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Removal of dispersant-stabilized carbon nanotubes by regular coagulants

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Abstract

Coagulation followed by sedimentation, as a conventional technique in the water treatment plant, can be the first line of defense against exposures of carbon nanotubes (CNTs) to aquatic organisms and human beings, which has been rarely documented. This study investigated the removal of dispersant-stabilized CNT suspensions by poly aluminum chloride (PACl) and $KAl(SO_4)_2 \cdot 12H_2O$ (alum), with a focus on the effects of dispersant type, coagulant type and dosage. PACl performed better than alum in the removal of tannic acid-, humic acid-, and sodium dodecyl benzenesulfonate-stabilized CNTs, but worse for polyethylene glycol octylphenyl ether (TX100)-stabilized CNTs. Neither coagulant could effectively precipitate cetyltrimethyl ammonium bromide-stabilized CNTs. The removal by PACl first increased up to a plateau and then decreased with the continued increase of coagulant dosage. However, the removal rates leveled off but did not decrease after achieving their highest level with the continued addition of alum. The coagulation and flocculation of the CNT suspensions by PACl could be regulated mainly by the mechanism of adsorption charge neutralization, whereas the coagulation by alum mainly involved electrical double-layer compression.

Key words: water treatment; coagulants; nanomaterial; surfactant; natural organic matter

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Introduction

Since the discovery by Iijima (1991), carbon nanotubes (CNTs) have been increasingly produced and used because of their unique electronic, thermal, optical, and mechanical properties (Mauter and Elimelech, 2008). CNTs can be discharged and present in the aquatic environment throughout their life cycle (Köhler et al., 2008; Gottschalk et al., 2009; Lin et al., 2010b). Increasing studies have confirmed toxicities of CNTs to aquatic organisms (Lin et al., 2010b), which creates a demand for the removal of CNTs from industrial and communal wastewaters.

Pristine CNTs are hydrophobic in nature. However, the released hydrophobic CNTs can be stabilized in surface water through the interaction with natural organic matter (NOM) (Hyung et al., 2007; Lin and Xing, 2008). CNTs can also be industrially utilized and discharged in the form of dispersant-facilitated suspensions (Hilding et al., 2003; Hansen et al., 2008) and remain stable in fresh surface waters (Lin et al., 2010a). The NOM- or dispersant-stabilized CNTs can therefore spread out in the aquatic environment and find their way into the water treatment system. The removal efficiency of the water treatment system for the stabilized CNTs can thus control the exposure of CNTs to aquatic organisms and human beings, which has attracted research attention.

Reijnders (2006) suggested that standard wastewater treatment may be ineffective in the removal of nanomaterials, whereas Wiesner et al. (2006) conclude the involvement of nanomaterials in current water treatment systems may not become a problem. Limbach et al. (2008) found that a significant fraction of cerium oxide nanoparticles could escape the clearing system of a wastewater treatment plant, although a majority of the nanoparticles were captured through adhesion to activated sludge. Biosorption of Ti-containing nano- or larger-sized particles from water by activated sludge bacteria was also observed by Kiser et al. (2009) through modeled and field studies. They reported that Ti-containing particles larger than 0.7 μm were effectively removed by a wastewater treatment plant; however, smaller particles could readily escape to the effluent. Further study by Kiser et al. (2010) revealed that 13%–97% of the suspended nanoparticles could be removed mainly by biosorption to the collected activated sludge samples and the removal efficiency was nanoparticle-type and surface-functionality dependent.

Zhang et al. (2008a) investigated the removal of quantum dots (CdTe) from tap water by the traditional coagulant, alum ($KAl(SO_4)_2 \cdot 12H_2O$). The removal rate of the quantum dots was about 70% by sedimentation alone and the addition of alum with dosage up to 2.86 meq Al(III)/L showed insignificant enhancement of the removal rate. Zhang et al. (2008b) also examined the effectiveness of alum in the removal of nanoparticulate

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TiO₂, SiO₂, ZnO, Fe₂O₃ and NiO from water. The removal rates at 60 mg/L of alum were 20%–60% and dependent on the sizes, surface properties and concentrations of the nanoparticles. Colloidal aggregates of C₆₀ (nC₆₀) were efficiently removed by a suite of coagulation, flocculation and sedimentation processes, with the removal efficiency dependent on nC₆₀ surface properties, NOM content and coagulant (alum) dosage (Hyung and Kim, 2009). Holbrook et al. (2010) specifically examined seven factors that affect CNT coagulation and concluded that the CNT removal was mainly affected by coagulant type and dosage and none of the other factors (method of CNT stabilization and concentrations of kaolin, organic matter, alginate and CNTs) were universally significant.

The above limited studies substantially help improve the understanding of the performance of conventional water treatment process for the removal of nanoparticles from water. However, more research is warranted to illustrate the complicated process of CNT removal in terms of the large varieties of CNTs and their stabilization methods. This study was therefore aimed to investigate the removal of dispersant-stabilized CNTs by coagulants with a focus on the effects of dispersant and coagulant types.

1 Materials and methods

1.1 Materials

A multiwalled CNTs with outer diameters of 20–40 nm and purity higher than 95% was purchased from Shenzhen Nanotech Port Co., China. It had been characterized and used in our previous work (Lin and Xing, 2008; Lin et al., 2009). Poly aluminum chloride (PACl) was purchased from Huabei Chemical Technology Co., Guangzhou, China, of which the alumina content was 27% (determined using an inductively coupled plasma mass spectrometer, Agilent7500a, USA), basicity 40%, and water-insoluble matter 1.5%. Alum (AR) was obtained from Hushi Chemical Reagent Co., Zhejiang, China. Five kinds of dispersants including tannic acid (TA), humic acid (HA), and three types of surfactants were used to prepare stable CNT suspensions. TA and HA were respectively purchased from Alfa Aesar (Ward Hill, USA) and Sigma Aldrich, Switzerland, and used as surrogates of NOM (Lin et al., 2009, 2010a). Sodium dodecyl benzenesulfonate (SDBS), cetyltrimethyl ammonium bromide (CTAB), and polyethylene glycol octylphenyl ether (TX100) are widely used anionic, cationic, and nonionic surfactants, respectively, and have been proved effective in stabilizing CNT suspensions (Lin et al., 2010). SDBS was purchased from Tokyo Chemical Industries Co., Japan, and CTAB and TX100 from Shanghai Ling-feng Chemical Reagents Ltd., China.

1.2 Methods

1.2.1 CNT suspensions

The dispersant solutions with concentration of 80 mg/L, which can be a realistic concentration in the aquatic environment (Han et al., 2008; Lin et al., 2009, 2010a), were used to make the stock CNT suspensions. HA solution was

prepared by dissolving the solid HA sample into ultra-pure water from a Milli-Q system using 0.1 mol/L NaOH, and the final solution pH was adjusted to 7.0 using 0.1 mol/L HCl. The other four dispersants were directly dissolved into ultra-pure water with pH adjusted to neutral. Two hundred mg of CNTs were mixed into 1 L of the dispersant solutions, followed by bath-sonication (40 KHz, 150 W, 25°C) for 1 hr and centrifugation at 3500 ×g for 30 min. The resultant supernatants were collected as the stock CNT suspensions.

Concentrations of the aqueous dispersants and the stabilized CNTs in the stock suspensions were measured with a method detailed in our previous articles (Lin et al., 2010; Lin and Xing, 2008). Briefly, the stabilized CNTs were determined with a TOC analyzer (Shimadzu, TOC-V_{CPH}) and calibrated to the absorbances at 800 nm; the concentrations of aqueous SDBS and TX100 after filtration through a 0.2 μm PTFE filter (Whatman) were measured by the absorbance at 223 nm, and the aqueous CTAB, TA, and HA were quantified by the TOC analyzer. Zeta potentials and hydrodynamic sizes of the stock CNT suspensions were determined using a zetasizer (Malvern, Nano-ZS90) at 25°C and pH 7.0.

1.2.2 Coagulation experiments

PACl and alum were dissolved into ultra-pure water with a concentration of 2% and diluted to the desired concentrations in the following coagulation experiments. Zeta potentials and hydrodynamic sizes of the coagulant solutions were also measured.

A jar test was used to evaluate removal of the dispersant-stabilized CNTs (dispersant-CNTs) by the coagulants on a magnetic mixer (Jintan, Jiangsu, China). The apparatus could accommodate six beakers simultaneously stirred at the same speed with magnets. Magnets of 2.7 cm in length and 0.8 cm in diameter and 100 mL beakers were used. Before the experiments, the stock CNT suspensions were semi-diluted using ultra-pure water. Forty five milliliters of the diluted CNT suspensions were added into the beakers. The jar tests were performed in three steps: (1) rapid mixing for 1 min at 730 r/min, (2) slow mixing for 20 min at 170 r/min, and (3) settling for 30 min. Five milliliters of the coagulant solutions of different concentrations were mixed into the 45 mL of CNT suspensions once the rapid mixing started. After the rapid mixing step, 5 mL of the mixtures were sampled for the zeta potential measurement using the zetasizer. After the settling step, the absorbances at 800 nm (UV₈₀₀) of the supernatants were measured as UV_{800-end}. UV₈₀₀ of the stock CNT suspensions were also determined and the initial UV₈₀₀ of the mixtures (45 mL of the diluted CNT suspensions and 5 mL of the coagulant solutions) were calculated as UV_{800-initial}. UV₈₀₀ has been widely used as an indicator of the concentration of stabilized-CNTs (Lin et al., 2010a). The removal rates of the dispersant-stabilized CNTs by the coagulants were then calculated by $(1 - UV_{800-end}/UV_{800-initial}) \times 100\%$. The pH values of the stock CNT suspensions and the supernatants after the settling step were also measured. Each coagulation test was performed in triplicate.

2 Results

2.1 Characteristics of the CNT suspensions and coagulant solutions

The mean outer diameter of the CNTs used was 28 ± 6 nm, the specific surface area calculated from the adsorption-desorption isotherm of N_2 at 77 K by multi-point BET method was $86 \text{ m}^2/\text{g}$, and the surface elemental contents of C and O measured by an X-ray photoelectron spectroscopy were 98.0% and 2.0%, respectively (Lin and Xing, 2008; Lin et al., 2009). The zeta potential and hydrodynamic diameter of the CNTs in ultra-pure water were -30 mV and 1000 nm , respectively, but could not be precisely determined due to the unstable nature of the suspensions. The initial concentrations, zeta potentials, and hydrodynamic diameters of the stabilized-CNTs and the aqueous concentrations of the dispersants in the stock CNT suspensions are shown in Table 1. The pH values of the stock CNT suspensions were around 6. The concentrations of the stabilized-CNTs ranged from 13.2 to 43.3 mg/L. HA and TA were proved to be more effective for the stabilization of CNTs than the surfactants. The stabilization could be due to the enhanced electrostatic and/or steric repulsions between CNTs by the CNT-adsorbed dispersants (Lin and Xing, 2008). TA, HA and SDBS delivered negative charges to the CNT surfaces, whereas CTAB introduced positive charges. TX100 did not significantly alter the zeta potential of the CNTs, but could disperse and stabilize CNTs mainly by steric repulsion. The dispersant-CNTs had similar hydrodynamic diameters of 235–250 nm. The aqueous concentrations of the dispersants in the stock CNT suspensions were 19.8–59.6 mg/L, which suggests about 60.2–20.4 mg/L of the dispersants were adsorbed by the CNTs.

Changes of the zeta potential and hydrodynamic diameter of the PACl solution with concentration are shown in Fig. 1. PACl in ultra-pure water formed positively-charged flocs with zeta potential of 24–46 mV. The zeta potential and hydrodynamic size of alum solutions could not be effectively measured, indicating the absence of flocs. The pH values of the coagulant solutions decreased from neutral to 4.5 with increasing concentrations of both PACl and alum due to the hydrolysis of aluminum ions.

2.2 Removal of dispersant-stabilized CNTs by PACl

Changes in the removal rates of the dispersant-CNTs against PACl concentrations are shown in Fig. 2, and the corresponding removal efficiency data are listed in Table 2. The removal curves in Fig. 2 appear as an inverted “U”

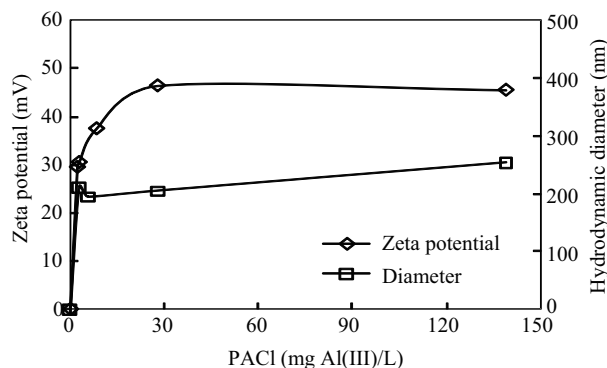


Fig. 1 Changes of zeta potential and hydrodynamic diameter of PACl solution against PACl concentration.

type and apparently can be divided into three zones with increasing PACl concentration (Luan and Tan, 1992): (1) “no significant removal zone”, where the removal rate remained low; (2) “coagulation and sedimentation zone”, where the removal rate sharply increased and reached a plateau; (3) “re-stabilization zone”, where the removal rate decreased due to the re-stabilization of precipitated CNTs. Several removal curves in Fig. 2 do not show a “no significant removal zone”, which is because the dose of PACl falling into this zone was too low to be examined in this study. The maximum removal rates of the dispersant-CNTs by PACl followed an order of SDBS-CNTs (98.9%) > TA-CNTs (92.4%) > HA-CNTs (78.6%) > TX100-CNTs (20.7%) > CTAB-CNTs (0.0). CTAB-CNTs could not be removed by PACl. Very small flocs in the TX100-CNT suspension were observed after the slow-mixing step, which however remained small and suspended during the settling stage. The effective concentration ranges of PACl for CNT removal varied with the dispersants, with the optimum PACl concentrations respectively being 2.78, 5.56, 2.78 and 0.22 mg Al(III)/L for TA, HA, SDBS and TX100.

The zeta potentials of TA-, HA-, SDBS- and TX100-stabilized CNT suspensions increased with increasing concentrations of added PACl (Fig. 2). In the “no significant removal zone”, the zeta potentials of the dispersant-CNTs increased but remained highly negative with increasing concentrations of added PACl, whereas they sharply increased to around 0 within the “coagulation and sedimentation zone” and kept rising up to a highly positive charge within the “re-stabilization zone” with further addition of PACl. The zeta potential of CTAB-CNTs slightly increased and remained at 70 mV with the addition of PACl.

Table 1 Characteristics of the stock dispersant-stabilized CNT suspensions

	TA-CNTs	HA-CNTs	SDBS-CNTs	TX100-CNTs	CTAB-CNTs
Stabilized CNTs (mg/L)	30.9	43.3	13.2	26.3	16.6
Zeta potential (mV)	-36.6	-45.8	-47.9	-30.1	53.7
Hydrodynamic diameter (nm)	249	250	240	246	235
Dispersants (mg/L)	19.8	59.6	25.8	24.8	60.0

TA-CNTs, HA-CNTs, SDBS-CNTs, TX100-CNTs, and CTAB-CNTs respectively stand for TA-, HA-, SDBS-, TX100-, and CTAB-stabilized CNT suspensions. The suspension pH values were around 6.

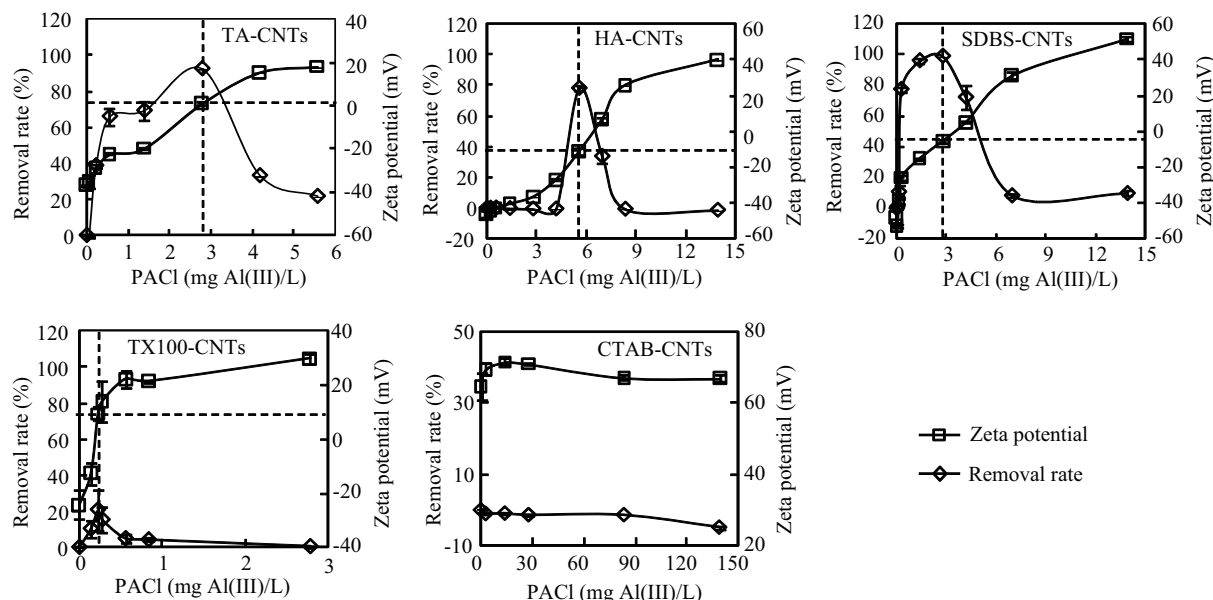


Fig. 2 Changes of the removal rates and zeta potentials of the dispersant-stabilized CNTs against PACl concentrations.

Table 2 Removal efficiency of the dispersant-stabilized CNTs from water by coagulants

	TA-CNTs	HA-CNTs	SDBS-CNTs	TX100-CNTs	CTAB-CNTs
Maximum removal rate by PACl (%)	92.4 ± 0.0	78.6 ± 1.6	98.9 ± 0.0	20.7 ± 11.1	0.0
Optimum PACl conc. (mg Al(III)/L)	2.78	5.56	2.78	0.22	/
Effective conc. range of PACl (mg Al(III)/L)	0.22–4.17	4.17–8.34	0.14–6.95	0.14–0.28	/
Maximum removal rate by alum (%)	88.5 ± 1.2	68.9 ± 5.3	97.7 ± 0.7	86.6 ± 2.2	12.1 ± 1.4
Optimum alum conc. (mg Al(III)/L)	0.7	5.0	2.5	250	250
Effective conc. range of alum (mg Al(III)/L)	> 0.5	> 1.5	> 0.5	> 5.0	/

“/” stands for no effective data could be obtained.

2.3 Removal of dispersant-stabilized CNTs by alum

The removal of dispersant-CNTs by alum showed a different trend compared to that by PACl (Fig. 3). There were “no significant removal zones” and “coagulation and sedimentation zones”, but no “re-stabilization zone”. The maximum removal rates of the dispersant-CNTs by alum followed an order of SDBS-CNTs (97.7%) > TA-CNTs (88.5%) > TX100-CNTs (86.6%) > HA-CNTs

(68.9%) > CTAB-CNTs (12.1%) (Table 2). TX100-CNTs could be effectively removed by alum, however, the optimum coagulant concentration for TX100-CNTs (250 mg Al(III)/L) was greatly higher than that for TA-CNTs (0.7 mg/L), HA-CNTs (5.0 mg/L) and SDBS-CNTs (2.5 mg/L). CTAB-CNTs could not be effectively removed by alum with the concentration up to 250 mg Al(III)/L.

The zeta potentials of TA-, HA-, SDBS-, and TX100-

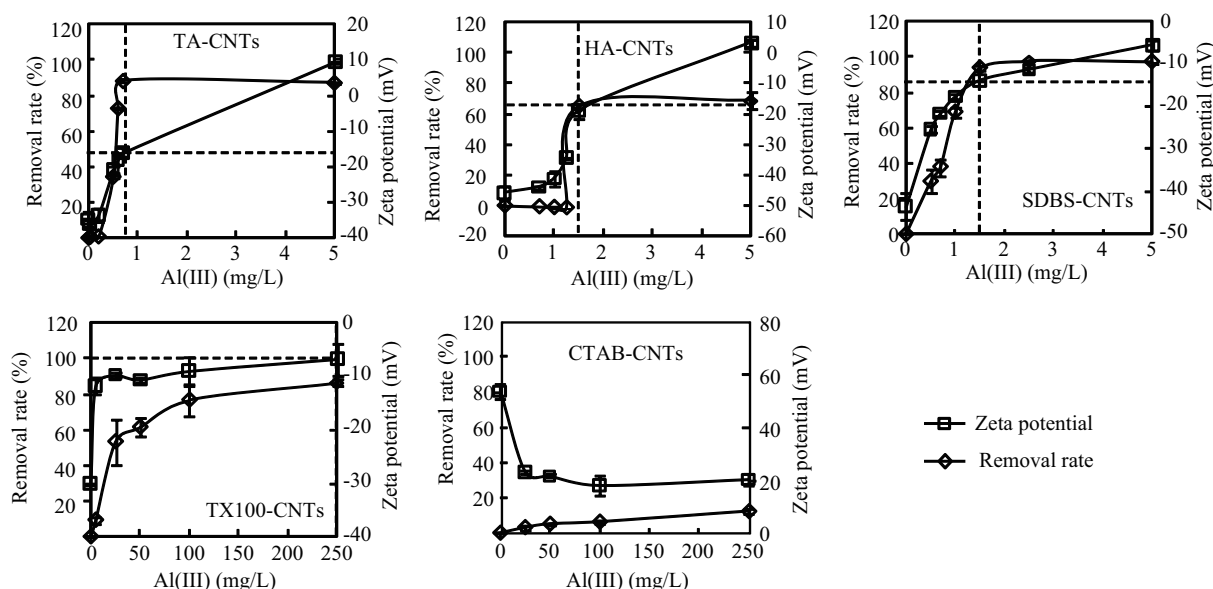


Fig. 3 Changes of the removal rates and zeta potentials of the dispersants-stabilized CNTs against alum concentrations.

CNTs increased and reached a plateau near 0 mV with the addition of alum (Fig. 3), but did not change from negative to positive as was the case with PACl. In contrast to PACl, the zeta potential of CTAB-CNTs decreased to 20 mV with the addition of alum.

Mixture with CNTs slightly reduced the pH levels of the five dispersant solutions from near neutral to about 6. The pH values of the stock dispersant-CNTs further lowered from 6 to 4.3–5.8 (Fig. 4a1–4a5) and 3.5–4.5 (Fig. 4b1–4b5) after the addition of PACl and alum, respectively, due to the hydrolysis of aluminum ions.

3 Discussion

Four mechanisms are generally described to regulate colloid removal by coagulants, which are electric double-layer compression, adsorption charge neutralization, intercolloid bridging, and sediment netting/sweep coagulation (Ahmad et al., 2006). They often play a role in the same time or alternate, but one mechanism may dominate the removal under certain circumstances.

Electric double-layer compression could be the main mechanism for the coagulation of the dispersant-CNTs by alum. Except for the positively-charged CTAB-CNTs, the other four dispersant-CNTs were all negatively charged. The positively-charged aluminum ions in single-core complexes formed by alum in the suspensions could compress the electric double-layers of the negatively-charged dispersants-CNTs, lower the absolute values of the zeta potentials, and eventually coagulate and precipitate the suspended CNTs.

The major mechanism for the removal of dispersant-CNTs by PACl could be charge neutralization by adsorption of PACl-formed multi-core complexes. PACl could form positively-charged flocs in water (Fig. 1). The chain-like and positively-charged PACl flocs could strongly adsorb to the negatively-charged dispersant-CNTs, and subsequently, neutralize the surface charges of the dispersant-CNTs, diminish the electrostatic repulsion between CNTs, and then coagulate and precipitate the stabilized-CNTs. However, as a type of polyelectrolyte, PACl could over-saturate the negatively-charged

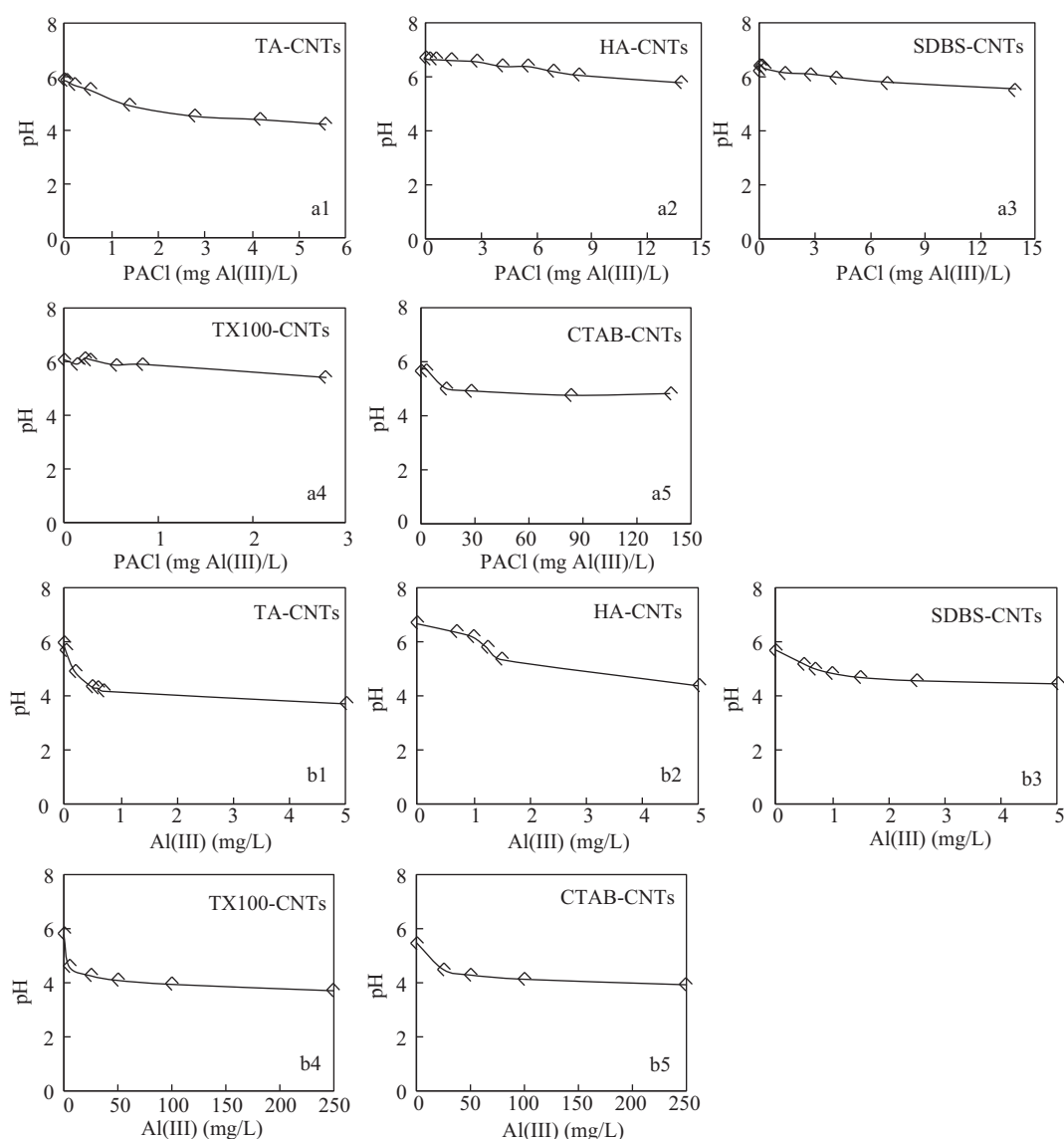


Fig. 4 Changes of pH of the dispersant-CNT suspensions with the addition of PACl (a) and alum (b).

CNT surfaces and make the surfaces positively-charged at high concentrations, which may then re-disperse and stabilize the precipitated CNTs due to the reproduced electrostatic repulsion between CNTs, as demonstrated by Fig. 2. Re-stabilization of coagulated colloids due to oversaturation of polyelectrolytes has been reported by Pinotti and Zaritzky (2001).

Aluminum in alum could form hydrated ions such as $\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^+$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in water at pH around 5 (Zhang, 2008a). These positively-charged ions may also adsorb to the negatively-charged CNT surfaces and destabilize the dispersant-CNTs by the mechanism of adsorption charge neutralization. However, the adsorption of aluminum ions in the single-core complexes formed by alum to the dispersant-CNTs could be weaker than that of the chain-like multi-core complexed Al(III) from PACl, and consequently, could not reverse the zeta potential of the dispersant-CNTs (Fig. 3). The stronger adsorption charge neutralization by PACl may also account for its better performance than alum in the removal of the negatively-charged TA-, HA-, and SDBS-CNTs. However, PACl performed worse than alum in the removal of TX100-CNTs, and both coagulants could not effectively remove the positively-charged CTAB-CNTs. The addition of PACl destabilized TX100-CNTs with very fine flocs observed, which however did not grow and precipitate during the settling stage (30 min). Positively-charged PACl neutralized the negatively-charged TX100-CNTs, which could facilitate the aggregation of TX100-CNTs by diminishing the electrostatic repulsion. However, the adsorbed layer of neutral TX100 on the CNTs may hardly be compressed by positively-charged PACl, which could thus limit the aggregation of TX100-CNTs and formation of large flocs due to steric repulsion. The reduction in the zeta potential (from 50 to 20 mV) of CTAB-CNTs by the addition of alum could be ascribed to alum-released SO_4^{2-} . The SO_4^{2-} (> 40 mg/L) from Na_2SO_4 could neutralize and precipitate CTAB-CNTs according to our previous research (Lin et al., 2010). However, the removal of CTAB-CNTs by SO_4^{2-} from alum was poor (12.1%) in this study.

The lowered pH values of the negatively-charged dispersant-CNT suspensions after the addition of the coagulants (Fig. 4) could also contribute to the removal of the stabilized CNTs. Absolute zeta potentials of the negatively-charged dispersant-CNTs could decrease with the decrease of solution pH (Lin et al., 2009), which would diminish the electrostatic repulsion between dispersant-CNTs and facilitate the aggregation. Moreover, oxygen-containing functional groups (such as -OH and/or -COOH) of TA and HA on the CNTs could not be dissociated at low pH and may form inter-colloid bridges through hydrogen bonding and consequently precipitate the dispersant-CNTs (Lin et al., 2009).

4 Conclusions

The removal of dispersant-stabilized CNT suspensions through the traditional coagulation and sedimentation process is dependent on dispersant type, coagulant type and

dosage. The CNT suspensions stabilized by the dispersants which deliver negative charges could be readily removed by PACl and alum, with better removal efficiencies observed by PACl; whereas, the positively-charged CTAB-CNTs could not be effectively removed by the coagulants. An inverted U type of removal rate curve against coagulant dosage was observed for PACl but not for alum, which suggests the optimum dosage of PACl should be predetermined before its application. The traditional water treatment plant may face challenges in removing CNTs stabilized by specific dispersants.

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