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Removal of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans by three coagulants in simulated coagulation processes for drinking water treatment

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ABSTRACT

Surface water from Guangzhou to which standard polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were added was treated by coagulation with ferric chloride (FC), polyaluminium chloride (PAC), and aluminium sulfate (AS) at optimum removal dosages for nature organic matter (NOM) to assess the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) removal efficiencies. PCDD/Fs in suspended particulate matter (SPM) and treated water (TW) after coagulation were analysed. Low residual levels of PCDD/Fs were found in treated water after coagulation: 0.8% for FC, 0.9% for PAC, and 3.1% for AS. The removal efficiency calculated using these results was >99% for FC and PAC and 97–98% for AS. Most PCDD/Fs congeners could be removed by the three coagulation processes; the removal efficiency of FC and PAC was similar, and slightly higher than that of AS. The results also demonstrate that coagulation with FC preferentially removed tetra- and penta-substituted PCDD/Fs from raw water.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are toxic, chemically stable and present in almost all environmental compartments [1,2], which may pose serious adverse effects on human health and ecosystems. PCDD/Fs in water body may occur on suspended particles by sorption or in water by desolvation. The concentration in water phase, however, is extremely low (pg/L or fg/L) owing to their low solubility and high octanol–water coefficients K_{ow} [3–5]. The most of PCDD/Fs bind strongly to suspended particulate matter (SPM) and associate with natural organic matter (NOM) present in water. The concentration of PCDD/Fs in water is a very important indicator of water quality [6,7]. For example, the US EPA has set an allowable concentration of 2,3,7,8-tetra-CDD in drinking water of 0.13–0.0013 pg/L based on risk assessment of human health exposure to PCDD/Fs (tumour incidence risk 0.13 pg/L for 10^{-5} and 0.0013 pg/L for 10^{-7}) [8]. The maximum contaminant level, based on a tolerable daily intake (TDI) of 10 pg toxic equivalent quantity (TEQ)/(kg body weight day), and the maximum contaminant level goal have been set to 30 and 0 pg-TEQ/L, respectively [9]. The strict limitation of PCDD/Fs in water by regulation facilitates the development of water treatment technologies to eliminate PCDD/Fs from water.

High PCDD/Fs removal efficiencies may be reached using membranes and activated carbon in treatment processes. However, these approaches are expensive and generally require pretreatment. The current preference is to coagulate PCDD/Fs with metal additives such as alum and ferric salts coupled to downstream physical separation methods and dissolved air flotation [3,10–13]. As PCDD/Fs are mainly associated with NOM, they will be removed together with NOM particle in the course of particle–coagulant interaction. The coagulation efficiency for PCDD/Fs removal is a function of NOM in particulates, which depends on several factors, including the coagulant type, dosage, pH, particle size and NOM properties. These factors are still not well investigated [14–19].

The objective of the present study was to investigate PCDD/Fs removal during coagulation using three common coagulants, ferric chloride ($FeCl_3{\cdot}6H_2O$; FC), polyaluminium chloride (PAC), and aluminium sulfate [$Al_2(SO_4)_3{\cdot}18H_2O$; AS] at the optimal dosage and pH for removal of NOM. Particulate organic carbon (POC) and dissolved organic carbon (DOC) were measured to assess the effect of NOM on the removal of PCDD/Fs.

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2. Materials and methods

2.1. Raw water (RW)

Three raw water samples were collected from the West Tributary of the Pearl River on 16 October 2005. The West Tributary of the Pearl River is the main water source for Guangzhou in Guangdong Province, a city that has experienced the fastest growth in the Chinese economy in the last three decades. PCDD/Fs and particulates in the upper streams of the West Tributary are low [20] and high in the lower reaches near Guangzhou. The sampling sites used for this study were located between the upper and lower reaches, where the water properties are similar to those in the lower reaches, but PCDD/Fs concentrations are low. These water samples were considered suitable for water treatment simulation. The characteristics of the raw water were: alkalinity, 37.5 mg/L $CaCO_3$; turbidity, 46.3 NTU; pH, 7.15; DOC content, 5.71 mg/L; SPM, 28.85 mg/L; and POC content, 5.46% in SPM.

Water samples were collected in 1.0 L amber glass flasks. PCDD/Fs concentrations in 1.0 L of raw water were below the analytical detection limit (see below), so all samples were spiked with 20 μL of Precision and Recovery Solution (PAR; CIL, EDF-7999) including 17 2,3,7,8-substituted PCDD/Fs; the levels added are shown in Table 1. Total PCDD/Fs concentrations were 6960 pg/L and 1000 pg WHO-TEQ/L which were all below their maximum solubility in water [3]. The samples were rapidly stirred at 100 rev/min (rpm) in an apparatus with six test jars and then at 50 rpm overnight at room temperature (23 °C) to achieve sufficient aggregation of PCDD/Fs with NOM in water. This water with added PCDD/Fs was named raw water.

2.2. Selection of coagulant dosages

The FC and AS coagulants used in bench-scale tests were reagent grade. PAC was produced by a local factory and contained 30% Al_2O_3. These materials are now used in water treatment factory of Guangzhou.

In the present study, the coagulation process was optimised mainly with regard to coagulant dosage and NOM removal efficiency. To determine the optimum coagulant dosage for NOM removal, jar tests were conducted using dosages from 20 to 140 mg/L. The optimum coagulant dosage was determined at maximum DOC removal. Fig. 1 shows that FC was the most efficient coagulant for NOM removal, with a DOC removal ratio of 49%, approximately 7.7% and 29% more efficient than PAC and AS for DOC removal at a dosage of 120 mg/L. We set the optimum coagulant dosage to 120 mg/L for coagulation experiments based on these results. The values of pH in all solutions for FC, PAC and AS were 5.5–6, 6.8–7 and 6.5–7, respectively, which lie in the range of optimised pH for iron-based coagulants (4.5–7) and aluminium-based coagulants (6–8).

Table 1

Summary data for 17 PCDD/Fs congeners and homologues in raw water (RW), treated water (TW) and suspended particulate matter (SPM) after coagulation

Compounds	RW (pg/L)	TW (pg/L)			SPM (pg/L)[a]			SPM + TW (pg/L)		
		TW1	TW2	TW3	SPM1	SPM2	SPM3	1[b]	2[b]	3[b]
2378-TCDF	80	3.74	3.21	6.92	73.2	61	60	77	64	67
12378-PeCDF	400	2.35	4.07	1.94	319	320	292	321	324	294
23478-PeCDF	400	5.14	1.72	16.2	322	311	293	327	313	309
123478-HxCDF	400	2.25	2.13	9.16	335	360	307	337	362	316
123678-HxCDF	400	1.01	0.00[c]	5.78	338	334	289	339	334	295
234678-HxCDF	400	3.69	0.663	5.81	312	335	291	316	336	297
123789-HxCDF	400	0.00[c]	0.00	6.75	356	330	306	356	330	313
1234678-HpCDF	400	0.00[c]	1.28	7.25	316	320	291	316	321	298
1234789-HpCDF	400	0.00[c]	0.00[c]	5.59	305	306	288	305	306	294
OCDF	800	2.34	4.07	10.5	724	797	698	726	801	709
2378-TCDD	80	0.00[c]	2.03	0.574	64	62	61	64	64	62
12378-PeCDD	400	3.46	5.26	15.9	367	354	317	370	359	333
123478-HxCDD	400	1.29	1.81	8.66	306	289	302	307	291	311
123678-HxCDD	400	0.00[c]	0.00[c]	6.39	305	314	288	305	314	294
123789-HxCDD	400	1.35	1.65	11.6	336	308	281	337	310	293
1234678-HpCDD	400	0.71	4.62	23.6	310	349	291	311	354	315
OCDD	800	2.98	2.26	19.7	737	725	711	740	727	731
Total $Cl_{4\text{-}5}$[d]	1360	14.7	16.3	41.5	1145	1108	1023	1160	1124	1065
Total Cl_6[d]	2800	9.59	6.25	54.1	2288	2271	2064	2298	2277	2118
Total $Cl_{7\text{-}8}$[d]	2800	6.03	12.2	66.7	2393	2497	2278	2399	2509	2345
Total PCDD/Fs[e]	6960	30.3	34.8	162	5826	5876	5365	5856	5911	5527
DOC (mg/L)[f]		2.86	3.31	4.54						
RW characteristics										
SPM (mg/L)										28.85
POC (%)										5.46
DOC (mg/L)										5.71
pH										7.15
Turbidity (NTU)										46.3
TDS (μS/cm)										712.4

[a] SPM (pg/L) is particulate PCDD/F concentration in SPM filtered from 1 L of raw water.

[b] 1 means the sum of PCDD/Fs for SPM1 and TW1, 2 the sum for SPM2 and TW2, and 3 the sum for SPM3 and TW3.

[c] 0.00, concentration below detection limit is designated the value of zero.

[d] TCDF, tetra-chlorinated dibenzofurans; PeCDF, penta-chlorinated dibenzofurans; HxCDF, hexa-chlorinated dibenzofurans; hepta-chlorinated dibenzofurans; OCDF, octa-chlorinated dibenzofurans; TCDD, tetra-chlorinated dibenzo-*p*-dioxins; PeCDD, penta-chlorinated dibenzo-*p*-dioxins; HxCDD, hexa-chlorinated dibenzo-*p*-dioxins; HpCDD, hepta-chlorinated dibenzo-*p*-dioxins; OCDD, octa-chlorinated dibenzo-*p*-dioxins; Total $Cl_{4\text{-}5}$, the sum of tetra- and penta-substituted PCDD/Fs; Total Cl_6, the sum of hexa-substituted PCDD/Fs; Total $Cl_{7\text{-}8}$, the sum of hepta- and octa-substituted PCDD/Fs.

[e] Total PCDD/Fs are the sum of 17 congener concentrations.

[f] DOC (mg/L) is residual DOC concentration in treated water (TW1, TW2 and TW3).

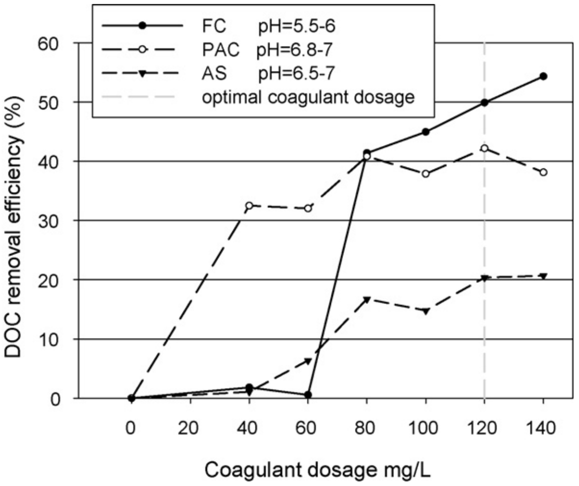

Fig. 1. Comparison of DOC removal efficiency for three coagulants (FC, PAC and AS) and selection of coagulant dosage. The values of pH in all solutions for FC, PAC and AS were 5.5–6, 6.8–7 and 6.5–7, respectively, which lie in the range of optimised pH for iron-based coagulants (4.5–7) and aluminium-based coagulants (6–8).

2.3. Treatment of RW

Coagulation experiments were performed in the same stirring apparatus. Three flasks containing 1.0 L of RW were rapidly mixed at 100 rpm for 2 min, slowly mixed at 30 rpm for 20 min, and then settled (0 rpm) for 60 min. During the rapid mixing period, 120 mg/L PAC, FC and AS was added to separate flasks. At the end of each test, samples were filtered through preheated (500 °C) glass fibre filters (GF/F; pore size 0.45 μm; Whatman, UK). After filtration, the FC, PAC and AS coagulant fractions were collected and designated SPM1, SPM2 and SPM3, respectively. The filtrates were percolated through preconditioned solid-phase extraction disks (ENVI-18 DISK 47 mm, Supelco, USA). Disks from water phases treated by FC, PAC and AS were designated TW1, TW2 and TW3, respectively.

2.4. Analytical methods

2.4.1. PCDD/Fs analysis

TW1, TW2, TW3, SPM1, SPM2 and SPM3 samples were dried in a desiccator and subjected to Soxhlet extraction with toluene (pesticide grade; Merck, Germany) for 24 h after being spiked with a mixture of 15 $^{13}C_{12}$-labeled internal standards (CIL, EDF-8999). Then 50 μL of *n*-tetradecane was added and each sample was concentrated to 1 mL on a rotary evaporator. Sample clean-up was carried out according to the following steps: (1) samples were pre-cleaned with 20 g of 40% H_2SO_4/silica gel (70–230 mesh, Merck, Germany) in 100 mL of hexane (pesticide grade; Merck, Germany) and stirred for 2 h. The entire contents of the flask was filtered through a funnel with glass wool covered with 10 g of Na_2SO_4, using 100 mL of hexane to rinse the flask and the slurry; (2) filtrates were further cleaned on a multilayer silica gel column (containing, from top to bottom, 1 cm of Na_2SO_4, 2 g of neutral silica gel, 8 g of 40% H_2SO_4/silica gel, 1 g of neutral silica gel, 4 g of 33% KOH/silica gel, 1 g of neutral silica gel and glass wool) and eluted successively with 20 mL of hexane (discarded) and 100 mL of 3% dichloromethane (pesticide grade; Merck, Germany)/hexane; (3) the latter fraction was cleaned on a 10-g basic alumina (Merck, Germany) column, eluted sequentially with 20 mL of hexane (discarded), 80 mL of 2% dichloromethane/hexane (discarded) and 50 mL of 50% dichloromethane/hexane. The last fraction was concentrated to 1 mL and then transferred to a 1.5-mL teardrop vial. Finally, injection standards ($^{13}C_{12}$-labeled 1,2,3,4-TCDD and $^{13}C_{12}$-labeled 1,2,3,7,8,9-HxCDD; CIL, EDF-5999) were added to the extracts and the final volume was adjusted to 15 mL. PCDD/Fs were identified and quantified using high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS, Trace GC 2000 and Finnigan MAT 95 XP). A CP-Sil 8 CB/MS column (60 m, 0.25 mm i.d., 0.25 mm film; Chrompak) was used. The temperature program was as follows: 90 °C for 1 min, increased to 220 °C at a rate of 76 °C/min and held for 7 min, then increased to 275 °C at 1.2 °C/min and finally to 301 °C at 1.7 °C/min. Measurements were conducted at high resolution ($R > 10{,}000$).

2.4.2. POC and DOC analyses

Concentrations of SPM, POC, and DOC were determined using 350–1200 mL samples of surface water that were passed through pre-combusted and pre-weighed glass fibre filters (GF/F, 0.45 μm pore size, 47 mm diameter; Whatman). The filters were then freeze-dried and re-weighed to determine the SPM content. After acid (HCl) treatment to remove inorganic carbon, the filters were analysed for POC on an elemental analyser (Elementar, Vario, EL III, Germany). The filtrates were analysed for DOC on a total organic carbon analyser (Shimadzu TOC-VCPH, Kyoto, Japan).

2.5. Quality control and quality assurance

Quality control and quality assurance were conducted using method blanks, ongoing precision and recovery, initial precision and recovery, duplicate samples, and standard reference material (EDF-2513). The method detection limits were ca. 0.1 pg for 2,3,7,8-TCDF, 0.2 pg for 2,3,7,8-TCDD, and 0.8 pg for OCDD. The recovery efficiency calculated for the surrogate standards ranged from 78% to 95%, which meets the recovery limit of US EPA Method 1613, and the relative standard deviation of the measurements was less than 10%. The WHO toxic equivalent factors were used to calculate the TEQ. Concentrations that were lower than the method detection limit were assigned a value of zero.

3. Results and discussion

3.1. PCDD/Fs levels in treated water (TW)

Table 1 presents summary data for the PCDD/Fs congeners and homologues found in TW and SPM after coagulation using FC, PAC and AS. Seventeen PCDD/Fs concentrations in TW1 and TW2 were below 5.23 pg/L, with values ranging from 0.663 to 5.23 pg/L, whereas concentrations in TW3 were 0.574–23.6 pg/L and most congener PCDD/Fs concentrations were >5 pg/L. The total PCDD/Fs concentration in TW1, TW2 and TW3 was 30.3, 34.8 and 162 pg/L, respectively. The lowest PCDD/Fs concentration was found in TW1, for which the concentration of TCDD and OCDD decreased from 80 to 3.74 pg/L and from 800 to 2.98 pg/L, respectively. Histograms of the concentration measured (pg/L) and toxic equivalent (pg-TEQ/L) for TW samples are shown in Fig. 2. Significant changes in concentration are evident for RW and TW after coagulation. The total PCDD/Fs concentration in RW decreased significantly from 6960 to 30.3–162 pg/L in TW. Residual PCDD/Fs account for only 0.43–2.3% of the RW levels. The total PCDD/Fs concentration in TW1 and TW2 was <35 pg/L, whereas total PCDD/Fs in TW3 were five-fold higher than in TW1 and TW2. In terms of TEQ units, the same trend was found, with PCDD/Fs levels in TW1, TW2 and TW3 of 7.53, 9.34 and 31.4 pg-TEQ/L, respectively. The residual TEQ concentration in TW1, TW2 and TW3 accounted for 0.8%, 0.9%, and 3.1% of the RW concentration, respectively.

In terms of the homologue distribution (Table 1) of PCDD/Fs in TW1, TW2 and TW3, the concentration of compounds with a low degree of chlorine substitution, i.e., tetra- and penta-CDD/Fs, was

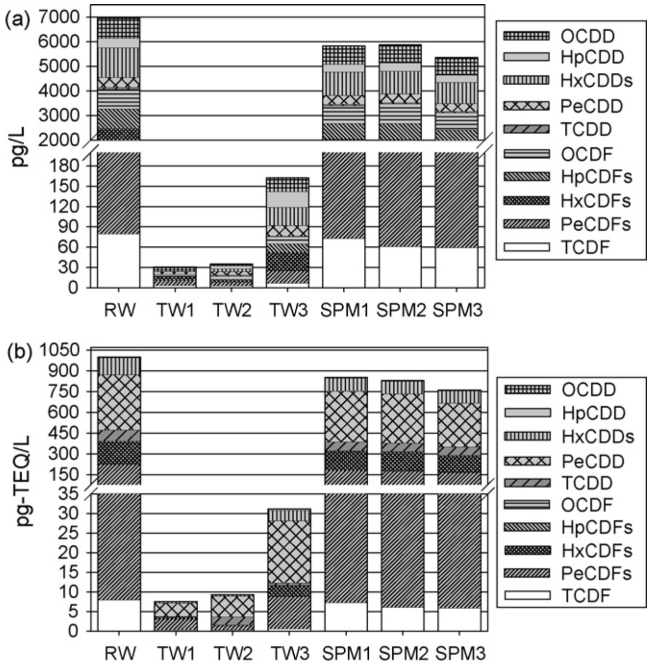

Fig. 2. Homologue patterns and total PCDD/Fs in raw water (RW), treated water (TW) and suspended particulate matter (SPM) after coagulation. Concentration in terms of pg/L (a) and pg-TEQ/L (b).

14.7, 16.3 and 41.5 pg/L, accounting for 48.4%, 46.7% and 25.5% of residual total PCDD/Fs, respectively. These percentages are much higher than the 19.5% in RW. However, for PCDD/Fs with a high degree of chlorine substitution, i.e., hexa-, hepta- and octa-CDD/Fs, the total homologue concentrations as a fraction of total PCDD/Fs in TW1, TW2 and TW3 were lower than those in RW by 5–14%. It seems that the coagulation process preferentially removes hexa-, hepta- and octa-CDD/Fs over tetra- and penta-CDD/Fs (Fig. 3a).

The changes in homologue ratio before and after coagulation generally agree with the solubility of PCDD/Fs in water, i.e., a gradual decrease in solubility with increasing chlorine substitution. Therefore, PCDD/Fs with a high degree of chlorine substitution are more likely to be present in the SPM phase compared to those with lower chlorine substitution.

3.2. PCDD/Fs levels in SPM

PCDD/Fs concentrations in SPM1, SPM2 and SPM3 were 5826, 5876 and 5365 pg/L and the corresponding TEQ values were 853, 830 and 761 pg-TEQ/L, respectively (Table 1 and Fig. 2). The concentrations in SPM were much higher than those in the water phase. As expected, most PCDD/Fs in RW were distributed in SPM during coagulation. Congener distributions of PCDD/Fs for SPM are shown in Table 1. The total concentration of tetra- and penta-CDD/Fs in SPM was 1023–1145 pg/L (18.9–19.7% of total 2,3,7,8-PCDD/Fs), compared to 1360 pg in RW (19.5% of total 2,3,7,8-PCDD/Fs). The concentration of hexa-CDD/Fs in SPM was 2064–2288 pg (38.5–39.3% of total 2,3,7,8-PCDD/Fs), compared to 2800 pg in RW (40.2% of total 2,3,7,8-PCDD/Fs). Hepta- and octa-CDD/F concentrations in SPM amounted to 2277–2497 pg (41.1–42.5% of total 2,3,7,8-PCDD/Fs), compared to 2800 pg in RW (40.2% of total 2,3,7,8-PCDD/Fs). Figs. 2(b) and 3(b) demonstrate that the concentrations and ratios of PCDD/Fs homologues in SPM are very similar to those in RW. There are also no differences in homologue patterns among SPM1, SPM2 and SPM3. Only a slight difference was observed for OCDF, HxCDDs and OCDD.

The ratios of PCDD/Fs concentrations in water to those in SPM ranged from 0.008 to 0.07, which is much lower than the ratio reported for natural aquatic systems (0.11–0.59, Gŏtz et al.) [21]. This may be attributed to the occurrence of coagulation. The congener and homologue patterns in TW and SPM indicate that coagulation is only a physical process and that other processes were not involved.

3.3. Comparison of coagulation efficiency

Coagulation of surface water samples with standard PCDD/Fs added was carried out using three coagulants (FC, PAC and AS) at the same dosage of 120 mg/L. The PCDD/Fs particulate removal efficiency (PRE) from the quantity of PCDD/Fs in SPM was calculated after the coagulation process according to $\mathrm{PRE} = Q_{\mathrm{SPM}}/Q_{\mathrm{RW}} \times 100\%$, where Q_{RW} is the concentration of PCDD/Fs in RW and Q_{SPM} is the concentration in SPM. The removal efficiency of the coagulants FC, PAC and AS was 83.7%, 84.4%, 77.1% in concentration terms and 85.3%, 83.0%, 76.1% in TEQ terms, respectively. Note that the PRE order for FC, PAC and AS is different for concentration (FC < PAC > AS) and TEQ (FC > PAC > AS), which may result from preferential removal of low chlorine substituted PCDD/Fs by FC. From Fig. 4 it is evident that the removal efficiency of FC for PCDD/Fs with a low degree of chlorine substitution (tetra- and penta-PCDD/Fs) is higher than that of PAC and AS. In general, PCDD/Fs with a low degree of chlorine substitution exhibit higher toxicity.

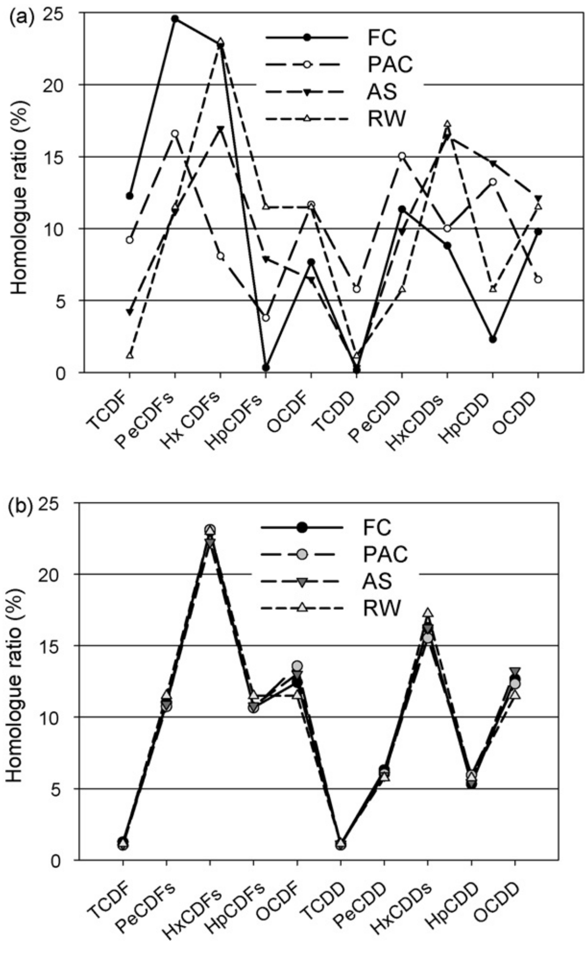

Fig. 3. Percentage of homologues in total PCDD/Fs in raw water (RW), treated water (a) and SPM (b) in terms of pg/g.

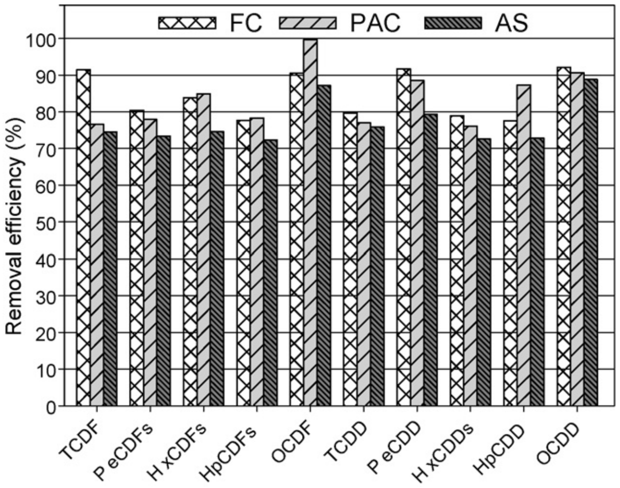

Fig. 4. Comparison of homologue PCDD/Fs removal efficiency by three coagulants (FC, PAC and AS) at a dosage of 120 mg/L.

These results generally agree with the NOM removal efficiency, since hydrophobic PCDD/Fs are highly associated with NOM. Fig. 1 shows that the order for NOM removal efficiency is FC, PAC > AS, which agrees with the PRE order for concentration and TEQ.

Another measure of PCDD/Fs removal efficiency is CRE, which is the removal efficiency calculated from residual PCDD/Fs in treated water as CRE = $(Q_{RW} - Q_{TW})/Q_{RW} \times 100\%$, (where Q_{RW} is as above and Q_{TW} is the PCDD/Fs concentration in treated water). In terms of both pg/L and TEQ results, the CREs are all >99% for FC and PAC and 97–98% for AS. Compared to the results reported by Kim et al. of 93% and 87% for treatment of whole drinking water [2], the CREs of the three coagulants were satisfactory during coagulation experiments. However, the sum of PCDD/Fs in SPM and TW (SPM + TW, Table 1) accounts for 80–85% of the PCDD/Fs in RW, leaving approximately 15–20% of PCDD/Fs not detected. These may initially be absorbed on particle and then be sequestered in SPM when particle grew. They could not be extracted by toluene in our experimental procedure.

3.4. *Effect of POC on the removal of PCDD/Fs*

In water, the particulate sorption dynamics of PCDD/Fs significantly influences their distribution between SPM and water. Sorption and desorption processes are governed by the coagulant type and coagulation mechanism. The major coagulation mechanisms for NOM and PCDD/Fs removal involve charge neutralisation of colloidal NOM, precipitation as humates or fulvates, and coprecipitation by adsorption on humates or fulvates or on the metal hydroxide [11,12,22]. This usually involves several of these mechanisms at the same time [18,19,23]. It is generally expected that PCDD/Fs interactions with POC during coagulation play an important role in this processes. An equilibrium expression commonly used to depict PCDD/Fs interactions with POC is the particulate–water partition coefficient K_p. K_p can be predicted as the product of the fraction of organic carbon of the sorbent (f_{oc}) and the hydrophobic partition tendency of the solute to NOM, expressed as the organic carbon–water partition coefficient (K_{oc}) [24]. To provide insight into the phase distribution processes that control the transport and fate of PCDD/Fs during coagulation, we calculated particulate–water partition coefficients (K_p) and particulate–organic carbon partition coefficients (K_{oc}) from the data set in Table 1 and the values of $\log K_{ow}$ from Doucette and Andren [25], Shiu et al. [4], Sijm et al. [26], Broman et al. [24], and Rantalainen et al. [27]. As shown in Fig. 5, the correlation equations for PCDFs are $\log K_{oc} = 1.06 \log K_{ow} + 1.78$ ($R^2 = 0.62$) for FC, $\log K_{oc} = 0.84 \log K_{ow} + 1.95$ ($R^2 = 0.42$) for PAC, and $\log K_{oc} = 0.21 \log K_{ow} + 5.96$ ($R^2 = 0.20$) for AS. The equations for PCDDs are $\log K_{oc} = 0.65 \log K_{ow} + 3.34$ ($R^2 = 0.51$) for FC, $\log K_{oc} = 0.91 \log K_{ow} + 1.21$ ($R^2 = 0.60$) for PAC, and $\log K_{oc} = -0.61 \log K_{ow} + 7.97$ ($R^2 = 0.02$) for AS. There is good correlation and high slope between $\log K_{oc}$ and $\log K_{ow}$ for 2,3,7,8-substituted congeners during coagulation with FC and PAC, whereas for AS coagulation the correlation is not as good and the slope is lower between $\log K_{oc}$ and $\log K_{ow}$. This finding is consistent with the explanation that the capacity of particles to sorb hydrophobic organic chemicals (HOCs) in water is related to their fraction of organic carbon [28]. The deficiency in correlation between $\log K_{oc}$ and $\log K_{ow}$ is possibly due to the poor DOC removal efficiency of AS (Table 1), which is lower than that of FC by approximately 29% (Fig. 1); moreover, the change in DOC concentration was not as distinct during coagulation with AS (Table 1). Removal of PCDD/Fs by AS seems to be controlled by a factor other than POC in SPM3. Furthermore, from the mechanism of coagulation [29,30] at high dosage, the three coagulants should have a similar mechanism of adsorption and precipitation for NOM removal. However, in the case of AS, sulfate is a moderately strong co-ordinator of aluminium, and the presence of sulfate in solution can significantly decrease the positive charge of aluminium hydrolysis products, so the hydrolysis of aluminium ions would be much slower than that for ferric ions. As a result, FC and PAC exhibit greater efficiency than AS for NOM and PCDD/Fs removal during water treatment.

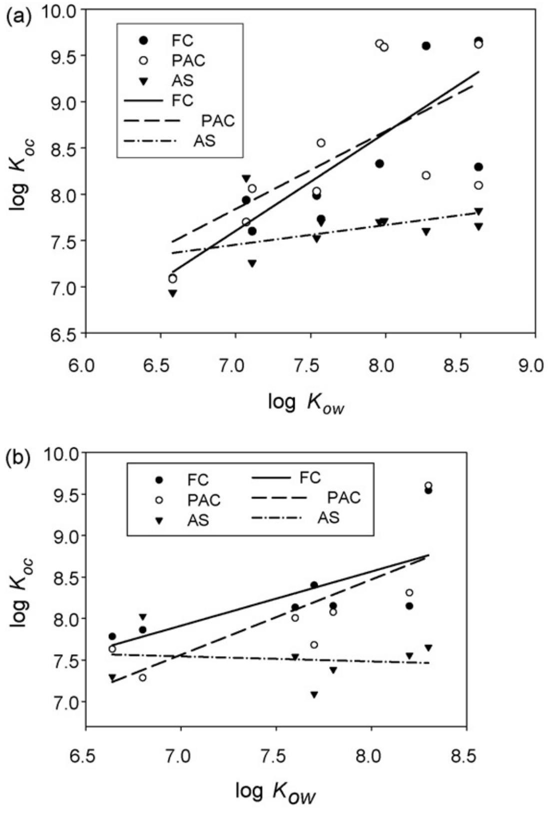

Fig. 5. Relationship between $\log K_{oc}$ and $\log K_{ow}$ for 2,3,7,8-substituted PCDD/Fs. The values of $\log K_{ow}$ are from literatures [4,24–27]. (a) Ten 2,3,7,8-substituted PCDFs; (b) seven 2,3,7,8-substituted PCDDs.

4. Conclusions

(1) In simulated coagulation experiments, the PCDD/Fs removal efficiency of FC and PAC was higher than that of AS, and the efficiency for FC and PAC was similar. FC exhibited higher removal efficiency for PCDD/Fs with a low degree of chlorine substitution (tetra- and penta-substituted). Nevertheless, PCDD/Fs in particulates after coagulation accounted for approximately >95% of the total PCDD/Fs.

(2) The PCDD/Fs removal efficiency is correlated to the DOC removal efficiency during coagulation. POC and DOC played a dominant role in PCDD/Fs sorption/desorption in water.

(3) The congener profile of residual PCDD/Fs in treated water is consistent with the solubility of the PCDD/Fs congeners, but the patterns varied for water treated with different coagulants.

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