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Pre-Treatment of Natural Organic Matters Containing Raw Water using Coagulation

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Coagulation is a commonly adopted process as a pretreatment step for minimizing membrane fouling. Three coagulants, polyaluminum chloride (PACl), alum, and $FeCl_3$ were tested under four mixing-settling schemes for turbidity and natural organic matters (NOM) removal. The organic matters in the raw waters were fractionated by high performance size exclusion chromatography (HP-SEC) system and were characterized using the excitation-emission matrix (EEM) fluorescence spectra. Sufficient rapid mixing and slow mixing or applying two-stage coagulation benefit turbidity removal using PACl or $FeCl_3$ under "electrostatic patch coagulation" (EPC) mechanism. The EPC mechanism is not efficient for alum coagulation. At higher coagulant doses, the NOM removal is not affected by mixing condition. Intensive rapid mixing alone benefits NOM removal using PACl or $FeCl_3$. Alum is a poor coagulant for NOM removal under EPC mechanism.

Keywords charge neutralization; coagulant; mechanism; organic matters

INTRODUCTION

Membrane separation presents a widely adopted nonthermal dehydration means in chemical and pharmaceutical industries (1–4). Fast filtration with minimum irreversible membrane fouling is desired (5–15). Coagulation is adopted by most drinking waterworks to agglomerate fine particles into rapid-settling flocs for separation. Colloidal destabilization can be achieved by adding aluminum or ferrous salts to form cations to be adsorbed onto the negatively charged surfaces, or to form hydroxide precipitation to enmesh fine particles in water.

An enhanced coagulation process was commissioned to remove natural organic matters (NOM) (16), which are precursors of disinfection by-products (DBP) and other synthetic organic compounds in the water (17). Mechanisms corresponding to the coagulation removal of organic substances had been discussed (18–20). Various mechanisms, such as colloidal destabilization, precipitation, co–precipitation, and adsorption, affected the NOM removal effectiveness (21). Narkis and Rebhun (22) showed that when both mineral particles and dissolved humic substances are present in raw water, the latter controls the coagulation process. Coagulation of humic substance–containing suspension would produce a highly turbid supernatant (23,24). Sung et al. (25) showed how the levels of mineral particles and of humic acid affect the stability of the blanket in full–scale floc blanket clarifiers.

The efficiency of an enhanced coagulation process was promoted by either acidifying the raw water or by applying an increasing dosage of coagulants. However, high dosages of coagulants lead to the corrosion of the iron pipe (26). Another concern is of excess coagulants in water as they are potential foulants to the membrane if the membrane filtration is the next step following the coagulation step. Yan et al. (27) demonstrated the role of the coagulant type on the NOM removal efficiencies from micro-polluted raw waters at high alkalinity. Jarvis et al. (28) compared the coagulation behavior of high-level NOM from water using ferric sulphate ($Fe_2(SO_4)_3$) and zirconium oxychloride ($ZrOCl_2$). Sam et al. (29) adopted four coagulants, i.e., two monomeric (aluminium sulphate and ferric sulphate) and two polymeric (polyaluminum chloride and polyferric sulphate) coagulants to remove organics from raw waters. Removal of humic acid by polyaluminum chloride (PACl) was studied for the effects on different sequences of rapid mixing, slow mixing, flocculation, and settling (30). The iron-based coagulants (e.g., ferric chloride and ferric sulfide) were reported to perform better in DOC removal than aluminium-based coagulants (e.g., alum and PACl), especially in those of low molecular weight organics (31).

Colloidal destabilization can be achieved by adding aluminum or ferrous salts to form cations to be adsorbed

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onto the negatively charged surfaces, or to form excessive hydroxide precipitation to enmesh fine particles. Chowdhury and Amy (32) proposed that precipitation is the main mechanism in the coagulation of alumina colloids with alum. Studies on PACl focused on the mode of charge neutralization (33). Dentel (34) proposed a combined coagulation model considering precipitation charge neutralization (PCN). The "electrostatic patch coagulation" (EPC) mechanism was proposed by Gregory (35). Restated, when part of the charged surface neutralized by adsorbing oppositively charged ions, particle coagulation could be induced by local contact between neutralized "patches" of surfaces could induce coagulation. Wang et al. (36) applied the EPC mechanism to interpret the coagulation behaviors of their PACl. The general mechanisms of coagulation have been summarized in a review by Duan and Gregory (37). Applying EPC mechanism, if feasible, can save excess coagulant dosage and produce less sludge.

This study aims at studying the coagulation behavior of three different commonly used coagulants on the removal of constituents of NOM of different molecular weights. The organic matters in the raw waters were fractionated by high performance size exclusion chromatography (HP-SEC) system and were characterized using the excitation-emission matrix (EEM) fluorescence spectra.

MATERIALS AND METHODS

Raw Water Characteristics

The raw water was sampled from the intake port of a major water treatment plant in Taipei city (Chang Shin Water works). Basic water qualities are shown in Table 1. Turbidity and dissolved organic matter (DOM) of the raw waters was 8.18 NTU and 0.50 mgl^{-1} as C, respectively. The EEM fluorescence spectra of the two raw water samples are also listed in Table 1.

Experimental Set-up and Procedures

Jar tests were performed in 2-liter square tanks equipped with a six-paddle stirrer. Prior to jar tests, the raw water samples were adjusted to pH 7 using sulfuric acid and sodium hydroxide. The water sample was then placed in the jar tester to evaluate the coagulation efficiencies with studied coagulants, aluminium sulphate salt, polyaluminum chloride (PACl), and ferric chloride under the scheme listed in Table 2. In Process 1–3 the coagulant was added at the start of the rapid mixing; while in process 4 the coagulants was added at half of the dosed quantity at the start of the first stage of rapid mixing, and at the other half at the second stage of rapid mixing. Process 1 was a typical coagulation process adopted in waterworks, which comprised a rapid mixing step at 100 rpm for 3 min followed by a slow mixing at 25 rpm for 20 min. The suspension was placed still for 30 min before sampling. Process 2 consisted of a rapid mixing stage of 180 rpm for 3 min followed directly by the 30 min settling. Process 3 had a rapid mixing step at 180 rpm for 3 min + slow mixing at 25 rpm for 3 min settling. Process 4 comprised of two rapid mixing steps, each at 100 rpm for 3 min, followed by slow mixing (25 rpm, 20 min) + 30 min settling. The suspension at two-of-third height of the tanks was sampled after 30 min settling. The turbidities of the collected samples were measured by a turbidimeter (2100P, Hach, USA). The NOM in the collected samples were fractionated by the HP-SEC.

TABLE 1
Characteristics of three studied water samples

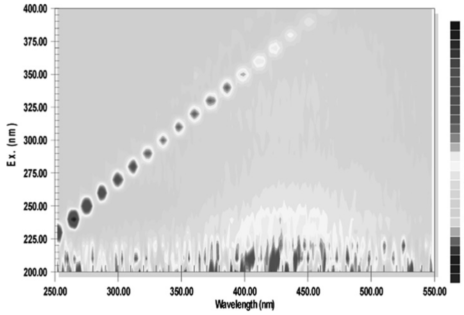
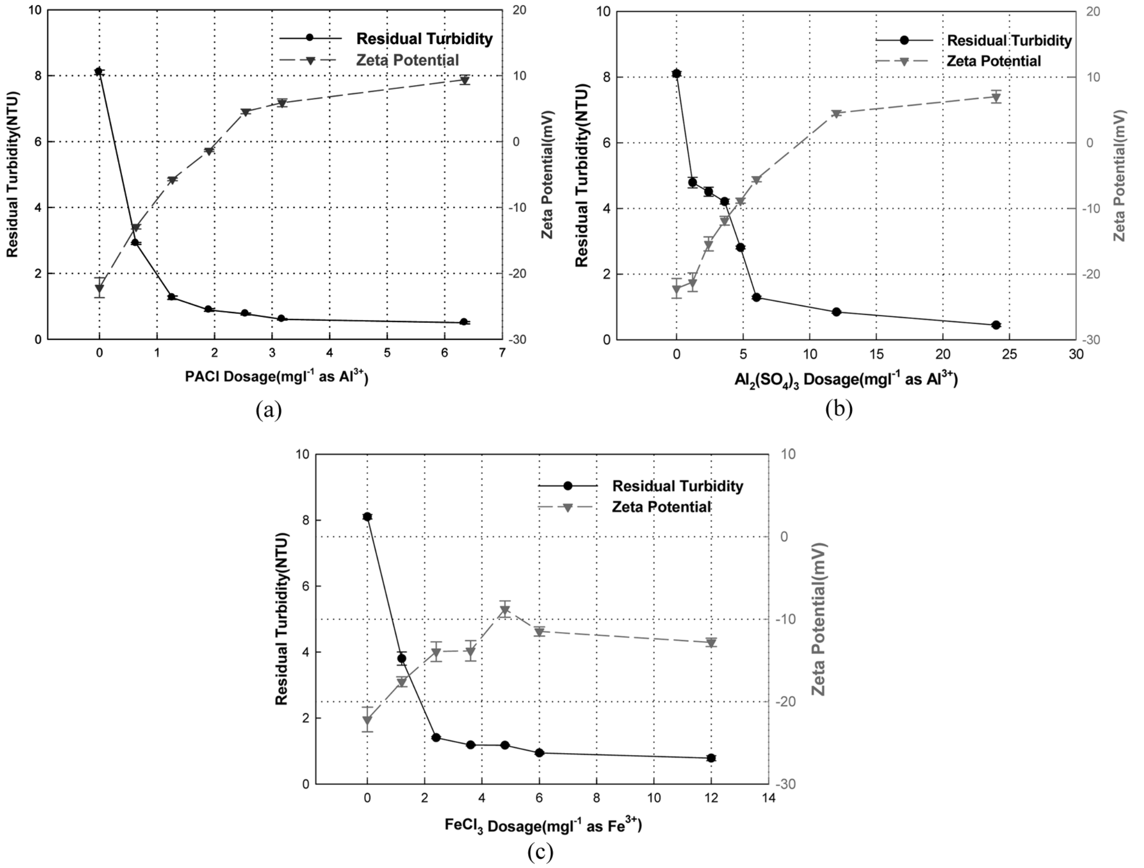
Sample	Raw water
Sampling date	2008.05.27
Water temperature (°C)	31
PH	7.39
Turbidity (NTU)	8.18
DOC(mgl^{-1} as C)	0.50
Alkalinity (mgl^{-1} as $CaCO_3$)	31
EEM plot	

TABLE 2
Coagulation scheme for the three tested coagulants

	Coagulant adding		Way of mixing				Setting time
			Rapid			Slow	
Coagulation process	Single-stage	Two-stage	180 rpm 3 min	100 rpm 3 min	100 rpm 3 min	25 rpm 20 min	30 min
0							●
1	●				●	●	●
2	●		●				●
3	●		●			●	●
4		●		●	●	●	●

Chemicals

Ferric chloride and aluminium sulfate were from ACROS (Geel, Belgium), which were used to make mother liquors containing 1000 mgl^{-1} as Fe^{3+} or as Al^{3+} for dosing. The PACl was purchased from Miaoli United Carbon Co., Taiwan, which supplies the coagulants used by the Changshin Waterworks (the sampled site), which contains 10% w/w Al_2O_3, with sulfate and nitrate contents less than 3.5% and 0.01% w/w, and the basicity and pH between 45–60 and 3.5–5, respectively. The contents of metals (Mn, As, Pb, Cd, Hg, and Fe) in the PACl were all less than 0.01% w/w.



(a) (b) (c)

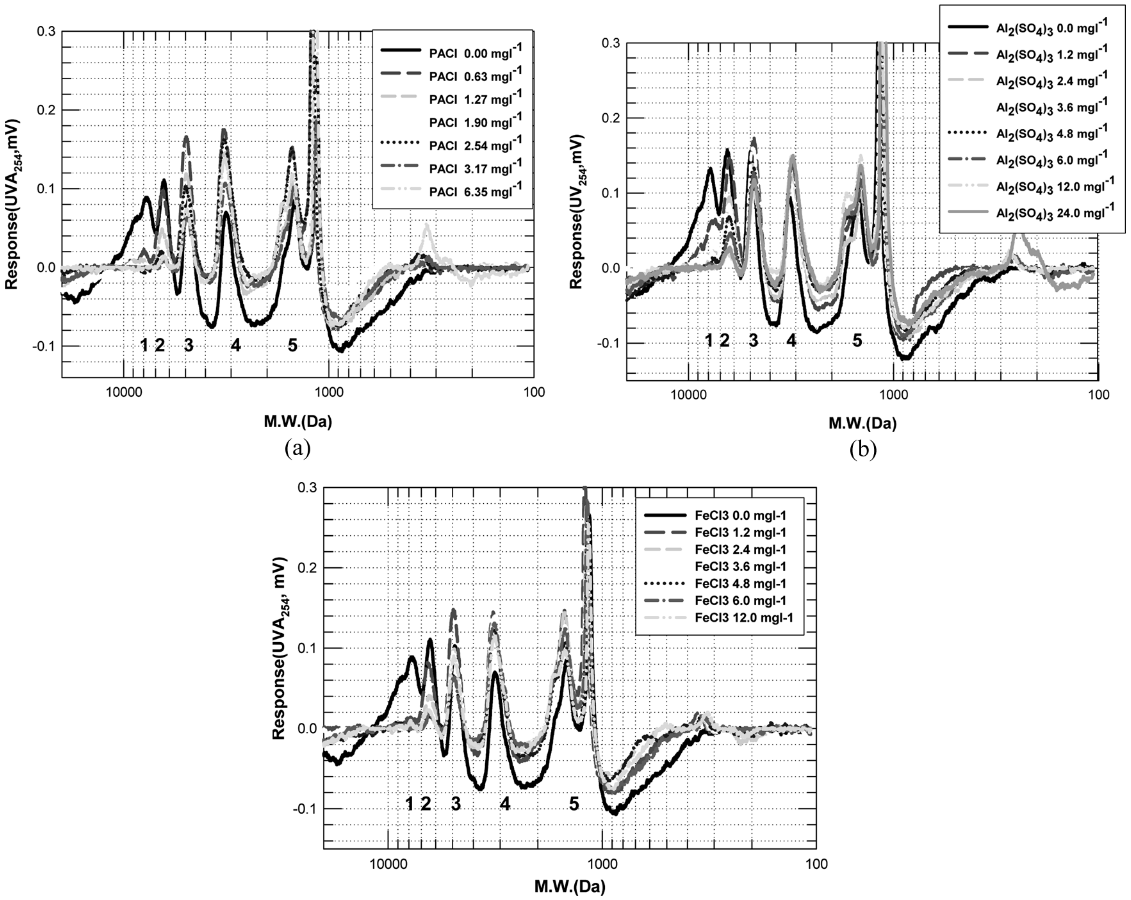
FIG. 1. Residual turbidities and zeta potentials of raw and coagulated water samples. PACl. (a) PACl; (b) Alum; (c) $FeCl_3$.

Analysis

Zeta potential measurement of particles in suspensions was carried out in a Zetasizer (Nano-ZS, Malvern Co., UK). The cell repeated flushing by DI water and ethanol several times before the measurement. The pH of the samples was measured using a calibrated pH meter (WTW pH-315, Weilheim, Germany). The TOC data of water samples were analyzed by Aurora Model 1030 TOC analyzer (OI Analytical, Co., College Station, USA). The non-purgable dissolved organic carbon (NPDOC) is an index of organic composition concentration. The DOC data were averaged over triplicate analysis.

The high performance size exclusion chromatography (HP-SEC) system was comprised of a degasser (DEGASYS DG-1310, Uniflows Co. Ltd, Tokyo, Japan), a feed pump (BETA 10 Gradient pump, Ecom spol. s.r.o., Prague, Czech Republic), a chromatography column (TSK G2000SWx1, TOSOH Co., Tokyo, Japan), and two on-line detectors. The first detector is a UV-vis variable wavelength detector (SAPPHIRE 600, Ecom spol. s.r.o., Prague, Czech Republic) and the second is a refractive index detector (IOTA 2, Precision Instruments, Marseille, France). Both detectors were connected in-series and monitored simultaneously via a software Peak-ABC on the computer. Since the characteristics of mobile phase affected the resolution of HP-SEC system significantly: the priority concern of the solvent is that it will not interfere with analytical samples. A phosphate mobile phase ($0.0024\,mol\,l^{-1}$ NaH_2PO_4 and $0.0016\,mol\,l^{-1}$ Na_2HPO_4, pH 6.8) was chosen for low UV absorbance and low interference with samples and freshly prepared for each experiment. The flow rate of the feed pump was set as $1\,ml \cdot min^{-1}$. The mobile phase and samples were conditioned by pH 7.0 ± 0.1 and filtered by $0.45\,\mu m$ PTFE membranes prior each HP-SEC measurements. $200\,\mu L$ sample was manually injected into the sample injector of the feed pump. Polyethylene glycols (PEG, 200, 1000, 4000, 8000, and 20000 Da) were used for apparent molecular weight (AMW) calibration of chromatograms. The absorption wavelength of the UV detector was set at 254 nm.

The EEM analysis was measured by a Cary Eclipse fluorescence spectrophotometer (Varian Inc., Palo Alto,



(a)

(b)

(c)

FIG. 2. SEC-UV$_{254}$ spectra for raw and coagulated water samples. (a) PACl; (b) alum; (c) $FeCl_3$.

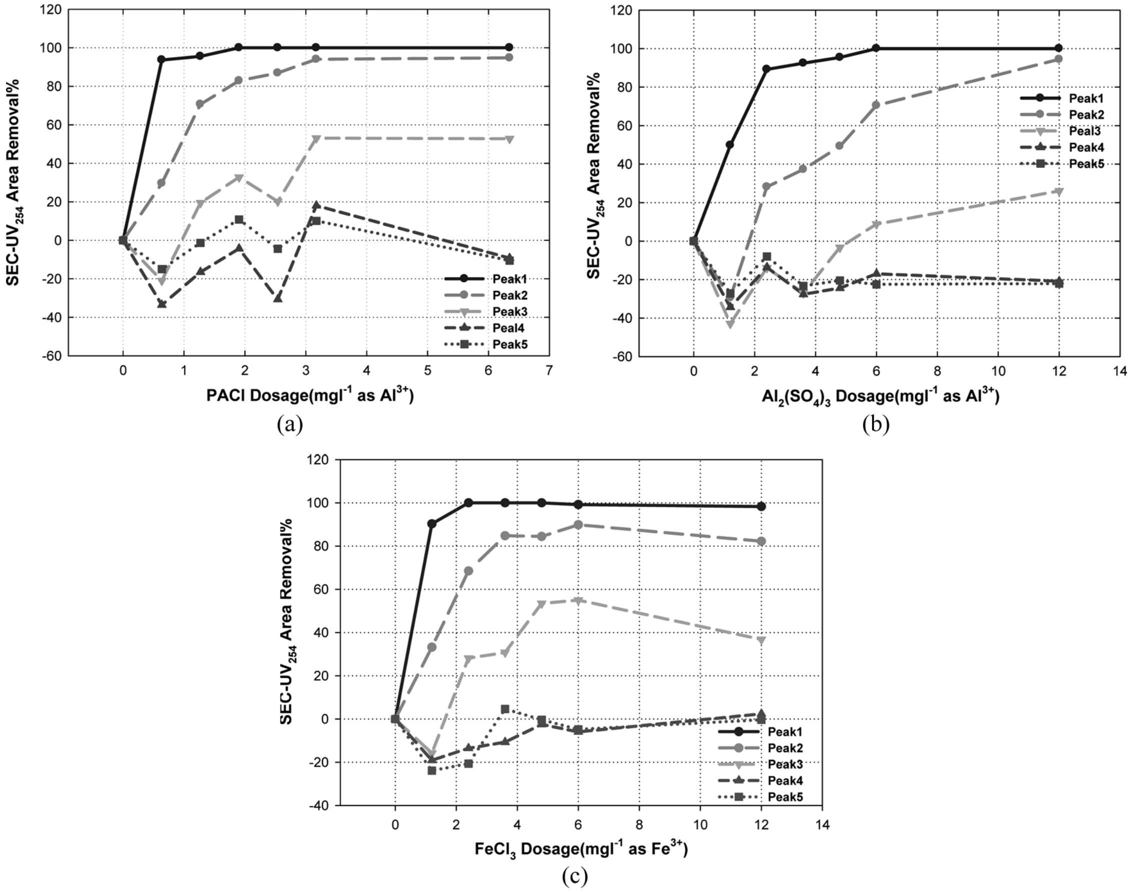
CA, USA). Due to the fact that the fluorescence measurement is more easily affected by instruments, sample preparation methods, sample pH, concentration, temperature, ionic strength, and solvent, it is necessary to control the samples in the same condition prior to each measuring. All samples were conditioned by pH 7.0 ± 0.1 and filtered by 0.45 μm PTFE membranes prior to each of the EEM measurements. EEM spectra were gathered with subsequent scanning emission spectra from 250 to 550 nm at 1 nm increments by varying the excitation wavelength from 200 to 400 nm at 10 nm increments. The spectra were recorded at a scan rate of $1200\,\mathrm{nm\,min^{-1}}$, using excitation and emission slit bandwidths of 5 nm. The voltage of the photomultiplier tube (PMT) was set to 800 V for low level light detection. Data were saved as ASCII format, and removed Rayleigh scattering by Perl code editing. The EEM fluorescence spectra listed in Table 1 revealed that the raw water contains more fulvic acid-like dissolved organic matters than the raw water A, based on the comparison of EEM signal intensity in "region III" according to the classification of Chen et al. (38).

RESULTS AND DISCUSSION

Coagulation of Raw Water in Process 1

The coagulation process 1 (100 rpm rapid mixing for 3 min + 25 rpm slow mixing for 20 min + settling) was conducted to determine the dosage quantity needed in the coagulation tests. Figures 1a–c show the residual turbidities and zeta potentials for the PACl, alum, and $FeCl_3$-coagulated water, respectively. PACl at $1.9\,\mathrm{mgl^{-1}}$ as Al^{3+} or alum at $12\,\mathrm{mgl^{-1}}$ as Al^{3+} were needed to neutralize the surface charge of the suspended particles in water. However, adding PACl of only $0.63\,\mathrm{mgl^{-1}}$ as Al^{3+} reduced the residual turbidity from 8.3 to 2.9 NTU or to 4.9 NTU, respectively. Further increase of the PACl dose to $12\,\mathrm{mgl^{-1}}$ or alum dose to $24\,\mathrm{mgl^{-1}}$ as Al^{3+} reduced the residual turbidity further to 0.75 NTU.

Dosing $FeCl_3$ up to $12\,\mathrm{mgl^{-1}}$ as Fe^{3+} could not neutralize the surface charge of the particles. The zeta potential of particles levelled off at around −12 mV. However, adding $FeCl_3$ at $1.2\,\mathrm{mgl^{-1}}$ as Fe^{3+} reduced the residual turbidity from 8.3 to 3.8 NTU. Further increase of the $FeCl_3$ dose to $12\,\mathrm{mgl^{-1}}$ reduced residual turbidity to around 1.0 NTU.



(a) (b)

(c)

FIG. 3. SEC-UV_{254} areal removal *versus* coagulant dosage curves for peak 1–5. (a) PACl; (b) alum; (c) $FeCl_3$.

We denoted the coagulation tests with PACl dose of 0.63, 1.90, and 6.35 mgl^{-1} as EPC, CN, and EM points studied for the water sample. The corresponding doses for alum were 1.2, 12, and 24 mgl^{-1} as Al^{3+} for the EPC, CN, and EM points, while the three doses for $FeCl_3$ were selected at 1.2, 4.0, and 12 mgl^{-1} at Fe^{3+} for the sake of comparison.

NOM and Turbidity Removal using Process 1

There exist five UV-254 absorption peaks for the SEC diagram for raw water (Figs. 2a–c), with apparent molecular weights at 8600 (peak 1), 7200 (peak 2), 5600 (peak 3), 3700 (peak 4), and 2200 Da (peak 5). The sharp peak at around 1500 Da is the water peak containing most dissolved ions. The present SEC resin system gives a distinct peak resolution for the organic matters in water compared with those applied by Chow et al. (39).

The addition of 0.63 mgl^{-1} PACl nearly completely removed the peak 1, but only partially removed peak 2. With the PACl dose of 1.27 mgl^{-1}, peak 2 was effectively removed. Then the intensity of peak 3 was gradually removed with the PACl dose further increased up to 6.35 mgl^{-1}. The PACl coagulation has negligible effects on peak 4. On peak 5, the peak intensity increased rather than decreased with increasing the PACl dose. Restated, the impurity in the dosed PACl contributed to the AMW of 2100 Da in the tested samples.

The addition of 2.4 mgl^{-1} alum nearly completely removed peak 1, but only partially removed peak 2. With the alum dose of 24 mgl^{-1}, peak 2 was effectively removed. The intensity of peak 3 was slightly removed with the alum dose. The alum coagulation has negligible effects on peak 4. On peak 5, the peak intensity also increased rather than decreased with the increasing alum dose.

The addition of 3.6 mgl^{-1} $FeCl_3$ nearly completely removed peak 1, but only partially removed peak 2. Peak 2 was gradually removed with the increasing $FeCl_3$ dose up to 12 mgl^{-1}. The $FeCl_3$ coagulation negligibly removed peaks 3 and 4.

The behavior of coagulation using three different coagulants is quite similar. The areas under UV_{254} (in mV) versus AMW (in Da) curves were numerically evaluated by Simpson's algorithm (Fig. 3). The PACl dosage at >2 mgl^{-1} completely removed peak 1. With >6 mgl^{-1} PACl, peak 2 could be completely removed. Similarly, the alum dosage at >2.4 mgl^{-1} or $FeCl_3$ dosage >6 mgl^{-1} completely removed peak 1. With >7 mgl^{-1} PACl, peak 2 could be completely removed.

Coagulation of Raw Waters using Process 1–4 by EPC, CN and Sweep Mechanism

The three tested coagulants removed most turbidity at the highest dose studied (Table 3). Among Process 1–4, process 2 always produced the worst turbidity removal efficiencies. The EPC coagulation efficiencies for turbidity removal using the three coagulants followed PACl > $FeCl_3$ > alum. Under high dosage, there is no difference between the performances from the three coagulants.

TABLE 3
Residual turbidities under process 1–4 with different coagulants. Initial turbidity 8.18 NTU

Coagulant	Dosage	Process	Residual turbidity (NTU)
PACl	EPC	P1	2.91
		P2	6.02
		P3	2.10
		P4	1.38
	CN	P1	0.89
		P2	1.75
		P3	0.73
		P4	0.59
	Sweep	P1	0.53
		P2	0.87
		P3	0.50
		P4	0.64
$Al_2(SO_4)_3$	EPC	P1	4.97
		P2	4.98
		P3	4.80
		P4	4.42
	CN	P1	0.84
		P2	2.47
		P3	0.55
		P4	0.57
	Sweep	P1	0.45
		P2	0.89
		P3	0.30
		P4	0.41
$FeCl_3$	EPC	P1	3.81
		P2	4.50
		P3	2.73
		P4	3.19
	4.0 mgl^{-1}	P1	1.18
		P2	1.67
		P3	0.77
		P4	0.78
	12 mgl^{-1}	P1	0.79
		P2	0.83
		P3	0.45
		P4	0.45

The EPC coagulation efficiencies for turbidity removal using the three coagulants followed Process 4 > Process 3 > Process 1 > Process 2. Intensive and prolonged rapid mix stage and the slow mix stage are needed for efficient turbidity removal using the EPC mechanism. At high dosage, the coagulation efficiencies for turbidity removal

TABLE 4
Aeral removal rates for UV-SEC peaks under process 1–4 with different coagulants

			SEC-UV_{254} areal removal rate (%)			
Coagulant	Dosage	Process	Peak 1	Peak 2	Peak 3	Total
PACl	EPC	P1	93.7	29.5	−21.0	7.7
		P2	94.2	46.3	−5.0	12.3
		P3	100.0	68.6	−0.2	22.2
		P4	100.0	64.2	3.8	38.3
	CN	P1	100.0	82.9	32.8	41.1
		P2	100.0	88.8	40.0	29.1
		P3	100.0	89.3	33.7	24.4
		P4	100.0	85.4	27.1	50.4
	Sweep	P1	100.0	94.7	52.8	46.9
		P2	100.0	97.1	57.9	40.6
		P3	100.0	91.3	42.0	28.9
		P4	100.0	100.0	58.7	53.2
$Al_2(SO_4)_3$	EPC	P1	49.8	−29.5	−42.9	−13.1
		P2	18.1	−38.0	−54.1	1.9
		P3	−14.2	−44.2	−53.7	−1.3
		P4	39.0	−32.0	−61.4	−0.1
	CN	P1	100.0	70.4	8.8	21.2
		P2	100.0	79.6	18.5	42.2
		P3	100.0	68.9	2.6	37.2
		P4	100.0	80.9	11.1	42.4
	Sweep	P1	100.0	94.4	26.0	24.1
		P2	100.0	84.9	22.2	42.7
		P3	100.0	83.2	13.1	39.6
		P4	100.0	87.3	23.6	43.1
$FeCl_3$	1.2 mgl^{-1}	P1	90.3	33.2	−15.8	9.4
		P2	95.8	47.4	−19.1	28.3
		P3	100.0	60.0	5.1	32.9
		P4	82.2	21.1	−61.1	−4.5
	4.0 mgl^{-1}	P1	100.0	84.8	30.8	36.7
		P2	100.0	93.2	39.5	50.6
		P3	100.0	88.5	37.7	43.5
		P4	100.0	94.4	48.2	44.1
	12 mgl^{-1}	P1	98.3	82.2	36.8	35.0
		P2	100.0	95.8	70.0	54.3
		P3	100.0	95.9	77.8	56.5
		P4	100.0	95.3	57.9	45.5

followed Process 4 = Process 3 = Process 1 > Process 2. The intensive and prolonged rapid mix stage is not a required stage at high dosing regime.

The EPC coagulation efficiencies for NOM removal using Process 1–4 were demonstrated in Table 4. The total peak aeral removal rate increased with increasing rapid mix time and intensity and with increasing dosage. The NOM removal rates for the three coagulants follows PACl > $FeCl_3$ > alum. Using PACl, the Process 4 yields >50% NOM removal rate. The use of $FeCl_3$ with Process 2–4 all produced >40% overall NOM removal. The use of alum led to poor NOM removal capability.

Comparing the performances for PACl and $FeCl_3$ using Process 1 and Process 3 under EPC mechanism in Table 3 revealed that intensive rapid mixing benefits turbidity removal, likely being attributable to the so-induced more uniform dispersion of dosed PACl or $FeCl_3$ over the entire suspension and the more frequent particle collision to form nuclei flocs at extensive mixing. However, the use of alum has yielded no such experimental observation. At a higher dose, the rapid mixing is not essential for improved turbidity removal. Comparing the turbidity removal rates for Process 2 and Process 3 reveals the significant role of slow mixing to allow large flocs to form for the separation. Rapid mixing without subsequent slow mixing left numerous fine particles that could not settle well. Again, such an observation is not justified for alum at the EPC dose. Comparing turbidity removal for Process 1 and Process 4 indicated that the use of two-stage coagulation with PACl produced nuclei flocs in the first 3-min rapid mix phase assisted the capture of fine particles to reach higher turbidity removal in slow mix and settling stages. This trend is not noticeable for alum or $FeCl_3$.

On peak 1 on SEC-UV_{254} spectra, comparing the performances for PACl and $FeCl_3$ using Process 1 and Process 3 under EPC mechanism in Table 4 revealed that intensive rapid mixing benefits NOM removal. The use of alum on the contrary led to the negative removal of peak 1. At a higher dose, the rapid mixing is not essential for the improved peak 1 removal. Comparing peak 1 removal for Process 2 and Process 3 reveals the insignificant role of slow mixing to the removal of NOM of AMW of 8600 Da. Slow mixing is not essential to remove NOM peak 1. Comparing peak 1 removal for Process 1 and Process 4 indicated that the use of the two-stage coagulation with the three studied coagulants is not significant for enhancing NOM removal.

On peak 2 on SEC-UV_{254} spectra, comparing the performances for PACl using Process 1 and Process 3 under CN mechanism in Table 4 revealed that intensive rapid mixing benefits NOM removal. The use of alum on the contrary led to the negative removal of peak 2. At a higher dose, the rapid mixing is not essential for improved peak 1 removal. Comparing peak 2 removal for Process 2 and Process 3 reveals the certain role of slow mixing to the removal of NOM of AMW of 7200 Da. Comparing peak 2 removal for Process 1 and Process 4 indicated that the use of the two-stage coagulation with PACl is significant for enhancing NOM removal. However, two-stage coagulation had no role on alum or $FeCl_3$ coagulation.

Restated, the mechanisms corresponding to NOM removal differ from those for turbidity removal. The association with particle aggregation does not correlate with the NOM removal. Hence, the proposal that NOM was adsorbed on the suspended particles or on the coagulated particle flocs is not physically relevant. Additionally, the PACl is much better than alum for NOM removal. $FeCl_3$ has an intermediate performance.

CONCLUSIONS

Polyaluminum chloride (PACl), alum, and $FeCl_3$ for turbidity and natural organic matters (NOM) removal were tested under four mixing-settling schemes. The EPC coagulation efficiencies for turbidity removal or NOM removal using the three coagulants followed PACl > $FeCl_3$ > alum. Under high dosage, there is no difference between the performances from the three coagulants. Sufficient rapid mixing and slow mixing or applying two-stage coagulation benefit turbidity removal using PACl or $FeCl_3$ under EPC mechanism. The EPC mechanism is not efficient for alum coagulation. At higher coagulant doses, the NOM removal is not affected by the mixing condition. Intensive rapid mixing alone benefits NOM removal using PACl or $FeCl_3$ at low coagulant dosage. Alum is a poor coagulant for NOM removal under the EPC mechanism.

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