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Coagulation performance and residual aluminum speciation of $Al_2(SO_4)_3$ and polyaluminum chloride (PAC) in Yellow River water treatment

Zhonglian Yang, Baoyu Gao*, Qinyan Yue

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 effect of pH and coagulant dosage on the coagulation performance of aluminum sulphate and polyaluminum chloride (PAC) with respect to the treatment of Yellow River water was investigated in this paper. The separation and measurement of residual aluminum (Al) speciation were also conducted. The results indicated that PAC showed superior coagulation performance compared to that of $Al_2(SO_4)_3$ in most cases during the Yellow River water treatment. At a dosage of 15 mg/L as Al_2O_3, PAC achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 96.3, 57.1, 32.7%, respectively, and $Al_2(SO_4)_3$ also achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 94.5, 53.5 34.8%, respectively. For PAC and $Al_2(SO_4)_3$, the optimum pH during the treatment of Yellow River water could be determined at 6.0. Different residual Al speciation exhibited different trends with dosage and pH variation. For the two coagulants studied, no matter the dosage or pH, the majority of residual total Al existed most in the form of total dissolved Al, among which, dissolved organically bound Al was the predominant speciation. Most of the dissolved monomeric Al in the effluent was dissolved inorganically bound monomeric Al. PAC showed lower concentration for the several kinds of residual aluminum species, except the dissolved organically bound Al; and PAC could effectively reduce the concentration of dissolved monomeric Al.

1. Introduction

Chemical coagulation followed by separation (sedimentation or flotation and filtration) are two basic water treatment processes in which the physical or chemical properties of colloidal or suspended particles are altered such that agglomeration is enhanced to an extent that these solids will settle out of solution by gravity or will be removed by filtration [1–4]. During the coagulation and flocculation processes, some Al-based compounds or polymers such as aluminum sulphate (alum), aluminum chloride, polyaluminum chloride (PAC) can change surface charge properties of solids to promote agglomeration and/or enmeshment of smaller particles into larger flocs. These coagulants are widely used in surface water treatment to enhance the removal of particulate, colloidal, and dissolved substances [5–8].

Although effective for removing turbidity and organic materials, Al-based coagulants, particularly alum, may result in elevated concentrations of residual Al in finished water [9,10]. The occurrence of Al in treated water or as a precipitate in distribution system has been considered to be an undesirable aspect of treatment practice and associated with several problems, including increased turbidity, reduced disinfection efficiency, and a loss in hydraulic capacity [9]. High concentrations of residual dissolved Al indicate incorrect coagulant dosing, inefficient use of the coagulant, or problems in the chemistry of treatment process. High concentrations of particulate Al may lead to problems in solid–liquid separation of postprecipitation of Al. Thus, Al fractionation measurements can provide the treatment plant operator with valuable information about various aspects of plant performance [9].

Moreover, the ingestion of high concentrations of Al is also of concern because of potential adverse effects such as Alzheimer's disease [10–12]. Furthermore, Al is widely diffused in natural waters in which various Al species exhibit different toxicity [11,13]. Thus the determination of Al speciation is very important from the standpoint of human and ecosystem health. In addition, most regulatory agencies have established guidelines/standards for the control of Al in drinking water. The Al limits in drinking water should not exceed 0.2 mg/L in China. However, it should be stressed that all guidelines refer to total Al and most water treatment plants and researchers pay attention to only total Al or dissolved Al. That is to say, profiles of various forms of Al in raw and treated water are rarely performed [14]. So reports of compliance with guidelines may have less toxicological significance. Thus, from a research perspective, knowledge of Al speciation can provide

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* Corresponding author. Tel.: +86 531 88364832; fax: +86 531 88364513.
E-mail address: baoyugao_sdu@yahoo.com.cn (B. Gao).

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insights into coagulation chemistry and the mechanisms for contaminant removal.

So, from the standpoint of both health field and research field, it seems reasonable to carry out the Al fractionation studies systemically during the surface water treatment. Moreover, pH and dosage were essential parameters influencing the coagulation performance of Al-based coagulants as well as the contents of different residual Al species [15–18]. In this paper, the Al characterization (speciation) studies were conducted with respect to the treatment of the Yellow River water [Jinan section, Shandong, China] using $Al_2(SO_4)_3$ and PAC. The effect of dosage and pH on the coagulation performance of $Al_2(SO_4)_3$ and PAC were also studied. The contents and changes of different residual Al species in the purified water under different dosage and pH were systematically investigated. It was intended to discuss the relationship between the coagulation performance of the two coagulants and content and speciation of residual Al and to provide some references on how to reach the national standard of residual Al content in drinking water.

2. Materials and methods

2.1. Experimental materials

High-purity Al sheet, obtained from Beijin Purchasing and Supply Station of Chinese Medicine Company, was used for the preparation of standard stock solution of Al. Concentrated reagent-grade nitric acid (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), a guaranteed reagent, was used for the acidification of the test water samples. Cetyl pyridinium bromide (CPB) and Triton X-100 (OP) were chemically pure grade agents and were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Reagent-grade CH_3COONa, Chrome azurol S, xylenol orange, ascorbic acid, NaCl, NaOH, Na_2CO_3, anhydrous ethanol and EDTA were analytically pure grade agents and were obtained from Guangcheng Chemical Reagent Plant, Tianjin, China. Other analytically pure grade agents, including concentrated hydrochloric acid (HCl), $Al_2(SO_4)_3{\cdot}18H_2O$, $AlCl_3{\cdot}6H_2O$, KF, 4-nitrophenol, anhydrous ethylenediamine and ammonia solution were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. All the reagents exploited were used as received, without any further purification. Deionized water and laboratory-grade glassware were used for all reagent preparation and stock dilutions.

All containers used in this study were cleaned using acid and deionized water as follows: cleaned with 1 + 9 HNO_3 solution and then stored in 1 + 9 HNO_3 solution for 12 h; rinsed with deionized water. It was reported that membrane filters should be used immediately after purchase and the first 50 mL of sample should be avoided to prevent any contamination due to filters [13].

2.2. Experimental methods

2.2.1. Test water

Raw water was collected from Jinan section of the Yellow River (Shandong, China) and quiescently settled for 24 h to remove any silt. The physicochemical characteristics of the test water used after settling were as follows (number of measurements: 4): pH 8.25 ± 0.20, turbidity = 12.5 NTU ± 0.5 NTU, UV_{254} absorbance = 0.060 ± 0.010, DOC = 2.026–2.985 mg/L. If necessary, the pH of the test water was adjusted to the predetermined value by 0.1 mol/L HCl and NaOH solutions.

2.2.2. Preparation and synthesis of Al-based coagulants and measurement of total Al content in PAC

The initial $Al_2(SO_4)_3$ solution was prepared by directly dissolving certain amount of $Al_2(SO_4)_3{\cdot}18H_2O$ to deionized water and it was used immediately after preparation. PAC was synthesized by solid–solid mixed method [19,20]. In this technique, each reaction was conducted in a 250 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer and glass plug. After the reactor was heated to about 80 °C from ambient temperature using a thermostated water bath, predetermined amount of $AlCl_3{\cdot}6H_2O$ and Na_2CO_3 mixed powder after grind was added slowly into the beforehand added 100 mL deionized water with vigorous agitation within 30 min. After that, the reactor was still kept at constant temperature with continuous and intense stirring for 1 h until the solid mixture was solubilized and the solution was optically transparent. At the end of the reaction the PAC product was homogeneous and clear and then was stored in refrigerator for later use.

Table 1
The Al speciation distributions of $Al_2(SO_4)_3$ and PAC.

Coagulants	B	Al_a (%)	Al_b (%)	Al_c (%)
$Al_2(SO_4)_3$	0.0	98.7	1.3	0.0
PAC	2.0	24.8	50.5	24.7

Al_a: monomeric species; Al_b: medium polymer species; Al_c: colloidal or solid species.

The total Al content in PAC was determined by titrimetric method according to the national standard of China [21]. The properties of PAC used were indicated as follows: total Al (Al_T) content = 0.8556 mol/L, basicity value (B, molar ratio of OH and Al) = 2.0, pH 2.85 ± 0.10.The dosages of $Al_2(SO_4)_3$ and PAC were calculated as mg/L of Al_2O_3 in order to standardize the mass of reactive Al to provide a direct comparison between the two coagulants. Al speciation data were measured by Ferron complexation timed spectrophotometry [22,23] and is summarized in Table 1. The characteristic absorption wavelength for the Al–Ferron complex is at 370 nm. From the results shown in Table 1, it can be seen that the initial $Al_2(SO_4)_3$ coagulant can be considered as monomeric Al speciation, and PAC can be considered as the mixture of various Al species.

2.2.3. Coagulation experiments

Standard jar tests for Yellow River water treatment were conducted on a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at a temperature of 20 ± 1 °C. The test water of 1 L was transferred into each of the 2.0 L plexiglass beakers and a six-paddled stirrer was used for mixing. Under rapid stirring of 200 rpm ($G = 102.5\ s^{-1}$), predetermined amount of coagulant was dosed. And then the solutions were stirred rapidly at 200 rpm for 60 s after coagulant addition, followed by slow stirring at 40 rpm ($G = 11.8\ s^{-1}$) with a duration of 15 min and then 25 min of quiescent settling. After depositing, samples were collected from 2 cm below the solution surface for subsequent measurements.

Collected water sample was filtrated through a 0.45 μm filtration membrane to measure the UV_{254} absorbance and dissolved organic carbon (DOC). UV_{254} was measured at 254 nm with a UV-754 UV/VIS spectrophotometer (Jinghua Precision Scientific Instrument Co. Ltd., Shanghai, China) using 1 cm quartz cells. DOC was measured with a Total Organic Carbon Analyzer (Shimadzu, Japan). The Zeta potential was measured with a Zetasizer 3000HSa (Malvern Instruments, UK) after rapid stirring (60 s after coagulant addition). Turbidity was measured using a portable turbidimeter 2100P (Hach, USA).

2.2.4. Separation method of different residual Al speciation

Nalgene 500 mL high-density polyethylene bottles were used for water sample collection and storage. Nucleopore polycarbonate 0.45 μm filters were used for the separation of total and dissolved Al. The initial filtrate volume (50 mL) was discarded prior to Al

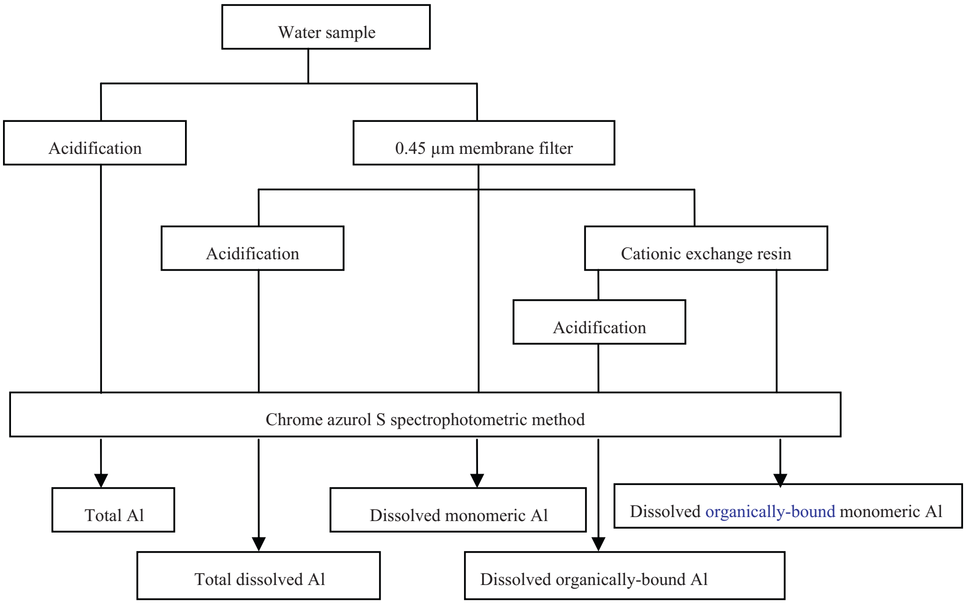

Fig. 1. Separation procedure of different residual aluminum speciation.

fractionation to avoid sampling bias caused by potential Al adsorption through the filter material [13].

The strongly acidic styrene type cation exchange resin (hydrogen form, 20–40 mesh standard screens) was purchased from Damao Chemical Reagent Plant, Tianjin, China, and was used for separation of organic-bound Al and inorganic-bound Al speciation. The pretreatment procedures of the cation exchange resin were revealed as follows: cleaned with 1 mol/L HCl solution and then stored in 1 mol/L HCl for 30 min; rinsed with deionized water; cleaned with 1 mol/L NaOH solution and then stored in 1 mol/L NaOH for 30 min; rinsed with deionized water; washed with 1 mol/L NaCl solution to convert hydrogen form resin to sodium form resin. All the procedures were implemented in a column of strongly acidic cation exchange resin [24]. The diameter of the cation exchange column was 8 mm and the height of the resin bed was 15 cm. The water sample passed through the exchange column was 100 mL. Accordingly, the ratio of resin bed volume to sample volume was approximately 19:1.

The Al fractionation method was carried out under a modification of previously developed procedures – the Van Benschoten and Edzwald method [9] and allowed the determination of the following operationally defined Al fractions (the analytical scheme is presented in Fig. 1) [25]:

- Total Al: an unfiltered sample was acidified with nitric acid and was then analyzed.
- Total dissolved Al: particulate and dissolved Al forms were operationally isolated by filtering the water samples with a 0.45 μm membrane filter, acidified and analyzed.
- Dissolved monomeric Al: a filtered sample was analyzed without acidification.
- Dissolved organically bound Al: a strong acidic cation exchange resin was used to fractionate dissolved Al into two fractions, namely, inorganic and organically bound Al; a filtered sample was passed slowly (about 13–14 mL/min) through a column of the strongly acidic cation exchange resin and effluent was analyzed after acidification.
- Dissolved organic monomeric Al: a filtered sample was passed through the cation exchange column and analyzed without acidification.

Additional fractions were obtained by subtraction, i.e.:

- Particulate Al is the difference between total reactive and total dissolved Al.
- Dissolved inorganically bound Al is the difference between total dissolved and dissolved organically bound Al.
- Polymeric colloidal and strongly bound Al is the difference between total dissolved and dissolved monomeric Al.

All the digestion procedure (for total Al/dissolved plus colloidal Al) involved lowing sample pH to 1 using guaranteed grade concentrated nitric acid and then heating the sample for 1 min after the sample was boiled at pH 1 before the subsequent cooling and measurement.

2.2.5. Measurement of residual Al content

Different residual Al speciation content was measured by spectrophotometer according to the national standard GB/T5750.6-2006 of People's Republic of China. During the experiment, the residual Al contents of raw and purified water after flocculation were analyzed by chrome azurol S colorimetric analysis [26]. The residual Al content was obtained through consulting the standard curve of Al content after measuring the absorbances at 620 nm wavelength with spectrophotometer of UV-754 type spectrophotometer using 1 cm glass cells. Precision of the method was verified by analyzing 10 replicates of a raw water sample. The precision for total, total dissolved, and dissolved organic Al determinations of the same water sample, separated and then measured 10 times as relative standard deviation, was all within 10%. The detection limit of the method was 0.008 mg/L.

3. Results and discussion

3.1. Coagulation performance of $Al_2(SO_4)_3$ and PAC under different dosages

The evaluation of the coagulation–flocculation performance and mechanisms of $Al_2(SO_4)_3$ and PAC for the treatment of Yellow River water were comparatively investigated in terms of turbidity removal efficiency, DOC removal efficiency, UV_{254} removal efficiency as well as Zeta potential in this study. The dose ranges for

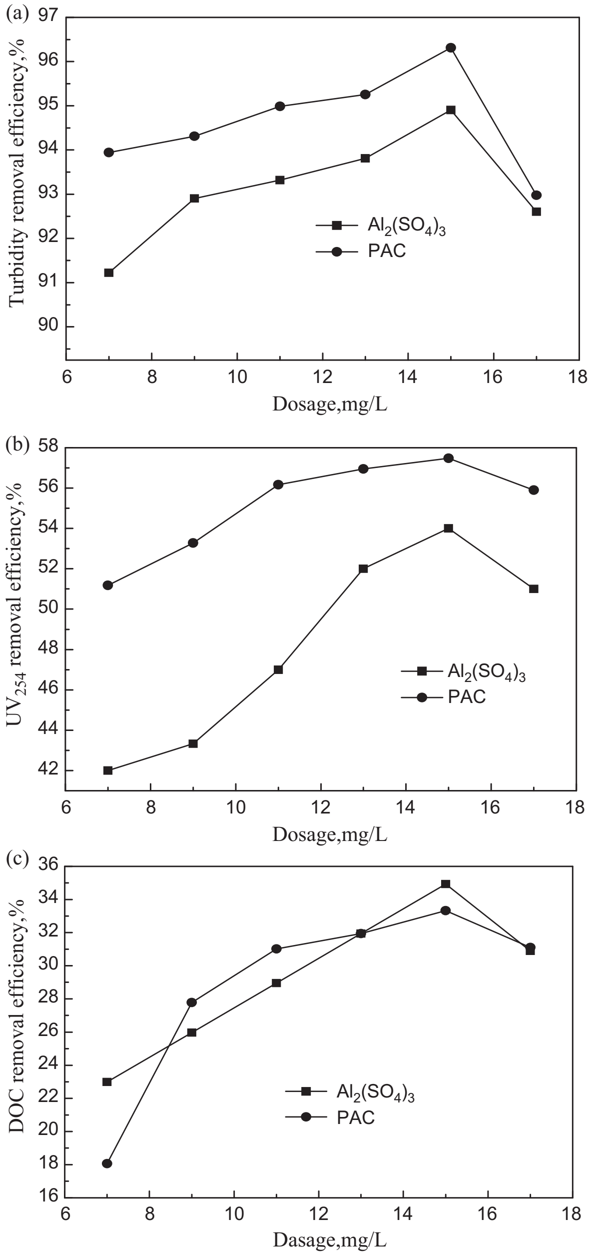

Fig. 2. Effect of dosages on coagulation performance of $Al_2(SO_4)_3$ and PAC in Yellow River water treatment: under raw water conditions.

both $Al_2(SO_4)_3$ and PAC were 7, 9, 11, 13, 15 and 17 mg/L as Al_2O_3. The removal efficiency for turbidity, UV_{254} and DOC using either $Al_2(SO_4)_3$ or PAC are shown in Fig. 2. The pH data of the effluent after coagulation and sedimentation under different dosage are shown in Table 2.

As shown in Fig. 2, the coagulant dosage had a great effect on their removal efficiency upon turbidity, UV_{254} and DOC. Removal efficiencies for turbidity, UV_{254}, and DOC with either coagulant increased significantly first with the increase of coagulant dosage and then decreased slightly when the coagulant dosage was higher than 15 mg/L. At a dosage of 15 mg/L, PAC achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 96.3, 57.1, 32.7%, respectively and $Al_2(SO_4)_3$ also achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 94.5, 53.5 34.8%, respectively. Specifically, the exact values of final turbidity, UV absorbance and DOC concentration corresponding to the highest removal efficiencies of alum and PAC were 0.69 NTU, 0.028 cm^{-1}, 1.63 mg/L (for alum coagulation) and 0.46 NTU, 0.026 cm^{-1}, 1.683 mg/L(for PAC coagulation). With either a decrease or increase coagulant dosage, the turbidity, UV_{254} and DOC removal efficiency decreased. The results demonstrated that PAC showed superior coagulation–flocculation performance compared to $Al_2(SO_4)_3$ in most cases. The reason was that Al speciation between the two coagulants varied was dependent on the pH and NOM characteristics.

It has been recognized that the performance of Al-based coagulants depends largely on their speciation, presenting as Al_a, Al_b and Al_c [27]. The Al speciation in $Al_2(SO_4)_3$ was most monomeric species (Al_a), while medium polymer species (Al_b) and colloidal or solid species (Al_c) were the main component in PAC (Table 1). The apparent molecular weight of the three Al speciations varies according to the following order: $Al_a < Al_b < Al_c$. It is found that Al_a is the most unstable species [27]. Under the raw water conditions, most Al_a would hydrolyze immediately after dosing and most of Al salts were in the form of hydroxide before reacting with organic matter. Therefore, sweep-flocculation, entrapment and adsorption effect played an important role and was less efficient in the treatment of Yellow River water with $Al_2(SO_4)_3$. While the Al_b content in PAC was correlated well with the removal of turbidity, UV_{254} and DOC due to its high charge neutralization ability. In the low dosage situation, more Al_b species is present in the solution to neutralize the negatively charged organic matter to enhance the removal. From the results indicated in Table 2, it can be seen that pH of the effluent after coagulation and sedimentation with $Al_2(SO_4)_3$ was a little lower than that with PAC. This was correlated well with different velocity and degree for alum and PAC hydrolysis. PAC was a pre-hydrolyzed products and it showed much slower hydrolysis after added in raw water. In contrast, since $Al_2(SO_4)_3$ was a monomeric salt, it hydrolyzed as soon as added into water and it would go through extremely rapid and uncontrolled hydrolysis when solution pH reached a certain value [28,29]. As a result, the two coagulants manifested different influence on sample pH. In addition, taking into consideration the phenomenon that residual Al (and dissolved residual Al) was less in the case of PAC and the fact that most of residual Al in the case of PAC was found to be organically bound; it is more likely that the charge of Al species was neutralized. These are two additional reasons for the lower impact of PAC on the final pH. Specially, pH of effluent after coagulation and sedimentation with both $Al_2(SO_4)_3$ and PAC changed little within the whole dosage. In $Al_2(SO_4)_3$ case, the higher removal of DOC under relatively higher coagulant concentration (15 mg/L) could result from the sweep-flocculation process [30] due to the fact that the concentration was close to the saturation level (overdosing effect, the efficiency of the coagulant decreases at 17 mg/L). The other explanation could be denoted to the in situ formation of Al_b under lower pH conditions [27].

Table 2
The pH of the treated water after coagulation and sedimentation with $Al_2(SO_4)_3$ and PAC (the dosage ranges for both $Al_2(SO_4)_3$ and PAC were 7, 9, 11, 13, 15, and 17 mg/L as Al_2O_3).

Water Samples	Solution pH					
Coagulant dosage (Al, mg/L)	7	9	11	13	15	17
Purified water after coagulation with $Al_2(SO_4)_3$	8.05	7.95	7.89	7.85	7.73	7.67
Purified water after coagulation with PAC	8.10	8.08	7.90	7.93	7.73	7.78

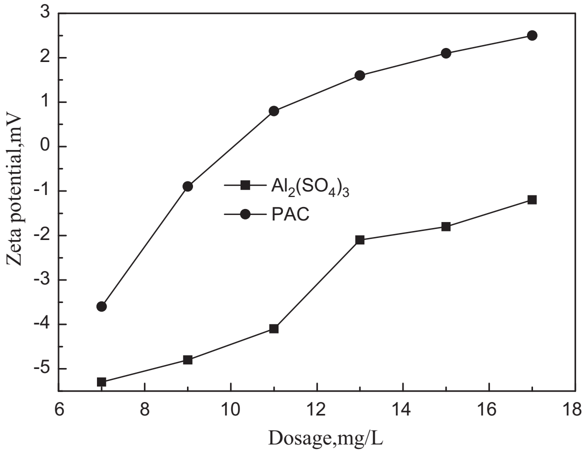

Fig. 3. Zeta potential of flocs formed of $Al_2(SO_4)_3$ and PAC in Yellow River water treatment under different dosage and raw water conditions.

From Fig. 3, it could be also seen that DOC removal was similar for both coagulants, but absorbance removal was much higher with PAC. This inconsistency was due to the characteristics (functional groups, hydrophobically/hydrophilically and aromaticity) of organic matter itself together with the different Al species distribution in the two coagulants. UV_{254} was the ultraviolet absorbance of filtrated water sample at 254 nm. It reflected a class of organic compounds that displayed intense absorbance at 254 nm such as lignin, tannin, humus and the aromatic organic compounds. However, these organic compounds fraction accounted for only 40–60% in dissolved organic carbon (DOC, mg/L) present in natural water [31]. That is to say, UV_{254} and DOC represented different classes of organic materials and this was the reason for their different removal trend. It indicated that the two coagulants removed different organic matter fraction during the treatment of the specific surface water.

The Zeta potential of flocs formed of $Al_2(SO_4)_3$ and PAC after rapid stirring as a function of coagulant dosage for the Yellow River water treatment is shown in Fig. 3. It can be seen that PAC gave much higher Zeta potential and represent much stronger charge neutralization effect than $Al_2(SO_4)_3$ for the removal of turbidity, UV_{254} and DOC. For $Al_2(SO_4)_3$, the Zeta potential increased dramatically and was below zero within the dosage range investigated. For PAC, the Zeta potential of flocs increased sharply at lower dosage and then decreased along with the continuous increase of coagulant dosage. When the PAC dosage was between 11 and 17 mg/L, the Zeta potential shifted into the positive region. The results demonstrate that the mechanisms of turbidity, UV_{254} and DOC were strongly related to the distribution of the Al species. As exhibited, the removal mechanism of PAC is mainly charge neutralization, which resulted in more favorable turbidity, UV_{254} and DOC removal at lower dosage and it lead to more possible particle restabilization at higher dosage. Therefore, it seemed reasonable to contribute to the superior coagulation performance of PAC in most cases, in which Alb and Alc were the majority component.

3.2. Effect of dosages on residual Al speciation in the effluent

The use of Al salts coagulants may either increase or decrease Al concentration in the solution, depending on Al speciation in source water, Al species in the coagulants, Al species transformation during water treatment [13]. In recent years, the physiological toxicity of Al is more and more recognized by people and the toxicity of Al is highly dependent on its speciation ("free" and complexed Al) and mobility (soluble, colloidal or precipitated) [32–34], accordingly, the fractionation and measurement of different Al speciation were conducted in this paper, in order to discuss the effect of dosage on the content and speciation of residual Al of $Al_2(SO_4)_3$ and PAC with respect to the treatment of the Yellow River water. The results are shown in Fig. 4. In addition, the proportion of different residual Al speciation in the total residual Al at various dosage is displayed in Table 3.

It was clear from the result that distribution of residual Al speciation shifted with different predominant speciation. Residual total Al and dissolved organically bound Al species first decreased at lower coagulant dosage and then increased when the coagulant dosage further increased. However, Residual dissolved Al and dissolved monomeric Al species decreased straightly within the dosage investigated for both $Al_2(SO_4)_3$ and PAC. And there was very little amount of residual dissolved organically bound monomeric Al speciation existed in the purified water. In addition, PAC showed lower concentration for each kind of residual Al species implied in Fig. 4, except the concentration of dissolved organically bound Al. Specially, PAC could effectively reduce the concentration of dissolved monomeric Al.

The speciation and fate of dissolved Al in treatment plants are determined by the competition of Al cation with ligands such as hydroxyl ion, fluoride, sulfate and the functional groups of dissolved organic materials. The colloidal and organic materials with a high Al complexation capacity was partially removed in the coagulation progress and the residual organic matter exhibited a different Al-binding capacity. For Al_a, the main component in $Al_2(SO_4)_3$ and the most reactive species out of Al_a, Al_b and Al_c, it performs inferiorly during the coagulation progress and can result in high residual Al in the finished water due to the complexation with organic matter [27].

The results in Table 3 revealed that, for $Al_2(SO_4)_3$ and PAC, the majority of total residual Al existed in dissolved form (about 60–80% for $Al_2(SO_4)_3$ coagulation, 48–73% for PAC coagulation), among which, dissolved organically bound Al was the predominant speciation. And, dissolved inorganically bound monomeric Al was the main component in the dissolved monomeric Al. This phenomenon can be explained as follows. Suspended or particulate Al could be removed from the water column very easily,

Table 3
Proportion of different residual aluminum speciation in the total residual aluminum of $Al_2(SO_4)_3$ and PAC (the dosage ranges for both $Al_2(SO_4)_3$ and PAC were 7, 9, 11, 13, 15, and 17 mg/L as Al_2O_3).

Proportion in the total Al (%)	Coagulant	Dosage (mg/L)					
		7	9	11	13	15	17
Proportion of total dissolved Al (%)	$Al_2(SO_4)_3$	80.01	73.85	73.55	60.05	58.66	46.18
	PAC	66.90	65.51	72.76	64.29	60.00	48.36
Proportion of dissolved monomeric Al (%)	$Al_2(SO_4)_3$	51.86	50.95	43.21	31.04	27.54	19.74
	PAC	28.77	24.19	24.80	21.60	18.50	16.30
Proportion of dissolved organically bound Al (%)	$Al_2(SO_4)_3$	41.30	40.23	41.11	39.02	43.29	35.54
	PAC_{20}	56.84	54.49	54.07	54.59	54.88	48.24
Proportion of dissolved organically bound monomeric Al (%)	$Al_2(SO_4)_3$	0	0	0	0	0	0
	PAC	5.03	0	0	0	0	0

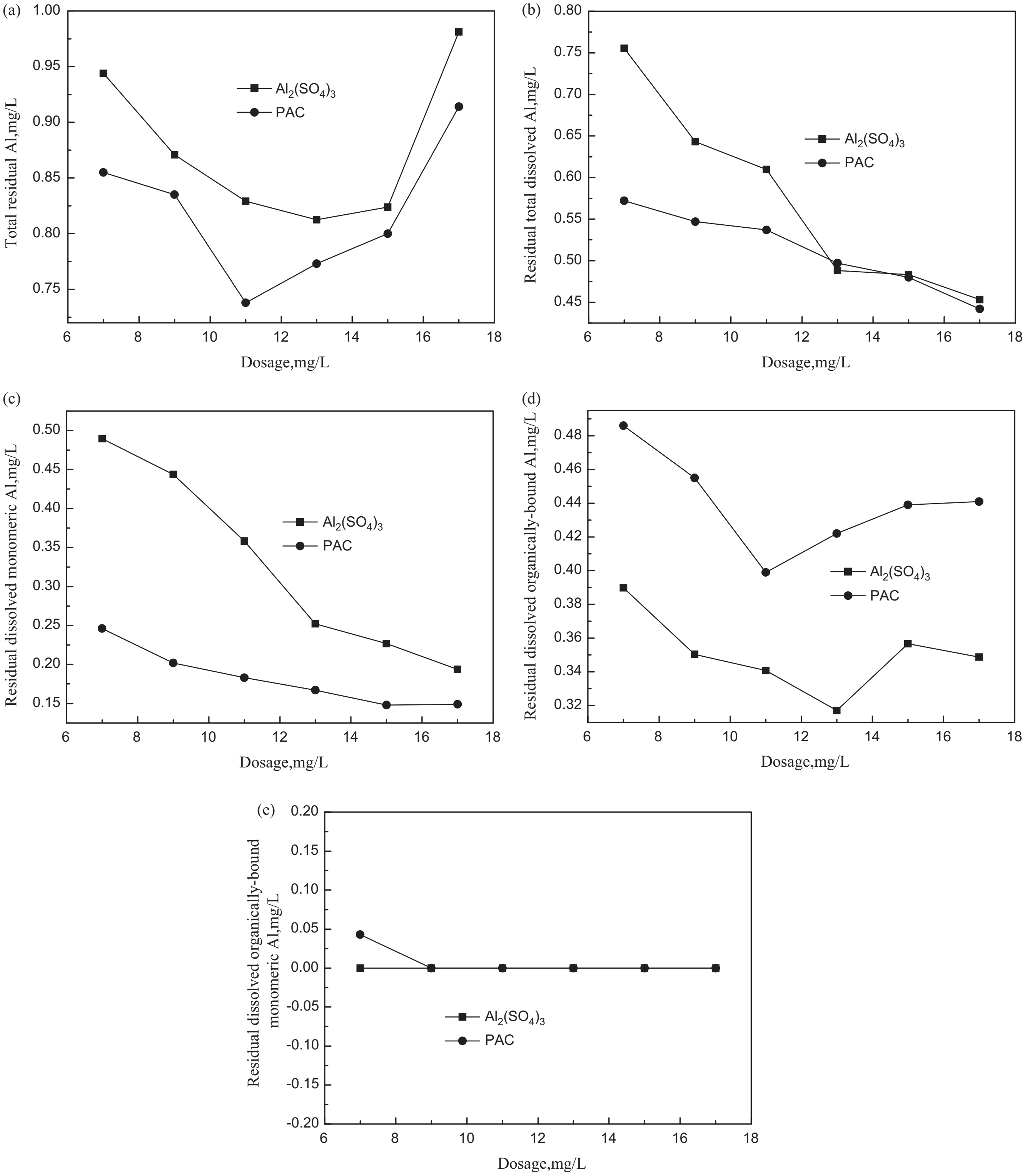

Fig. 4. Effect of dosage on residual aluminum speciation content in Yellow River water treatment: under raw water conditions.

while, dissolved Al fraction exhibited high activity and was partially removed during coagulation process. Therefore, the dissolved Al speciation was the main component in residual total Al of the effluent. The total dissolved Al concentration consists of inorganic Al species (e.g., Al^{3+}, Al $(OH)_2{}^+$, AlF^{2+}) and soluble complexes of Al with dissolved organic carbon. Among the dissolved Al speciation, inorganically bound Al was almost all monomeric cation, while organically bound Al existed mostly in oligomers or complexes formed between Al and natural organic matter or polymeric colloidal materials in the water, which was non-labile, negatively charged and could not be easily removed through conventional coagulation process [10]. Thus, in the total dissolved Al, dissolved organically bound Al was the predominant fraction. Additionally, the resulted expressed in Fig. 4(e) showed that there existed no dissolved organically bound monomeric Al which also indicated that most of the dissolved Al was strongly bound or polymeric colloidal.

3.3. Coagulation performance of $Al_2(SO_4)_3$ and PAC under different pH

A treatment set-up comprising of only $Al_2(SO_4)_3$ and only PAC at 15 mg/L Al_2O_3 was selected to examine the effect of different solution pH on the removal of turbidity, UV_{254} and DOC in the Yellow River water. In view of the dosage effect and good coagulation performance, the dosage of $Al_2(SO_4)_3$ and PAC was determined at 15 mg/L Al_2O_3, which was determined through preparatory experiments shown in Sections 3.1 and 3.2. In addition, considering the acidic, alkaline and neutral condition together, the initial pH of the raw water was adjusted to 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0, respectively. The results of turbidity removal (a), UV_{254} removal (b) and DOC removal (c) with pH variation is shown in Fig. 5. The pH of raw water and the effluent after coagulation and sedimentation with $Al_2(SO_4)_3$ and PAC in the Yellow River water treatment is shown in Table 4.

Consistent with the reported results [35], initial pH had an important effect on the coagulation behavior of the two Al-based coagulants. As indicated in Fig. 5(a), turbidity removal efficiency increased obviously with pH when initial pH is lower than 6.0 and could reach about 85.7 and 85.0% for PAC and $Al_2(SO_4)_3$ at the dosage of 15 mg/L (Al_2O_3) and at initial pH 6.0. When the initial pH is between 7.0 and 9.0, the turbidity removal efficiency increased insignificantly for PAC, while it decreased slightly for $Al_2(SO_4)_3$. And the turbidity removal performance of PAC was better than that of $Al_2(SO_4)_3$ within the whole pH range investigated. Similarly, as seen in Fig. 3(b), UV_{254} removal efficiency increased at the lower initial pHs and could reach about 55 and 52% for PAC and $Al_2(SO_4)_3$ at the dosage of 15 mg/L (Al_2O_3) and at initial pH 6.0. When the initial pH range is between 7.0 and 9.0, the UV_{254} removal efficiency decreased sharply for both the two coagulants. The UV_{254} removal performance of PAC was better than that of $Al_2(SO_4)_3$ within the whole pH range investigated. The DOC removal of the two coagulants manifested the similar trend as the UV_{254} removal and it could reach about 45 and 38% for PAC and $Al_2(SO_4)_3$ at the dosage of 15 mg/L (Al_2O_3) and at initial pH 6.0. For PAC and $Al_2(SO_4)_3$, the optimum pH during the treatment of Yellow River water could be determined at 6.0, which corresponded well with the reported optimums for Al coagulants [36].

The mechanisms to explain the coagulation of particle and organic substances include charge neutralization, precipitation, bridge-aggregation, adsorption and sweep-flocculation [37]. Under different conditions, the different mechanisms or their combination may be dominant. As indicated in the pH of raw and treated water, the effect of the initial pH on the particle and organic materials removal was correlated with the coagulant hydrolyzates. For $Al_2(SO_4)_3$, when pH was lower than 5.0, the polymerization of Al^{3+} was inhibited at a certain degree and the primary Al speciation was the positive monomer hydrolyzates, like $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, and $Al_3(OH)_4^{5+}$,etc. [38,39]. These positive hydrolyzates were easy to neutralize the exterior negative charges of particle and organic materials in Yellow River water, and further destabilize the colloids. They are also of benefit to the physical or chemical adsorption of the destabilized colloids, which lead to floc growth. When the initial pH range was between 6.0 and 8.0, there were some high polymeric positive hydrolyzates and $Al(OH)_3$ formed in solution [38,39]. The colloids were easily adsorbed and co-precipitated by the hydrolyzates, which had low solubility and large surface area. When pH was higher than 8.0, the suspension system was difficult to be destabilized because the hydrolyzates were transformed to $Al(OH)_4^-$ [38,39]. While for laboratory tailor-made PAC product, the polymeric and colloidal species remained quite stable once they were preformed [29]. Correspondingly the coagulation performance of PAC was less influenced by the solution pH variation compared with $Al_2(SO_4)_3$.

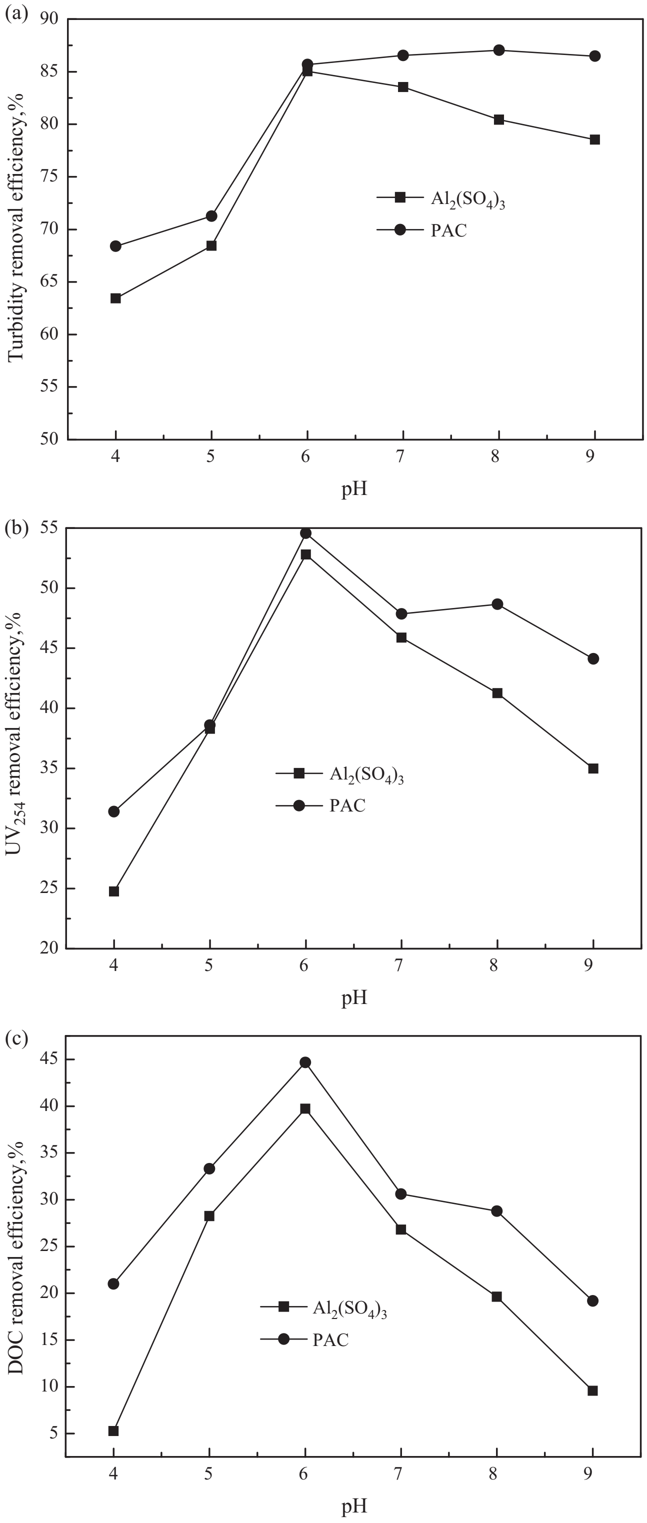

Fig. 5. Effect of pH on coagulation performance of $Al_2(SO_4)_3$ and PAC in Yellow River water treatment at the dosage of 15 mg/L as Al_2O_3.

Fig. 6 presented the Zeta potential of flocs formed after rapid stirring for the two Al-based salts coagulation. In acid region, the Zeta potential of flocs formed after coagulation with both $Al_2(SO_4)_3$ and PAC increased dramatically with the increase of pH, while it reduced significantly at an initial pH range between 6.0 and 9.0. As pH increased, Zeta potential moved into the positive side first and then the negative side and it reached a peak value at pH 6.0.

Table 4
The pH of the treated water after coagulation and sedimentation with $Al_2(SO_4)_3$ and PAC at different initial pH (the coagulant dosage for both $Al_2(SO_4)_3$ and PAC was 15 mg/L as Al_2O_3).

Water Samples	pH					
Raw water	4.0	5.0	6.0	7.0	8.0	9.0
Purified water after coagulation with $Al_2(SO_4)_3$	4.20	5.12	6.40	7.48	7.94	8.29
Purified water after coagulation with PAC	4.21	5.34	6.49	7.46	7.97	8.64

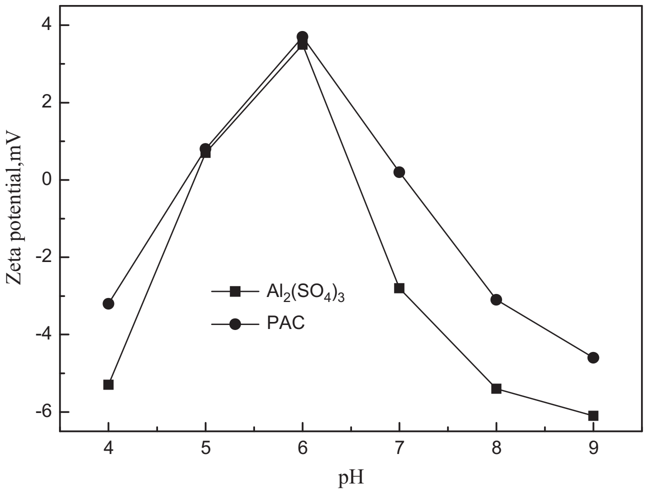

Fig. 6. Zeta potential of flocs formed of $Al_2(SO_4)_3$ and PAC in Yellow River water treatment at the dosage of 15 mg/L as Al_2O_3 under different pH.

This indicated that charge neutralization effect of $Al_2(SO_4)_3$ and PAC at acid ambience was superior to that at alkaline and neutral ambience. In addition, at lower pH range, there was minor difference between Zeta potential of flocs with $Al_2(SO_4)_3$ coagulation and that with PAC. Yet, when pH was higher than 6.0, the Zeta potential of flocs formed with PAC coagulation was obviously higher than that with $Al_2(SO_4)_3$ coagulation. And this was in accordance with the relatively better coagulation performance of PAC in most cases.

Furthermore, pH also affected the physical or chemical properties of particle and organic materials in surface water. The natural organic matter was less hydrophilic and the protonation was improved at weak acid condition (such as pH 6) to make the organic matter easier to be charge-neutralized and destabilized. Not merely, pH could affect the balance between the reactions of organic functional groups with hydrogen ions and Al hydrolysis products [27]. At weak acid conditions (such as pH 6–7), hydrogen ions could outcompete the metal hydrolysis products for organic ligands; thus, the amount of unsatisfied organic ligands is decreased and then colloids and organic materials could be removed more efficiently by metal salts. In alkaline conditions, $Al_2(SO_4)_3$ underwent rapid and strong hydrolysis after contacting with water and only a small portion of Al could react with organic materials to form complexes. Majority of Al salts existed in the form of negatively charged $Al(OH)_3$ and $Al(OH)_4{}^-$ ions, which gave weak charge neutralization effect and the particle and organic materials could not be removed efficiently. However, the existence of the polymerized Al species in PAC prevented at a certain degree the hydrolysis process. This was the reason for the higher efficiency of PAC compared to alum at the alkaline pH range. At the significantly acidic pH range ($pH < 5$), the formation of $Al(OH)_3$ is retarded and therefore alum was again less efficient than PAC at this pH range. PAC contains already the pre-hydrolyzed polymerized Al species, which were more effective than the simple monomeric Al^{3+}. At pH 6, $Al(OH)_3$ formation was favored and therefore the removal efficiencies of PAC and alum were similar to each other.

3.4. Effect of pH on residual Al speciation in the effluent

In order to gain more insight into the roles of different coagulant species, jar test experiments were carried further out to investigate the effect of pH on the speciation and contents of residual Al during the treatment of Yellow River water with $Al_2(SO_4)_3$ and PAC. These effects are shown in Fig. 7. And the proportion of different residual Al speciation in the total residual Al at various initial pH is denoted in Table 5.

The Al present in Al-based coagulants and naturally present in raw water are transformed into various forms during water treatment. As suggested in Fig. 7, the concentration of different Al speciation varied regularly along with the pH variation. The concentration of the tested several Al species represented the similar tendency, expressing as going down at the beginning and then going up later. It seemed reasonable to attribute to the pH variation and the solubility of Al species. As listed in literature [39], the very scarce solubility of Al (III) varied with physiological pH values and the ill-defined nature of the $Al(III)–H_2O–OH^-$ system under practical operational conditions. When pH was lower than 6.0, Al in the solution existed mostly in soluble and labile form such as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2{}^+$ [39], which was hardly removed by coagulation and sedimentation process [10], and tended to remain in the purified water. While under the neutral and the weak alkaline ambience, the gel–$Al(OH)_3$, suspended Al and soluble $Al(OH)_4{}^-$ together were the predominant species and were conveniently removed during water treatment [39,40]. And this was in accordance with the change trends of residual Al concentration. It seemed reasonable to induce the lower residual Al concentration of the coagulants at an initial pH range from 6.0 to 8.0. In addition, as can be seen from the results listed in Table 5, coincidence with the results expressed in Section 3.2, for the two coagulants under different pH, the majority of total residual Al also existed in the form of total dissolved Al (accounting for about 54–97% for $Al_2(SO_4)_3$ coagulation, 51–92% for PAC coagulation), among which, dissolved organically bound Al was the predominant speciation.

Table 5
Proportion of different residual aluminum speciation in the total residual aluminum of $Al_2(SO_4)_3$ and PAC at different initial pH (the coagulant dosage for both $Al_2(SO_4)_3$ and PAC was 15 mg/L as Al_2O_3).

Proportion in the total Al (%)	Coagulant	Solution initial pH					
		4	5	6	7	8	9
Proportion of total dissolved Al (%)	$Al_2(SO_4)_3$	97.90	83.49	69.47	54.19	57.20	78.75
	PAC	92.51	90.07	63.23	51.82	62.20	75.61
Proportion of dissolved monomeric Al (%)	$Al_2(SO_4)_3$	95.03	70.48	52.83	12.70	20.22	49.59
	PAC	74.53	58.55	33.79	9.83	18.30	41.49
Proportion of dissolved organically bound Al (%)	$Al_2(SO_4)_3$	17.58	18.60	26.55	32.52	42.48	31.18
	PAC_{20}	27.81	26.79	33.23	45.83	52.39	41.77
Proportion of dissolved organically bound monomeric Al (%)	$Al_2(SO_4)_3$	10.73	11.61	3.41	2.72	1.47	5.48
	PAC	10.97	8.27	1.16	1.07	0	2.37

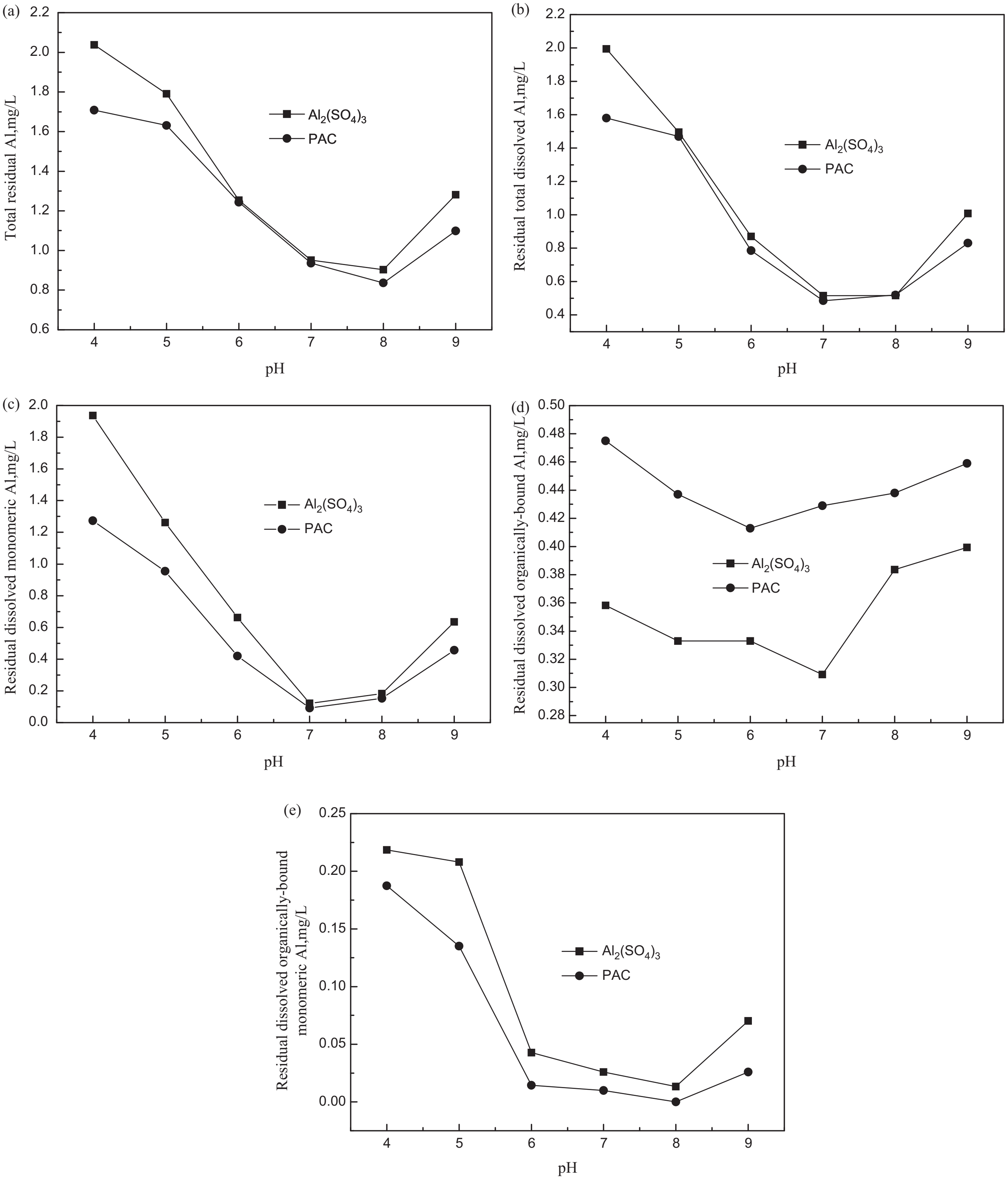

Fig. 7. Effect of pH on residual aluminum speciation content in Yellow River water treatment at the dosage of 15 mg/L as Al_2O_3.

And, dissolved inorganically bound monomeric Al was the main component in the dissolved monomeric Al.

Besides, PAC also exhibited lower concentration for each kind of residual Al species implied in Fig. 7, except the concentration of dissolved organically bound Al, which seemed consistent with the results appeared in the previous research [25]. And PAC could effectively reduce the concentration of dissolved monomeric Al. From the results indicated in Figs. 4 and 7, it was clear that PAC showed higher content of dissolved organically bound Al in the purified water than that with $Al_2(SO_4)_3$. It shows that Al_b could destabilize particles and colloidal materials efficiently to form aggregates. However, it could not form flocs large enough to settle down efficiently, and remained most in the colloidal form.

As can be seen, PAC showed a better coagulation performance in most cases for turbidity, UV_{254} and DOC removal under both different dosage and pH. Specifically, compared with $Al_2(SO_4)_3$, PAC also gave lower concentration of residual Al, except the dissolved organically bound Al. From the standpoint of coagulation–flocculation performance together with the residual Al concentration and its speciation distribution, PAC was a preferable coagulant for the treatment of Yellow River water in Jinan, China. The higher total residual Al concentration (more than 1.0 mg/L) can be explained by the high Al concentration in the raw water (particles materials containing Al_2O_3 component as well as some possible impurities in the Yellow River water) together with the fraction caused by the Al-based coagulants. Additionally, the water treatment units utilized in this study only included coagulation–flocculation and sedimentation and it was necessary and crucial to investigate the effects of the subsequent treatment units (flotation, filtration, adsorption, disinfection, etc.) on the residual Al concentration for the purpose of the reduction of residual Al concentration.

4. Conclusions

(1) PAC showed superior coagulation–flocculation performance compared to $Al_2(SO_4)_3$ in most cases during the Yellow River water treatment. At a dosage of 15 mg/L, PAC achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 96.3, 57.1, 32.7%, respectively, and $Al_2(SO_4)_3$ also achieved an optimum removal efficiency of turbidity, UV_{254} and DOC of 94.5, 53.5 34.8%, respectively. For PAC and $Al_2(SO_4)_3$, the optimum pH during the treatment of Yellow River water could be determined at 6.0. At initial pH 6.0 and the dosage of 15 mg/L (Al_2O_3), for PAC and $Al_2(SO_4)_3$, the turbidity removal efficiency could reach about 85.7 and 85.0%, UV_{254} removal efficiency about 55% and 52%, and the DOC removal efficiency could reach about 45 and 38%.

(2) Residual total Al and dissolved organically bound Al first decreased at lower dosage and then increased when the dosage further increased. However, dissolved Al and dissolved monomeric Al decreased straightly within the dosage for both $Al_2(SO_4)_3$ and PAC. And there was very little amount of dissolved organically bound monomeric Al speciation existed in purified water. The concentration of the several Al species represented the similar tendency under different pH, expressing as going down at the beginning and then going up later. The lower residual Al concentration of the coagulants could be achieved at an initial pH range from 6.0 to 8.0.

(3) For the two coagulants, no matter under different dosage or pH, the majority of residual total Al existed in dissolved form, among which, dissolved organically bound Al was the predominant speciation. And, dissolved inorganically bound monomeric Al was the main component in the dissolved monomeric Al. PAC exhibited lower concentration for each kind of residual Al species, except the concentration of dissolved organically bound Al; and PAC could effectively reduce the concentration of dissolved monomeric Al.

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