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Effect of coagulant basicity on virus removal from water by polyferric chloride

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Short title: Effect of coagulant basicity on virus removal by polyferric chloride

Abstract

We investigated the effect of coagulant basicity on bacteriophage removal from river water by polyferric chloride (PFC). PFC at three basicities (basicity 0.9−2.1) was prepared by means of base titration (NaOH was added to ferric chloride [$FeCl_3$] solution) and the virus removal efficiencies of those PFCs were compared with that of $FeCl_3$ (basicity 0). The virus removal efficiencies of the PFCs were equal to or less than that of $FeCl_3$ both at pH 6 and pH 8. This suggests that, unlike aluminum-based coagulants, increasing the basicity of iron-based coagulants does not improve virus removal efficiency. Furthermore, the relative abundance of monomeric iron(III) species in the PFCs decreased whereas that of precipitated iron(III) species increased with increasing basicity, as assessed with a ferron method. Colloid charge density also decreased with increasing basicity. Therefore, it is likely that the reduction in the abundance of monomeric iron(III) species led to the reduction in colloid charge density, which then reduced virus removal efficiency. Thus, the development of novel iron-based coagulants with increased virus removal efficiency may not be possible by simply increasing the basicity of the coagulant.

Keywords: bacteriophage, basicity, coagulation, colloid charge density, iron(III) hydrolyte species

Introduction

Coagulation is a drinking-water treatment process that removes contaminants such as particulate and organic matter. Aluminum and iron salts are widely used coagulants that destabilize and combine contaminants into large flocs that can be easily separated from the source water by sedimentation and filtration processes. Waterborne enteric viruses that do not settle from suspension under the influence of gravity can also be removed by coagulation with aluminum- and iron-based coagulants (Abbaszadegan *et al.* 2007; Mayer *et al.* 2008; Shirasaki *et al.* 2010; Shin & Sobsey 2015). Therefore, coagulation is an essential part of the multiple-barrier approach to controlling the risk to human health posed by virus contamination in drinking water.

The efficiency of virus removal by coagulation is strongly influenced by factors such as source water quality, the nature and concentrations of coagulants used, and the mixing conditions (Hijnen & Medema 2010). The quality of source drinking water is being deteriorated by continued population growth and urbanization, resulting in increased contamination of drinking-water sources with wastewater, biosolids, and emerging contaminants (Shi *et al.* 2012). This deterioration reduces the overall efficiency of commercially available aluminum- or iron-based coagulants, and thus the efficiency of virus removal. Therefore, coagulation processes that effectively and inexpensively remove contaminants, including viruses and precursors of disinfection by-products (i.e., natural organic matter [NOM]), are urgently needed.

Prepolymerized aluminum coagulants (e.g., polyaluminum chloride [PACl]) and prepolymerized iron coagulants (e.g., polyferric chloride [PFC]) with improved coagulation efficiency have been developed. Since coagulant basicity is an important factor in determining the relative abundances of the aluminum or iron hydrolyte species produced in these coagulants, and in turn the coagulation efficiency (Lei *et al.* 2009), the influence of the aluminum or iron hydrolysis ratio (basicity = $[OH^-]/[Al^{3+}]$ or $[OH^-]/[Fe^{3+}]$) on the coagulation process has been investigated (Yan *et al.* 2007; Lei *et al.* 2009; Yang *et al.* 2011; Kimura *et al.* 2013). We recently investigated the effect of basicity on the ability of PACl to remove viruses from water by comparing the virus removal efficiencies of PACl at several different basicities and reported that the PACls with higher basicities (basicity ≥2.1) had greater virus removal efficiency than did commercially available aluminum-based coagulants (aluminum chloride solution or alum, basicity 0) or the PACls with lower basicities (basicity, 0.9, 1.5, or 1.8) (Shirasaki *et al.* 2014). However, the relationship between the basicity and virus removal efficiency of PFC is yet to be fully investigated.

Here we investigated the relationship between the basicity and virus removal efficiency of PFC by comparing the virus removal efficiencies of PFC at several different basicities with that of ferric chloride ($FeCl_3$) solution.

Materials and Methods

Source water and coagulants

River water was sampled from the Toyohira River (Sapporo, Japan) on 4 December 2012 and subjected to water quality analyses (Table 1). $FeCl_3$ solution (basicity 0) was prepared by dissolution of reagent-grade iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$; Wako Pure Chemical Industries, Osaka, Japan) in Milli-Q water (Milli-Q Advantage; Millipore Corp., Billerica, MA, USA). PFCs with basicities of 0.9, 1.5 and 2.1 (PFC-0.9, PFC-1.5, and PFC-2.1, respectively) were prepared by means of a base titration method as described previously (Lei *et al.* 2009). Briefly, a certain amount of 0.1 M $FeCl_3$ solution was transferred to a glass beaker and then the solution was titrated with 0.5 M NaOH at a constant rate (4 μL/s) with a peristaltic pump until the target basicity was reached. Throughout the titration, the solution in the beaker was kept at 20 °C and stirred at 630 rpm with a magnetic stirrer. Immediately before use, the coagulants were diluted with Milli-Q water to the concentration required for each experiment.

Coagulant characterization

Ferron method

The relative proportions of the iron(III) hydrolyte species in the coagulants were determined by means of the ferron method described by Gao *et al.* (2007), with minor modifications, after the coagulant was diluted with Milli-Q water to a concentration of 2.8 g-Fe/L (i.e., 0.05 M-Fe). Based

on the kinetic differences between the reactions of the iron(III) species and the ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid; Wako Pure Chemical Industries), iron(III) hydrolyte species were categorized as monomeric species, polymeric species, or precipitated species (Fe_a, Fe_b, and Fe_c, respectively) (Gao *et al.* 2007). After addition of the ferron reagent to the diluted coagulant, the mixture was magnetically stirred for 10 s at 400 rpm, and then the absorbance at 600 nm was measured with a UV-1700 PharmaSpec spectrophotometer (Shimadzu Corp., Kyoto, Japan) at predetermined reaction times. The iron(III) hydrolyte species were operationally divided into three categories as follows: Fe_a, species that reacted with ferron within 30 s; Fe_b, species that reacted with ferron within 120 min (absorbance at 120 min minus the absorbance due to Fe_a); and Fe_c, species that did not react with ferron ($Fe_c = Fe_t - [Fe_a + Fe_b]$, where Fe_t = total Fe). To obtain Fe_t, we adjusted the pH of the diluted coagulant to approximately 0.5 with ultrapure nitric acid (Kanto Chemical Co., Tokyo, Japan), heated the mixture for 3 h at 85 °C in a muffle furnace, cooled it to room temperature, and then analyzed it by means of the ferron method as described for Fe_a.

Colloid titration method

The positive colloid charge of each coagulant was determined by means of a colloid titration method after dilution of the coagulant with Milli-Q water to 2.1−4.1 mg-Fe/L, as we reported previously (Shirasaki *et al.* 2014).

Bacteriophages

Escherichia coli phage MS2 (NBRC 102619), an F-specific RNA bacteriophage, was obtained from the National Institute of Technology and Evaluation Biological Research Center (Kisarazu, Japan). MS2 is a prototype member of the genus *Levivirus* in the Leviviridae family. The genome of this bacteriophage contains a single molecule of linear, positive-sense, single-stranded RNA, which is encapsulated in an icosahedral protein capsid with a diameter of 24–26 nm (Fauquet *et al.* 2005). Because of its morphological similarities to hepatitis A virus and poliovirus, the removal of which is important during drinking-water treatment, MS2 is widely used as a surrogate for waterborne enteric viruses in coagulation experiments (Abbaszadegan *et al.* 2007; Mayer *et al.* 2008; Shirasaki *et al.* 2010; Matsushita *et al.* 2011; Kreissel *et al.* 2014; Shirasaki *et al.* 2014; Shin & Sobsey 2015). MS2 was propagated and purified prior to the preparation of a bacteriophage stock solution as described previously (Shirasaki *et al.* 2010).

Coagulation experiments

Batch coagulation experiments were conducted with 1000 mL of bacteriophage-spiked river water in square plastic beakers at 20 °C. The bacteriophage stock solution was added to the river water at approximately 10^8 plaque forming units (PFU)/mL (C_0), and the spiked water was then mixed with an impeller stirrer. After enough HCl or NaOH was added to the water to bring the final pH to 6 or 8, coagulant was injected into the water at a dosage of 2.24, 4.48, or 11.2 mg-Fe/L (i.e., 40, 80, or 200

μM-Fe). The water was stirred rapidly for 1 min (G = 200 s^{-1}, 136 rpm) and then slowly for 10 min (G = 20 s^{-1}, 29 rpm) and left at rest for 60 min to allow the floc particles generated to settle. A sample of the supernatant was then used for quantification of bacteriophage concentration (C_s) and turbidity. A portion of the supernatant was also filtered through a polycarbonate membrane filter (nominal pore size, 0.4 μm; Isopore, Millipore Corp.) and then used for quantification of bacteriophage concentration in the filtrate (C_f). In addition, a portion of the supernatant was filtered through a polytetrafluoroethylene membrane filter (nominal pore size, 0.45 μm; Dismic-25HP; Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and then used for quantification of the ultraviolet absorbance at 260 nm (an indication of NOM concentration) and for measurement of the residual iron concentration after settling. Turbidity and ultraviolet absorbance at 260 nm were quantified with a 2100AN turbidity meter (Hach Company, Loveland, CO, USA) and a UV-1700 PharmaSpec spectrophotometer, respectively. After ultrapure nitric acid (Kanto Chemical Co.) was added to the membrane filtrate (1% v/v), the iron concentration was determined by means of inductively coupled plasma–mass spectrometry (Agilent 7700 series, Agilent Technologies, Inc., Santa Clara, CA, USA).

Bacteriophage assay

PFU method

Infectious bacteriophages were enumerated by determining the number of PFUs according to the

double-layer method (Adams 1959) with *Escherichia coli* (NBRC 13965) as the bacterial host. The average plaque count of triplicate plates prepared from one sample was considered the infectious bacteriophage concentration for that sample.

Real-time reverse transcription-polymerase chain reaction (RT-PCR) method

Viral RNA of bacteriophages was quantified by means of a real-time RT-PCR method as described previously (Shirasaki *et al.* 2010). This method detects all bacteriophages regardless of their infectivity or the presence of aggregates.

Results and Discussion

Effect of coagulant basicity on the removal of turbidity and UV260-absorbing NOM, and on the residual iron concentration after settling

At the Moiwa drinking water treatment plant (Sapporo, Japan), which is the treatment plant for the water source used in the present study, the coagulation process is conducted by using PACl at an approximate pH of 7. Since the optimum pH for iron-based coagulants is generally lower than that for aluminum-based coagulants (American Water Works Association 1990), we decided to use a pH of 6 in the present study. In addition, because approximately 1–2 mg-Al/L (i.e., 40–80 μM-Al) of PACl is usually dosed in the Moiwa drinking water treatment plant, 80 μM-Fe (i.e., 4.48 mg-Fe/L) of coagulant dosage was used in the present study at pH 6.

The coagulants examined in the present study removed 70% to 80% of the turbidity present in the water (Figure 1). In addition, after settling, a very low concentration of residual iron (<0.003 mg-Fe/L) was detected for all of the coagulants regardless of their basicity. These results indicate that, at pH 6, coagulant basicity did not affect the amount of turbidity removed from the water or the concentration of residual iron after settling. In contrast, the amount of UV260-absorbing NOM removed did differ depending on the basicity of the coagulant used; $FeCl_3$ removed approximately 70% of the UV260-absorbing NOM, whereas PFC-2.1 removed only 40%, indicating that NOM removal efficiency decreased with increasing coagulant basicity. However, Lei *et al.* (2009) reported that at pH 6 the amount of humic acid removed from water by PFC increased from 40% to 80% with increasing basicity (basicity range, 0–0.8), and that this removal efficiency remained stable when the basicity was further increased to 2.4. Despite the PFCs being prepared by using similar methods, the quality of the source water (UV260- or UV254-absorbing NOM; 0.026 vs. 0.151 cm^{-1}) and the coagulant dosage used (4.48 vs. 14.0–16.8 mg-Fe/L) were markedly different between our study and that of Lei *et al.* (2009), which may explain the differences seen regarding the effects of coagulant basicity. Nevertheless, in the present study, $FeCl_3$, which has a basicity of 0, removed more UV260-absorbing NOM than did the PFCs at pH 6.

Effect of coagulant basicity on bacteriophage removal

The effect of coagulant basicity on the removal ratio of infectious MS2 (log[C_0/C_s]) during the coagulation process was evaluated by means of a PFU method after settling at pH 6 (Figure 2a). Because MS2 has a small diameter and is stably monodispersed in water from the Toyohira River, as confirmed in our previous study (Shirasaki *et al.* 2009), no removal of infectious MS2 was observed in the absence of coagulant (data not shown). Coagulation with the PFCs did remove infectious MS2. The addition of PFC destabilizes the dispersion of MS2, resulting in their entrapment within or adsorption onto floc particles generated during coagulation that then settle from suspension under the influence of gravity. The removal ratio of infectious MS2 depended on the PFC used: whereas infectious MS2 removal was ≥1-log with $FeCl_3$ and PFC-0.9, the removal ratio decreased with increasing coagulant basicity (PFC-2.1, 0.5-log removal) (Figure 2a). In addition, although the removal ratio of infectious MS2 was increased after coagulation and membrane filtration compared with after coagulation and settling alone for all of the PFCs examined, which was probably due to the removal of additional floc particles containing infectious MS2 that were not removed from the suspension by gravity during settling, the removal ratios (log[C_0/C_f]) obtained with $FeCl_3$ and PFC-0.9 were approximately 1–2-log larger than those obtained with PFC-1.5 and PFC-2.1.

The removal ratios for total MS2, as evaluated by means of an RT-PCR method, were also larger when $FeCl_3$ or PFC-0.9 was used than when PFC-1.5 or PFC-2.1 was used, not only after settling

but also after membrane filtration (Figure 2b). These results indicate that virus removal efficiency was reduced at higher coagulant basicities. Since this trend of increasing basicity reducing the effectiveness of the PFC was also observed for the removal of UV260-absorbing NOM (Figure 1), it is likely that the mechanisms that destabilize the dispersion of viruses and NOM during the coagulation process, that is, the coordination reactions between coagulant species and the carboxyl groups of the virus surface proteins or NOM, are similar for the two types of contaminant (Bratby 2006).

Because the removal ratios of MS2 with PACl were previously reported to increase with increasing PACl basicity (0.9–2.1), particularly under weakly alkaline pH conditions (Shirasaki *et al.* 2014), the effect of coagulant basicity on the removal of MS2 was also evaluated at pH 8 (Figure 3). The removal ratio of infectious MS2 with $FeCl_3$ (4.48 mg-Fe/L) at pH 8 (Figure 3a) was lower compared with that at pH 6 (Figure 2a). Even when the dosage of $FeCl_3$ was increased from 4.48 mg-Fe/L to 11.2 mg-Fe/L and membrane filtration was conducted after coagulation and settling, the removal ratio was <1-log. A similar trend was observed for the PFCs, regardless of basicity or coagulant dosage. In addition, the total MS2 removal ratios observed for all iron-based coagulants and all coagulant dosages used in the present study were <0.5-log, even after membrane filtration (Figure 3b). These results indicate that coagulant basicity did not affect virus removal at pH 8. Taken together these results suggest that, unlike with aluminum-based coagulants, increasing the

basicity of PFC from 0 to 2.1 does not improve virus removal efficiency, not only under weakly acidic pH conditions but also under weakly alkaline pH conditions. In addition, the removal efficiency of UV260-absorbing NOM remained ≤30%, regardless of coagulant basicity or coagulant dosage, although the removal of approximately 60% and 70–80% of turbidity was achieved with coagulant doses of 4.48 mg-Fe/L and 11.2 mg-Fe/L, respectively, irrespective of the type of coagulant used and even at pH 8 (data not shown). Together, our results suggest that the development of novel iron-based coagulants for efficient virus and NOM removals cannot be achieved simply by increasing the basicity of the coagulant.

Coagulant characterization

To investigate the distribution of iron(III) species in the coagulants, we used a ferron method (Figure 4). The major iron(III) species in $FeCl_3$ was a monomeric iron(III) species (Fe_a). In the PFCs, the percentage distribution of precipitated iron(III) species (Fe_c) increased whereas that of Fe_a decreased with increasing basicity; the major iron(III) species in PFC-2.1 was Fe_c. Because the virus removal ratio decreased as the amount of Fe_c in the coagulant increased (that is, as Fe_a decreased), Fe_c was likely not the species involved in the mechanism of virus removal. This is in contrast to PACl, where, as we reported previously, colloidal aluminum species (i.e., those that did not react with ferron within 120 min) were involved in the improvement of virus removal efficiency (Shirasaki *et al.* 2014). The present results suggest that Fe_a plays a more important role than Fe_c in

the removal of viruses during coagulation with iron-based coagulants. Lei *et al.* (2009) reported that Fe_a mainly contributes to contaminant removal through electric-double-layer compression and charge neutralization, while Fe_b and Fe_c can capture contaminants by adsorption and interparticle bridging. Therefore, coprecipitation into growing iron hydroxide during charge neutralization is possibly the main mechanism for virus removal during coagulation with iron-based coagulants.

The positive colloid charges of the coagulants were determined by means of a colloid titration method (Figure 5). The colloid charge densities of the iron-based coagulants used in the present study were all increased with increasing iron concentration. However, the colloid charge densities of the coagulants decreased with increasing basicity; the colloid charge densities of PFC-1.5 and PFC-2.1 were the lowest among the coagulants used in the present study. Because the Fe_c content increased and the Fe_a content decreased with increasing basicity, the reduction in Fe_a content (i.e., the increase of Fe_c content) may have led to the reduction in colloid charge density. Lei *et al.* (2009) reported that increasing PFC basicity facilitated the formation of large molecule species with low positive charge densities. However, in a previous study, we found that the colloid charge densities of PACls were increased with increasing PACl basicity (i.e., the increase of the total amount of Al_b and Al_c in the PACl; basicity range, 0.9–2.1), and that a PACl with a high colloid charge density removed more virus than did one with a low colloid charge density (Shirasaki *et al.* 2014). Because a high colloid charge density confers on coagulants a high capability to neutralize negatively

charged viruses during coagulation, the reduction of the colloid charge density of the iron-based coagulants used in the present study with increasing basicity is likely associated with the reduction in virus removal efficiency. Nevertheless, the virus removal efficiencies of the PFCs were similar to or less than that of $FeCl_3$, suggesting that, unlike with PACl, preparation of PFCs by means of a base titration method (i.e., NaOH addition to $FeCl_3$ solution) does not produce PFCs with greater virus removal efficiency.

Conclusions

(1) Virus removal efficiencies of PFCs were similar to or lower than that of $FeCl_3$ (basicity 0), suggesting that increasing the basicity of iron-based coagulants does not improve virus removal efficiency. Therefore, the development of novel iron-based coagulants for efficient virus removal may not be achievable simply by increasing the basicity of the coagulant.

(2) Monomeric iron(III) species likely play a more important role than precipitated iron(III) species in virus removal during coagulation with iron-based coagulants, because the virus removal ratio decreased as the amount of monomeric iron(III) species in the PFCs decreased (that is, as precipitated iron(III) species increased).

(3) The reduction of the colloid charge density of the PFCs used in the present study with increasing

coagulant basicity was likely associated with the reduction in virus removal efficiency.

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Table 1. Toyohira River water quality properties.

pH	7.3
Turbidity (NTU)	2.5
DOC (mg/L)	1.0
UV260 (cm^{-1})	0.026
Alkalinity (mg-$CaCO_3$/L)	16.0

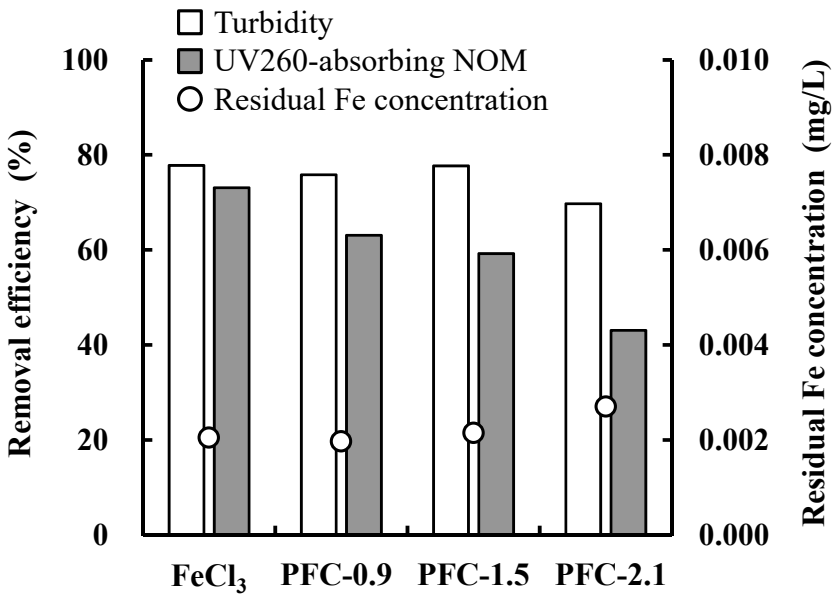


Figure 1. Effect of the basicity of polyferric chloride (PFC) on removal of turbidity and UV260-absorbing natural organic matter (NOM), and residual Fe concentration after settling, after coagulation at pH 6. Coagulant dosage, 4.48 mg-Fe/L. The numbers after "PFC" represent the basicity of the coagulant.

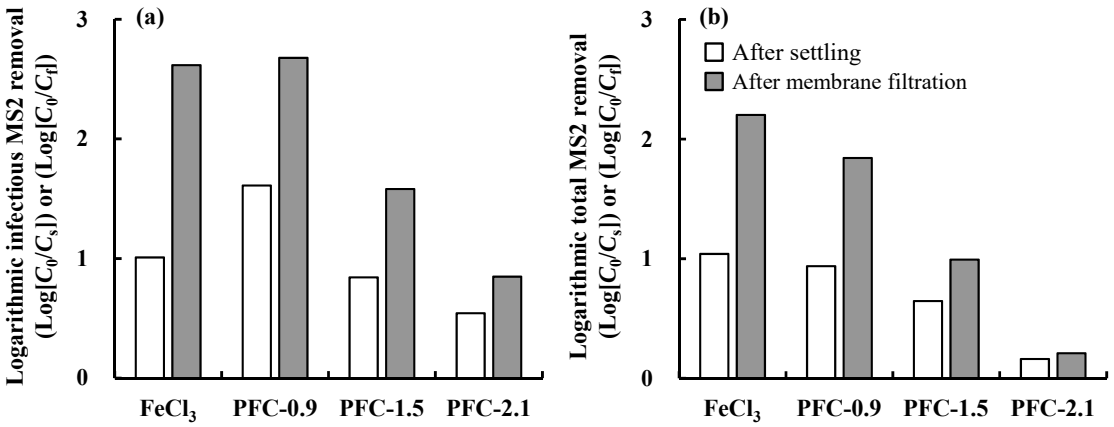


Figure 2. Effect of the basicity of polyferric chloride (PFC) on infectious MS2 removal as evaluated by using a plaque-forming unit method (a), and total MS2 removal as evaluated by using a real-time polymerase chain reaction method (b) after settling and after membrane filtration at pH 6. Coagulant dosage, 4.48 mg-Fe/L. The numbers after "PFC" represent the basicity of the coagulant.

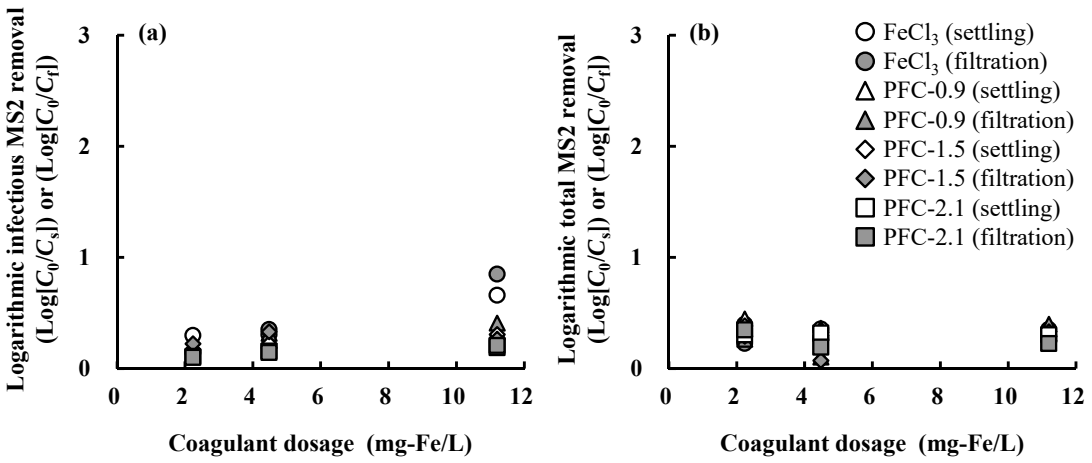


Figure 3. Effect of the basicity and dosage of polyferric chloride (PFC) on infectious MS2 removal as evaluated by using a plaque-forming unit method (a), and on total MS2 removal as evaluated by using a real-time polymerase chain reaction method (b) after settling and after membrane filtration at pH 8. The numbers after "PFC" represent the basicity of the coagulant.

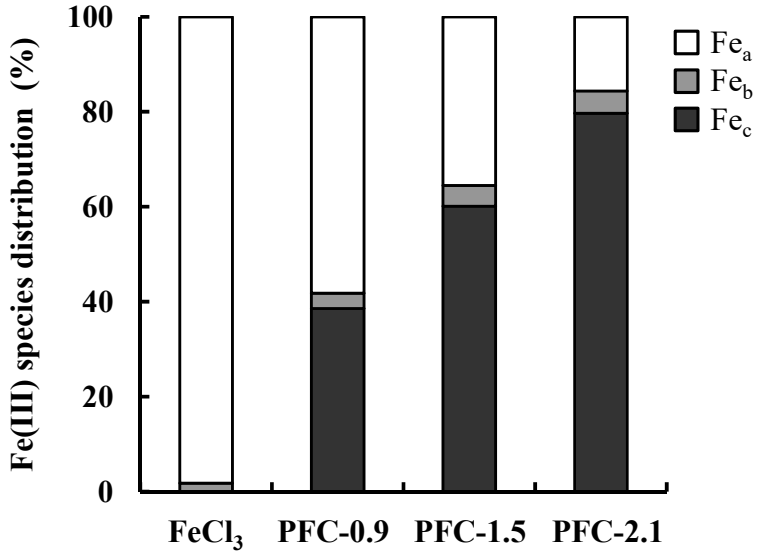


Figure 4. Distribution of iron(III) species in the polyferric chloride (PFC) coagulants used in the present study as evaluated by a ferron method. The numbers after "PFC" represent the basicity of the coagulant. Fe_a, monomeric species; Fe_b, polymeric species; Fe_c, precipitated species.

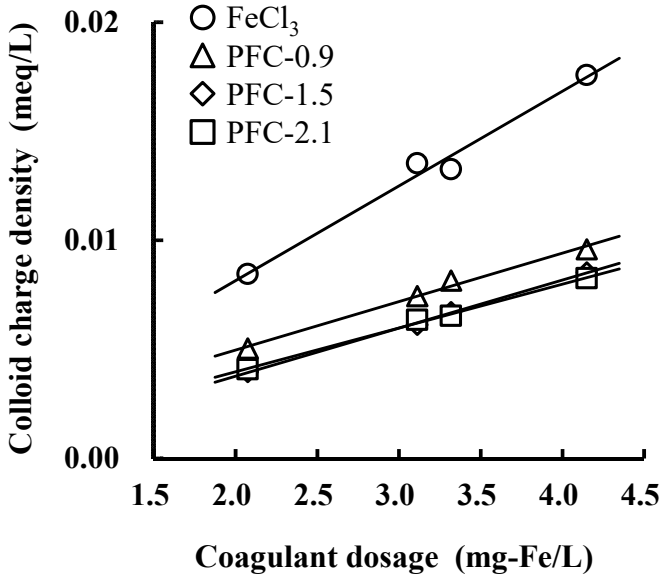


Figure 5. Positive colloid charge densities of the polyferric chloride (PFC) coagulants used in the present study as evaluated by means of a colloid titration method. The numbers after "PFC" represent the basicity of the coagulant.