\% \tag{2}$$

$$\%10k\text{--}5k\ Da = \frac{C_{10kpermeate} - C_{5kpermeate}}{C_{raw}} \times 100\% \tag{3}$$

$$\%30k\text{--}10k\ Da = \frac{C_{30kpermeate} - C_{10kpermeate}}{C_{raw}} \times 100\% \tag{4}$$

$$\%100k\text{--}30k\ Da = \frac{C_{100kpermeate} - C_{30kpermeate}}{C_{raw}} \times 100\% \tag{5}$$

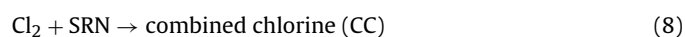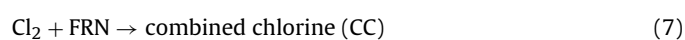$$\% > 100k\ Da = \frac{C_{raw} - C_{100kpermeate}}{C_{raw}} \times 100\% \tag{6}$$

where $C_{ipermeate}$ is the DOC concentration of the effluent after filtering through i ultra filtration membrane (i = 1k, 5k, 10k, 30k, 100k). C_{raw} is the DOC concentration of the raw water after filtering through 0.45 μm membranes.

2.5. Chlorine decay experiments

500 mL of samples were collected from: (i) treated water collected from 2 cm below the surface after coagulation; (ii) treated water filtered through the sand core funnel (G2) after coagulation and subsequent adsorption; and (iii) treated water filtered through the sand core funnel (G2) after adsorption and subsequent coagulation. In the experiments, the collected samples were dosed with 2.0 and 2.5 mg/L chlorine, respectively. Dark brown bottles were used to prevent light penetration or algal growth and thus to obtain the decay of chlorine due to reducing compounds present in water samples. Free and total chlorine concentrations were measured immediately after dosing (1 min), then at short intervals for the first 1 h and at longer intervals for the next 3 days.

2.6. Chlorine decay model

There are some kinds of models for chlorine decay and DBPs formation available in the literature [23–26]. In this study, a simple and efficient model proposed by Kastl et al. [27] is used. The model estimates the initial rapid decay as well as the slow continuing decay of chlorine in the test sample. The model considers the initial rapid decay due to fast reducing agents (FRA) and fast reducing nitrogenous compounds (FRN) and the continuing slow decay due to slow reacting agents (SRA) and slow reacting nitrogenous compounds (SRN). FRN and SRN will react with chlorine to produce combined chlorine (CC). The sum of free and combined chlorine will be the total chlorine (TC). The organic compounds of FRA and SRA are considered as the DBPs formation precursors. The reactions used in the model can be described as follows:

$$Cl_2 + FRN \rightarrow combined\ chlorine\ (CC) \tag{7}$$

$$Cl_2 + SRN \rightarrow combined\ chlorine\ (CC) \tag{8}$$

$$Cl_2 + FRA \rightarrow inert\ products + DBPs \tag{9}$$

$$Cl_2 + SRA \rightarrow inert\ products + DBPs \tag{10}$$

$$CC \rightarrow inert\ products \tag{11}$$

While Cl_2 indicates the available free chlorine present in the water, the sum of Cl_2 and CC indicates the total chlorine present in the water. The reaction rates for the above equations are k_1, k_2, k_3, k_4 and k_5, respectively. Thus the equations of the decay of free and combined chlorine can be written as:

$$\frac{d[Cl_2]}{dt} = -k_1[Cl_2][FRN] - k_2[Cl_2][SRN] - k_3[Cl_2][FRA]$$
$$- k_4[Cl_2][SRA] \tag{12a}$$

$$\frac{d[CC]}{dt} = -k_5[CC] + k_1[Cl_2][FRN] + k_2[Cl_2][SRN] \tag{12b}$$

$$[TC] = [Cl_2] + [CC] \tag{12c}$$

The model is constructed in AQUASIM 2.0 and the parameters are estimated to find the best fit of the model to the experimental data [28].

2.7. Analytical methods

Zeta potential was measured with a Zetasizer 3000HSa (Malvern Instruments, UK). Collected sample was filtered through a 0.45 μm membrane to measure UV_{254} and DOC. UV_{254} was measured at a 254 nm wavelength using a UV-754 UV/VIS spectrophotometer (Shanghai Jinhua Group Co., Ltd., China). DOC was analyzed with a TOC analyzer (Shimadzu, Japan). Turbidity was measured using a portable turbidimeter 2100P (Hach, America). The free and total chlorine was tested with a Free&Total chlorine measuring meter HI93711 (Hanna, Italy). The measurements of permanganate index (COD_{Mn}) were performed according to the standard methods established by the China National Environmental Protection Agency [29].

3. Results and discussion

3.1. Coagulation efficiency

Fig. 2 shows the effect of PFC and PAC dose on turbidity, UV_{254}, DOC and COD_{Mn} removal for the settled Yellow River water treatment. PFC and PAC dosages range from 0.02 mmol/L to 0.24 mmol/L as Fe or Al. The results showed that the two coagulants gave similar turbidity removal trend: a sharp increase with the increase of coagulant dosage and the removal efficiency exceeded 90% at a dosage of 0.08 mmol/L. As the dosage further increased, PFC reached a plateau. In the case of PAC, the turbidity removal presented a slight decrease at a dosage more than 0.18 mmol/L due to the restabilization of flocs. The reason may be that: when PAC is over dosage, the positive charge of flocs increases, furthermore, repulsion interaction among flocs is enhanced and so flocs are restabilized and dispersed in treated samples.

The trend of the UV_{254}, DOC and COD_{Mn} removal curves was similar for PAC and PFC. The higher the coagulant dosage, the better the coagulation performance. PAC was a bit better for removing UV_{254}, DOC and COD_{Mn} than PFC within the dose investigation. Considering turbidity removal efficiency, a dose of 0.18 mmol/L of PAC was chosen for the subsequent chlorine decay experiments, while the dose that gave the maximum turbidity, UV_{254}, DOC and COD_{Mn} removal was 0.24 mmol/L for PFC which was chosen for the subsequent tests.

The variations of zeta potentials and pH after coagulation against coagulant dosage are shown in Fig. 3. It can be seen that after coagulation, the solution pH was slightly decreased with the increased dosage of coagulant. In the term of zeta potential, PFC gave only a very slight increase and remained below zero in flocs zeta potentials within the dosage investigation. While the coagulation efficiency of PFC increased as the dosage increasing, which indicated that both adsorption-bridging and electric neutralization implicated into the coagulation process for Yellow River water treatment. When PFC was dosed into the test water, initially, the NOM would be coagulated by charge neutralization ability of PFC, then flocs formed and increased gradually through the adsorption-bridging
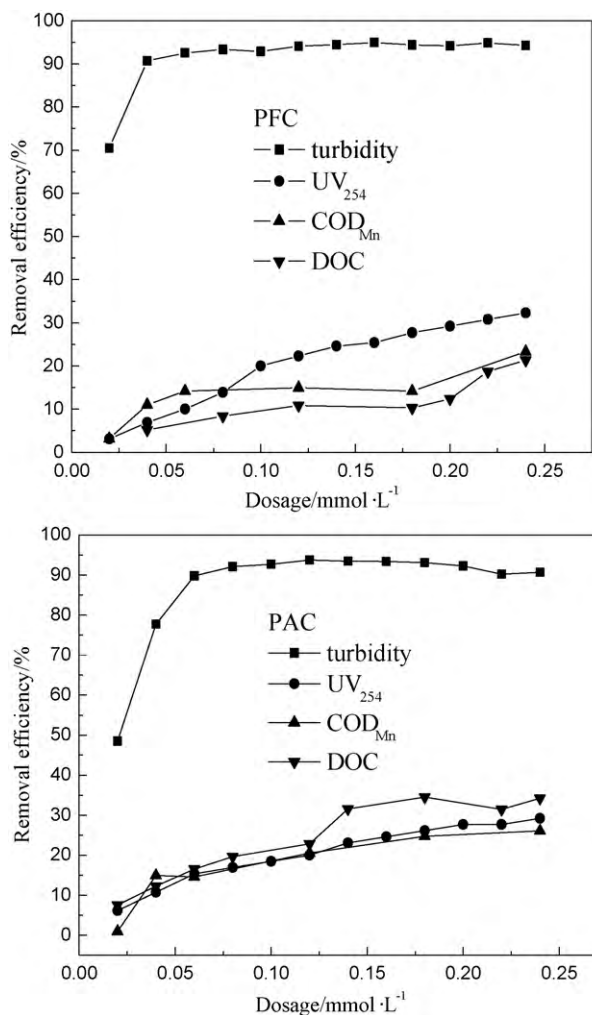
Fig. 2. Turbidity, UV_{254}, COD_{Mn} and DOC removal for PFC and PAC coagulation.

ability of coagulant. Finally, the flocs settled and was removed from the water. Zeta potentials of flocs formed by PAC increased gradually and reached the isoelectric points at a dosage of about 0.17 mmol/L. It was noted that turbidity removal efficiency of PAC reached the optimal values when zeta potential was close to the isoelectric point, which suggested that the electric neutralization played an important role in the treatment of Yellow River water by PAC.

3.2. Adsorption efficiency

The variations of UV_{254}, DOC and turbidity removal efficiencies with MWS dosages as well as the pH after adsorption are illustrated in Fig. 4. As shown in Fig. 4, the solution pH was slightly decreased after adsorption. An increase of coagulant dosage resulted in a rapid increase of turbidity removal. However, the increasing rate became slight when the dosage was higher than 0.025 g/L. The minimum residual turbidity was 7.86 NTU which was much higher than that of coagulation effluent (<1 NTU). Both UV_{254} and DOC removal increased with the increasing MWS dose. Compared with the results shown in Fig. 2, it indicated that MWS gave higher UV_{254} and DOC removal efficiency than PFC and PAC. The adsorption of NOM can be ascribed to the amino groups which are used as adsorption sites for removing NOM [20]. The zeta potential of the NOM in the raw water was negative. There may be an electrostatic attraction between the NOM and the amino groups. Trying to model
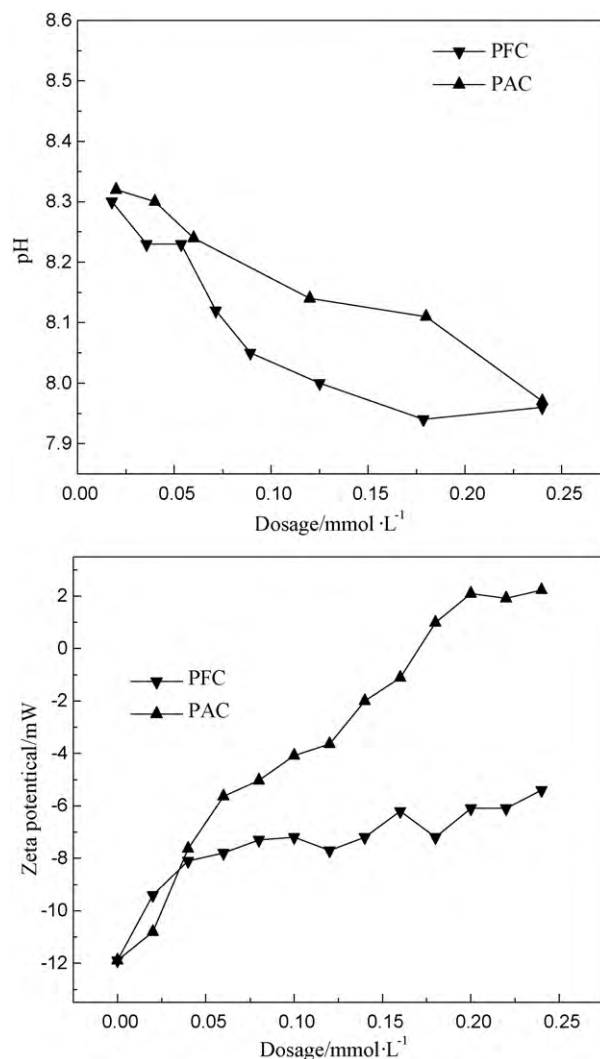

Fig. 3. Zeta potentials and pH after coagulation as a function of coagulant dose in Yellow River water treatment.

the NOM removal results according to the Langmuir or Freundlich isotherm were problematic because NOM in natural water is not a pure chemical and could not be 100% adsorbed by MWS even at a high adsorbent dosage [30].
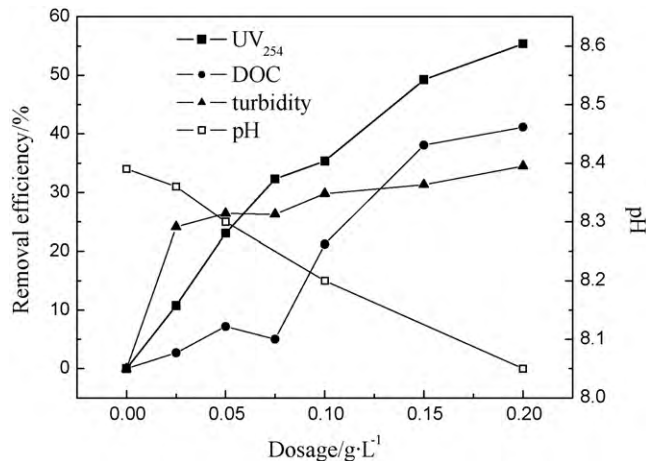

Fig. 4. Turbidity, UV_{254} and DOC removal for MWS adsorption as well as the pH after adsorption.
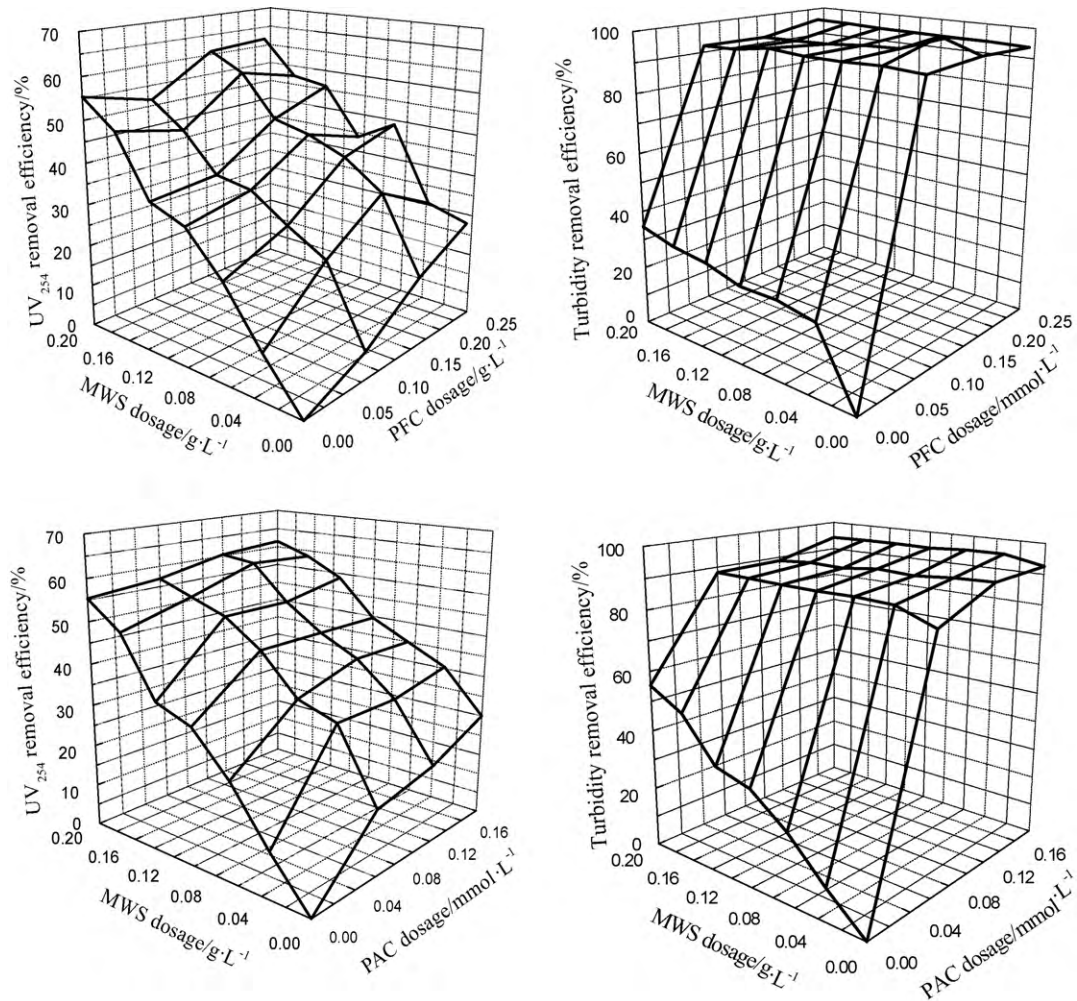
Fig. 5. Turbidity and UV_{254} removal for combination of coagulation (PFC or PAC) and adsorption (MWS) at different dosages.

3.3. Combination of coagulation and adsorption

In order to investigate the effectiveness of combined coagulation and adsorption processes for NOM removal, coagulant PAC or PFC was used together with MWS. As seen in Fig. 5, at the fixed coagulant dosage, increase in adsorbent dosage resulted in greater influence on UV_{254} removal than on turbidity removal, whereas increase in coagulant dosage at the constant adsorbent dosage reduced the turbidity to a larger extent, which was consistent with the results presented above (Figs. 2 and 4). Compared with the individual treatment, the combined process gave higher turbidity and UV_{254} removal efficiency. However, UV_{254} removal efficiency of the combined coagulation and adsorption system was less than the superposition of individual treatment efficiencies (Figs. 1 and 3), indicating that NOM removed by coagulation was partially similar to that removed by adsorption.

3.4. Combination sequence

Combination sequence, including coagulation and subsequent adsorption (PAC–MWS/PFC–MWS), adsorption and subsequent coagulation (MWS–PAC/MWS–PFC), was investigated under the condition of a fixed MWS dosage of 0.2 g/L and various PFC or PAC dosages. The turbidity, UV_{254}, COD_{Mn} and DOC removal efficiencies are shown in Fig. 6. It can be seen that for turbidity removal, whether for PFC or PAC, coagulation preceded by

adsorption was more effective than coagulation first. The turbidity removal efficiency could reach about 90% at a low coagulant dosage (0.04 mmol/L). This may due to the adsorption function of MWS which can supply the attachment points for NOM and improve flocs settlement performance.

MWS–PFC was slightly efficient in removing UV_{254}, while PFC–MWS was slightly efficient in reducing DOC. It was found that MWS–PAC and PAC–MWS showed no significant differences in removing UV_{254}. MWS–PAC was favorable to remove DOC at low dosage of PAC, however, when the dosage of PAC was higher, PAC–MWS was favorable. In the term of COD_{Mn}, PAC–MWS/PFC–MWS gave higher removal efficiency than MWS–PAC/MWS–PFC.

3.5. DOM size distribution

DOC was analyzed for each size fraction of DOM after filtering through different ultra filtration membranes, and the DOC percentage of different fractions was calculated from DOC concentration. Fig. 7 shows the DOC concentration of different DOM fractions after treatment and the raw water. It was found that the molecular weight distribution of DOM in Yellow River water covered several orders of magnitude with a mean value characteristically skewed toward lower molecular weight fractions. DOM was mainly consisted of low molecular weight constituents with fraction lower than 10k Da accounted for 64.11% of DOC. Previous studies [31] also found that low molecular weight fraction was predominant for sur-
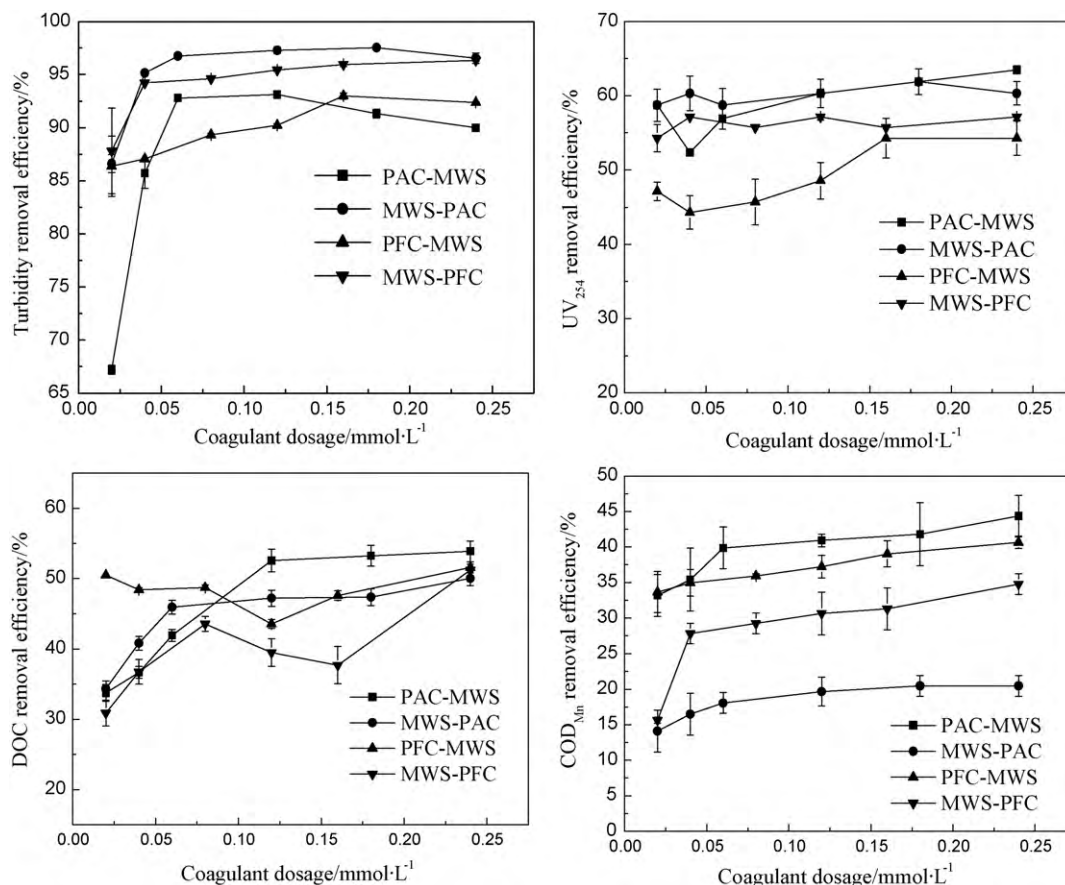
Fig. 6. Turbidity, UV$_{254}$, DOC and COD$_{Mn}$ removal for combination sequence at different coagulants dosages.

face water samples. The percentage of molecular weight >100k Da was less than 10%.

As shown in Fig. 7, coagulation and the combined system were effective for removing higher molecular weight of DOM, e.g. >10k Da. One possible reason is that most low molecular weight NOM is hydrophilic, so it is hardly removed by both coagulation process and combined system. Compared with PFC–MWS process, MWS–PFC process gave better results for lower molecular weight

Fig. 7. DOC concentration of different fractions for the water sample.

constituents removal and the DOC removal efficiency was up to 76.27% for the fraction with molecular weight lower than 10k Da. For the fraction with molecular weight of 5k–1k Da, DOC content in the fraction treated by PFC, PFC–MWS and MWS–PFC process was higher than that in raw water, and the increase in DOC concentration was highest for PFC coagulation, followed by PFC–MWS and MWS–PFC processes. For PAC to be used alone or PAC–MWS process to treat the water, DOC content in the fraction with molecular weight of 5k–1k Da was higher than that in raw water, and the increase in DOC concentration was highest for PAC–MWS. DOC concentration of each fraction was very low; therefore small amount of organic matter that dissolved into the water can influence the DOC fraction greatly. However, there has not been a clear explanation on the DOC concentration in the fraction with molecular weight of 10k–1k Da increasing. Further research will be carried out in our subsequent work.

Removal of NOM with high molecular weight by coagulation can be enhanced when MWS was used. But MWS had a slight influence on removing NOM with low molecular weight. Both MWS adsorption and coagulation using PFC or PAC were effective in removing high molecular weight constituents which resulted in a similar reduction of NOM fraction. This can explain why the serial UV$_{254}$ removal efficiency was less than the superposition of individual treatment efficiencies.

3.6. Chlorine decay

Rapid assessment of chlorine consuming substances in the water will provide useful information on the quality of the treated water. The water samples for chlorine decay experiments were treated by coagulation (PAC or PFC), coagulation and subsequent
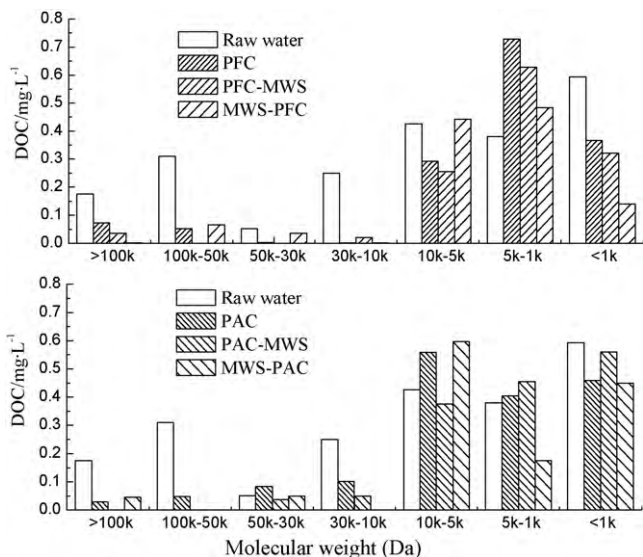
Table 3
Characteristics of samples after treatment.

	MWS	PAC	PAC–MWS	MWS–PAC	PFC	PFC–MWS	MWS–PFC
Turbidity/NTU	7.86	0.91	0.80	0.37	0.82	0.50	0.57
DOC/mg L^{-1}	1.286	1.575	1.270	1.125	1.512	1.174	1.165

Table 4
Chlorine decay model parameters.

Parameter	k_1 (L/mg h)	k_2 (L/mg h)	k_3 (L/mg h)	k_4 (L/mg h)	k_5 (L/mg h)	FRN (mg/L)	SRN (mg/L)	FRA (mg/L)	SRA (mg/L)
MWS	0.14	75.01	69.57	0.077	0.053	0.21	0.048	9.19	10.25
PFC	33.91	0.093	1.80	0.53	0.15	0.22	0.00	0.45	1.90
PFC–MWS	6.00	13.88	0.34	0.53	0.18	0.0010	0.22	0.89	2.31
MWS–PFC	16.00	14.89	3.05	1.37	0.21	0.013	0.24	0.00	1.46
PAC	73.69	35.46	1.80	0.19	0.010	0.0050	0.10	0.55	1.99
PAC–MWS	20.38	11.61	0.45	1.52	0.12	0.21	0.0080	0.021	1.81
MWS–PAC	0.50	8.38	17.02	0.99	0.38	0.077	0.14	0.43	1.50

adsorption (PAC–MWS or PFC–MWS), adsorption and subsequent coagulation (MWS–PAC or MWS–PFC), respectively. The quality parameters of the treated effluent are given in Table 3. The model fitting parameters of chlorine decay to the experimental data are shown in Table 4.

As shown in Table 3, the water quality, in terms of turbidity and DOC, improved significantly after the treatment. The Yellow River water obviously contained all four compounds (FRA, SRA, FRN and SRN) because the total chlorine measurements were due to both free and combined chlorine [32].

After the effluents dosed with chlorine, a higher degradation rate was observed in the solution in the first 1 h due to reaction between chlorine with FRA and FRN, and the residual chlorine became changing slightly afterward. When PFC coagulation effluent was dosed with 2.5 mg/L of chlorine, after 50 h the free and total chlorine concentrations were 0.27 and 0.43 mg/L, respectively. When PAC effluent was dosed with 2.5 mg/L chlorine, then the free and total chlorine concentrations were 0.09 and 0.25 mg/L after 42 h, respectively. There was a higher residual DOC in the sample coagulated using PAC resulting in higher chlorine decay and greater potential to form DBPs [33]. Furthermore, a lower residual DOC in the samples after the combined treatment (Table 3) resulted in lower chlorine decay and less amounts of DBPs being probably formed.

As shown in Table 4, MWS adsorption alone was not effective in reducing the total chlorine demand compared with coagulation and combined treatment. After the PAC coagulation, the model estimated a total chlorine demand of 2.645 mg/L. The combined demand due to FRA and SRA was 2.54 mg/L. The FRN reaction rate constant was the highest at 73.69 L/mg h, while the second highest reaction rate constant was 35.46 L/mg h due to the reaction of SRN. After the PFC coagulation, the model estimated a total chlorine demand of 2.57 mg/L. The combined demand due to FRA and SRA was 2.35 mg/L and was lower than PAC coagulation effluent which revealed that there was less reducing agent presented in the PFC coagulation effluent. The FRN reaction rate constant was the highest at 33.91 L/mg h while the second highest reaction rate constant was 1.80 L/mg h due to the reaction of FRA.

When using PAC as a coagulant, from the model it can be found that the chlorine demand due to both fast and slow reacting organic/inorganic compounds (FRA and SRA) was reduced by combined coagulation and adsorption process and was around 1.831 mg chlorine equivalent/L for PAC–MWS process and 1.95 mg chlorine equivalent/L for MWS–PAC process. For PFC, the chlorine demand due to both fast and slow reacting organic/inorganic compounds (FRA and SRA) was slightly increased by PFC–MWS treatment and was around 3.20 mg chlorine equivalent/L. However, the initial con-

centrations of FRA and SRA were reduced by MWS–PFC and were about 1.46 mg chlorine equivalent/L.

The model can also estimate the DBPs formed in different samples due to chlorination. In this study, a case was assumed: only SRA are responsible for the formation of DBPs and 5% of SRA reacted would produce DBPs [27]. According to the assumption, PAC–MWS effluent can produce 90.3 μg/L of DBPs, while MWS–PAC effluent can produce 75.0 μg/L of DBPs. When PFC was used, 115.5 μg/L of DBPs can be formed after PFC–MWS process and 73.2 μg/L of DBPs can be formed after MWS–PFC. Therefore, adsorption first was more effective in reducing SRA and then lowered the DBPs.

Sinha [34] suggested that the limited molecular weights (<1k) was more prone to form DBPs and adsorption first was more effective in reducing NOM with low molecular weight (Fig. 7). Therefore, MWS–PFC/MWS–PAC were useful to lower the DBPs formation. The results were consistent with those concluded from the residual DOC and chlorine experiment data that a lower residual DOC resulted in less amounts of DBPs.

4. Conclusions

A series of experimental procedures were developed in order to investigate the individual and combined treatment (coagulation and adsorption) efficiency in removing NOM from the Yellow River. It was found that both PFC and PAC had high turbidity removal efficiency (>90%), and UV$_{254}$, DOC and COD$_{Mn}$ removal efficiency increased with the coagulant dosage increasing. MWS adsorption at a dose 0.2 g/L resulted in better UV$_{254}$ and DOC removal (55.4% and 45.1%, respectively), compared with PFC and PAC. In addition, MWS was not effective in reducing turbidity and the efficiency was only 34.5% at a dosage of 0.2 g/L.

A combination of coagulation and adsorption can enhance the NOM removal in term of UV$_{254}$. MWS added to the treated solution acted not only as an adsorbent for NOM but also enhanced the settleability of flocs formed. Therefore, MWS–PAC or MWS–PFC process was superior to PAC–MWS or PFC–MWS process in turbidity removal. In the term of COD$_{Mn}$, coagulation with adsorption on MWS had better results when adsorption is preceded by coagulation than when the adsorption was carried out first. In general, coagulation and the combined treatment were effective in removing NOM with high molecular weight rather than with low molecular weight.

The performances of coagulation and different combined sequences were evaluated for their effectiveness in removing chlorine demand compounds from raw water. Chlorine demand was estimated by fitting the chlorine decay data to a model that describes the chlorine decay due to fast and slow reacting

nitrogenous and organic/inorganic compounds. It was found that chlorine demand due to both FRA and SRA was slightly reduced by combination treatment and was around 1.67 (PAC–MWS), 1.99 (MWS–PAC), 2.39 (PFC–MWS), 1.44 (MWS–PFC) mg chlorine equivalent/L, respectively. If DBPs are assumed to form due to reaction of chlorine and SRA, then it is possible that the DBPs formation potential in the effluents from PFC–MWS/PAC–MWS could be higher than that in the effluents from MWS–PFC/MWS–PAC.

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