Effect of polyferric chloride (PFC) doses and pH on the fractal characteristics of PFC–HA flocs

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ABSTRACT

Changes in the fractal characteristics of PFC–HA flocs with polyferric chloride (PFC) doses and coagulation pHs were investigated in this study. A type of PFC coagulant with a hydrolysis degree (B^*) of 0.6027 and a Fe(III) concentration of 0.202 mol/L was employed to coagulate HA solutions at five constant coagulation pHs. Zeta potential tests were employed to reveal the coagulation mechanisms. The physical properties of flocs formed in the coagulation process were analyzed by their CCD image morphology, size distribution, and fractal dimensions. Next, microscopic observations and nitrogen-adsorption-desorption methods were conducted to characterize the pore structure and surface fractal dimensions of powders prepared from these flocs through a cryofixation–vacuum-freeze-drying procedure. The PFC doses and coagulation pHs had an obvious effect on the physical characteristics of PFC–HA flocs and their corresponding powders. Generally, in the low PFC dose range, PFC–HA flocs formed under acidic coagulation pHs and charge neutralization mechanisms were larger, had less irregular boundaries or surfaces (lower D_1 value), a more compact structure (lower D_2 value) and more irregular pore surface or pore size distribution in their dried powder than those formed under neutral and alkaline coagulation pHs and physical enmeshment and/or fresh precipitate adsorption mechanisms involved in the coagulation process. After the PFC doses exceeded this range, a gradual reversal phenomenon occurred. Furthermore, there were different specific PFC dosages that were above the critical reversal point for each property of these flocs or powders, such as the median diameter, one-dimensional fractal dimension, two-dimensional fractal dimension, and pore surface fractal dimension. In addition to these characteristics, the most compact PFC–HA flocs were formed at coagulation pH = 6.00 ± 0.05 and a PFC dosage of 4.04×10^{-4} mol/L (Fe^{3+}), and the loosest flocs were produced at coagulation pH = 7.00 ± 0.05 and a PFC dose of 1.01×10^{-4} mol/L (Fe^{3+}).

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1. Introduction

Optimizing the drinking water treatment requires enhanced removal of natural organic matter (NOM). Indeed, humic substances represent the dominant portion of the dissolved organic matter (DOM) in most surface waterbodies used for drinking water supplies. Generally, elimination of these humic substances during drinking water treatment is carried out by coagulation with hydrolyzed metal species such as aluminum and iron salts. However, the presence of uncoagulated humic materials in clarified water is responsible for reduced adsorption capacity in activated carbon beds, taste and odor of the finished water, membrane fouling, trihalomethane formation during chlorine disinfection, or biological regrowth in the distribution network [1–3]. Accord-

ingly, considerable attention has been focused on the technologies and their own efficiency for eliminating these substances. The United States Environmental Protection Agency has proposed that enhanced coagulation technology (ECT) is the best available technology (BAT) for the removal of these compounds [4–6]. Previous studies have paid close attention to the reaction behavior between FeCl_3 and humic acids [4–6], and it has been shown that FeCl_3 performs well in the removal of HA during enhanced coagulation processes. Recently, several studies have focused on the removal of HA and coagulated flocs with polyferric chloride (PFC), an inorganic polymer flocculant (IPF) that performs well in particle removal from natural water or wastewater. Indeed, it has been shown that PFC is very effective at the removal of HA [7].

Usually, several main mechanisms such as charge neutralization/complexation, enmeshment, and adsorption [8–10] are used to explain the interaction of humic substances with these metal salts. Charge neutralization/complexation is believed to preferentially occur at acidic pH [9–11], while physical enmeshment

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and/or adsorption commonly occurs under conditions favoring metal hydroxide precipitation, and humic substances are primarily transferred onto freshly formed precipitate [9,10,12,13]. When FeCl_3 is employed in enhanced coagulation for HA removal, good performance has been gained at acidic pH and large doses, where in pH-coagulant concentration domains fresh iron hydroxide precipitation is formed [4–6]. Therefore the pH and iron concentration play key roles in coagulation mechanisms.

Since Mandelbrot introduced the concept of fractal theory in the 1970s, fractal geometry has become a well-established means of describing the irregular and complicated structure of floc aggregates [14–18]. Flocs are mass fractal objects because both the internal and surface structure of the aggregates exhibit fractal properties. Mass fractal or fractal characteristics under different topological dimensions can provide some hints of the formation dynamics and the microstructure of flocs induced by coagulants [19]. Generally, a mass fractal may have some effect on bulk physical structural characteristics, such as floc density, settling rates and floc strength [15–17]. In fact, the physical and chemical properties of floc surfaces also have an important effect on the kinetic growth process of flocs. More irregular and rough surfaces will imply greater collision and attachment rates between different flocs during treatment processes such as flocculation, flotation and filtration. However, the surface fractal dimension of flocs, which is an indication of surface irregularity and roughness [18–27], has rarely been investigated.

The morphology of the resulting aggregates is directly connected to coagulation mechanisms and is a primary factor in understanding these processes. In this study, PFC–HA flocs and their cryofixation–vacuum-freeze-dried powder were prepared at different pHs and doses. CCD images and an adsorption–desorption isotherm (N_2 , 77 K) data matrix were then used to calculate the fractal dimensions at different topological spaces. The influence of pH and PFC doses on the changes in the fractal dimensions could then be investigated. The goal of this study was to gain a comprehensive understanding of the PFC–HA aggregates formed during the coagulation process under different coagulation mechanisms when using fractal analysis in conjunction with morphology analysis and particle size distribution.

2. Methods and materials

2.1. Preparation of synthetic waters and coagulation procedure

A stock suspension was obtained by dissolving humic acid reagent (Tianjin Jinke Fine Chemical Institute, China) in deionized water under alkaline conditions and kept for two months. After the initial storage period, an amount of the stock suspension was passed through a 0.45- μm membrane filter and diluted with tap water of equal volume to give a solution with a mass concentration of 4.79 mg/L (as dissolved organic carbon (DOC)) and 0.33 cm^{-1} for UV absorbance at 254 nm (UV_{254}). The pH of the working solution is 8.92, and alkalinity is 205 mg/L (as CaCO_3). Moreover, the turbidity of these solutions was close to 1.40 NTU (Turbidimeter 2100N, HACH, USA). Next, synthetic water was subjected to a coagulation jar test. Prior to injection of the coagulant, the initial pHs of a 1 L sample solution were adjusted by the dropwise addition of 2% HCl or NaOH solution to maintain the pH values of the solutions at 9.00 ± 0.05 , 8.00 ± 0.05 , 7.00 ± 0.05 , 6.00 ± 0.05 , and 5.00 ± 0.05 during coagulation process. The coagulant, a commercial polyferric chloride (PFC) kindly supplied by Tianjin Tianshui Water Purifying Ltd., China, was FeCl_3 pre-hydrolyzed and polymerized solution with a basicity (B) of 14.1% ($[\text{OH}]/[\text{Fe}]$ molar percentage) or 0.4230 ($3[\text{OH}]/[\text{Fe}]$ molar ratio), a Fe_2O_3 content of 11.3% (w/w), and a pH of 0.43. The coagulant was diluted to a concentration of 0.202 mol/L

Fig. 1. Schematic methodology for the recording of floc images. (1) Flocculation mixer; (2) petri dish; (3) colorimetric tube; (4) CCD; (5) computer.

(as Fe(III)) with ultra-purified water, and the pH of this diluted solution was 1.79.

Coagulation experiments were conducted at 25 °C in 1 L cylindrical plexiglass beakers containing 1 L samples of water. Stirring was conducted using 50 mm $\times$ 40 mm flat paddle impellers in a JTY variable-speed jar tester (Tangshan Dachang Chemical Ltd., China). The following mixing procedure designed to yield a certain overall energy input into the coagulation suspension was used: a rapid mix period for 1.0 min at 200 rpm followed by a slow-stir phase at 30 rpm for 15 min. The coagulant was added under agitation as pure solution using a graduated pipette at a point just below the free surface of the suspension. At the end of mixing, the coagulated suspension was allowed to settle in the beaker for 30 min. A 50-mL supernatant sample was then withdrawn from about 25 mm below the free surface. The residual turbidity, pH and zeta potential (Zeta 2000, Malvern) were monitored, after which 30 mL of supernatant were filtered with a 0.45- μm membrane and then subjected to a UV_{254} test using a UV-vis spectrophotometer (UV8500, Shanghai Techcomp Ltd., China). During this stage, UV_{254} removal served as an indicator of dissolved humic acid removal.

2.2. Floc image acquisition and processing

To obtain the high-resolution images of real-time floc after 15 min flocculation, an image processing system (Fig. 1) was constructed. The main components of this system included a computer-controlled digital CCD camera (China Daheng Group Corporation, Beijing Image Vision Technology Branch), a Computar Macro Zoom lens (MLM-3XMP, GOYO OPTICAL Inc., Japan), lighting provided by a stroboscopic lamp, image acquisition, and image analysis software. The strobe light was placed on the opposite side of the jar from the camera to provide back-lighting, which produces particle images as shadows. As each focused floc was introduced into a colorimetric tube filled with deionized water and passed through the observation region in the tube, its images were recorded by a computer-controlled digital CCD camera. To interpret image sizes correctly, a graduated microscale was photographed to determine the number of pixels corresponding to a given standard length for each set of experiments.

2.3. Cryofixation and vacuum drying of PFC–HA flocs

Cryofixation of the PFC–HA floc samples was conducted by plunge-freezing in liquid nitrogen at 77 K. A 15-mL plastic centrifugal tube containing 10 mL of flocculated water with flocs was plunged into a liquid-nitrogen tank for 30 min, after which the cryofixation samples were placed in a vacuum-freeze dryer (FD-1A, Beijing Boyikang Laboratory Instruments Ltd., China) for 24–48 h. Sublimation of the ice formed from void or interstitial water of the sample was then induced by the vacuum-freeze drying process [28]. Finally, dry floc powder samples were obtained and stored in a desiccator.

SEM images of the freeze-dried samples were obtained on a scanning electron microscope (Quanta 200, FEI). The surface area and pore size distribution were measured by N_2 adsorption using ASAP 2000 (Micromeritics, USA).

2.4. Fractal geometry in different topological spaces

Geometric characteristics were derived for the images collected after slow-stirring. Unlike spherical particles that can be described based on their diameter alone, nonspherical particles can be characterized in many ways, and the software of Image pro Plus 5.0 determines the area, perimeter, and the second-order moments of the image for each floc. The procedure for geometrical characteristics identification was following: the boundary of each gray-level image was automatically or manually discriminated, sometimes the image was treated using contrast enhancement in order to produce the clearest possible particle images prior to above discrimination; then the number of pixels corresponding to a given standard length was determined through the calibration function of the professional software; finally, above geometrical parameters can be automatically calculated through pull-down menu of measure in Image pro Plus 5.0.

The one-dimensional fractal dimension (D_1) of flocs was calculated by regression analysis of the logarithm of their perimeters versus the logarithm of their corresponding characteristic lengths. The two-dimensional fractal dimension (D_2) of flocs was determined by regression analysis of the logarithm of their projected areas versus the logarithm of their corresponding characteristic lengths or perimeters [29]. In this study, the longest diameter of the particle image was taken as the characteristic length.

2.5. Pore surface fractal dimension

To evaluate the pore surface fractal dimension of PFC–HA, flocs were evaluated by employing a well-established method based on the fractal version of the Frenkel–Halsey–Hill (FHH) equations and thermodynamic model [30–32]. The length scale at which fractal behavior was observed in the above fractal FHH equation plots was also computed according to previously conducted studies [26,27,33,34].

The classical FHH theory for multilayer adsorption has been extended to the fractal surfaces in the following form:

$$\ln \frac{N}{N_m} = -\frac{1}{q} \ln(-\ln x) + C \quad (1)$$

where N/N_m represents the fractions of surface coverage and x is the ratio of p and p_0 , which are respectively the equilibrium and saturation pressures of the adsorbate; C is the intercept and the parameter q is related to the surface dimension of the sample. The determination of pore surface fractal dimension D_s can be achieved through Eq. (2), which suggests capillary condensation in the mesopore range is more important.

$$D_s = 3 - \frac{1}{q} \quad (2)$$

If fractal behavior was observed in the fractal FHH equation plots above, the length scale was computed from the number of absorbed layers n with the following equation [33]:

$$n = \left(\frac{N}{N_m} \right)^{1/(3-D_s)} \quad (3)$$

where the N_2 layer thickness is 0.35 nm and the length scale is the product of n and 0.35 nm. It is to be noted that the coverage, N/N_m , is always above the monolayer capacity when fractal behavior is observed in the capillary-force-controlled regime. Thus, the calculated length scale is always larger than the N_2 molecular size.

In addition to the fractal FHH theory discussed above, Neimark and Unger [34] and Neimark [35] proposed a different model based on the free energy of the liquid/gas interface to estimate the surface fractal dimension D_s from the adsorption isotherm data. It is called a thermodynamic model, in which the same adsorption mecha-

nism, i.e., capillary condensation, is assumed, as in the fractal FHH equation. The model reflects the idea that during the adsorption on a fractal surface, the surface is smoothed by the adsorbate and where the surface of the adsorbent, covered with an adsorbate, is smaller than the surface of the uncovered adsorbent. The equation of the thermodynamic model is:

$$\ln S = (D_s - 2) \times \ln(-\ln x) + C_2 \quad (4)$$

where S represents the area of the ‘condensed adsorbate-vapor’ equilibrium interface and C_2 is the intercept.

The area S can be calculated according to the Kiselev equation:

$$S = \frac{RT}{\gamma} \int_{N(p/p_0)}^{N_{\max}} \left[\ln \frac{p_0}{p} \right] dN \quad (5)$$

where $N_{\max}$ represents the amount absorbed when p/p_0 approaches unity and γ denotes the liquid surface tension.

The area S is related by the fractal law $S \propto r^{2-D_s}$ to the mean scaling radius of the curvature of this interface r which is calculated from Kelvin’s equation:

$$r = \frac{2\gamma V_L}{RT \ln x} \quad (6)$$

where V_L is the molar volume of the liquid adsorbate. Kelvin’s equation also indicates the range of the scale exhibited by fractal behavior.

3. Results and discussion

3.1. Destabilization of HA with PFC

Table 1 gives the initial pH values of working solution of HA before coagulant injection at different PFC doses. The amount of hydroxyl ions in original working solution can just neutralize the surplus hydrogen ions from PFS and keep the pH values of working solution constant to preset values during coagulation process. Once PFS solution was dosed, the hydroxyl ions in working solution will neutralize the surplus hydrogen ions from PFS and the pH values of working solution will change to preset values immediately. Then the coagulation process will happen at the corresponding constant pH values. As shown in Table 1, the initial pH values of working solutions of HA increased with PFC doses increasing, which indicates that more surplus hydrogen ions at higher PFC doses need to be neutralized by increased amounts of hydroxyl ions in working solutions of HA.

Fig. 2 presents the results obtained from a jar-test conducted at different coagulation pHs. Most turbidity curves displayed similar behavior, with the residual turbidity decreasing steeply at low PFC dosages and then fluctuating only slightly upon further addition of PFC coagulant until another rapid decrease begins. Finally, the residual turbidity reaches the least value among the PFC doses. This pattern may not be very fixed for the turbidity curve at a coagulation pH = 7.0 ± 0.05 ; rather, it is more likely that a gradual decrease is preserved until its minimum value at a coagulant concentration of 8.08×10^{-4} mol/L (Fe^{3+}) is reached. The residual turbidities for almost all samples decrease as the coagulation pH increases, and a much higher value is found at acidic coagulation pHs, with only close points being observed in turbidity curves of pH 8.0 ± 0.05 and 9.0 ± 0.05 at coagulant concentrations of 4.04×10^{-4} mol/L (Fe^{3+}) and 8.08×10^{-4} mol/L (Fe^{3+}). As shown in Fig. 2b, some different behaviors were observed in UV₂₅₄ absorbance curves, with the UV₂₅₄ absorbance decreasing sharply at low doses and then gradually decreasing upon further PFC addition at alkaline coagulation pHs. However, at acidic or neutral coagulation pHs a gradual decrease was shown in the UV₂₅₄ absorbance curves with the addi-

Table 1
Initial pH of working solution of HA.

PFC doses ($\times 10^{-4}$ mg/ L as Fe^{3+})	Initial pH of working solution of HA				
	Coagulation pH 5.00 ± 0.05	Coagulation pH 6.00 ± 0.05	Coagulation pH 7.00 ± 0.05	Coagulation pH 8.00 ± 0.05	Coagulation pH 9.00 ± 0.05
1.01	6.74 ± 0.05	7.26 ± 0.05	8.31 ± 0.05	9.39 ± 0.05	9.58 ± 0.05
2.02	7.09 ± 0.05	7.56 ± 0.05	9.30 ± 0.05	9.83 ± 0.05	10.04 ± 0.05
4.04	7.88 ± 0.05	8.92 ± 0.05	10.09 ± 0.05	10.35 ± 0.05	10.61 ± 0.05
5.65	9.18 ± 0.05	9.74 ± 0.05	10.52 ± 0.05	10.78 ± 0.05	10.91 ± 0.05
8.08	9.99 ± 0.05	10.44 ± 0.05	11.06 ± 0.05	11.24 ± 0.05	11.37 ± 0.05

tion of PFC. In general, lower UV_{254} absorbances were observed at coagulation pH = 6.0 ± 0.05 and 7.0 ± 0.05 . For all coagulation pHs, the least values of the UV_{254} absorbance were reached at a PFC dose of 8.08×10^{-4} mol/L (Fe^{3+}), and these minimum values at acidic or neutral coagulation pHs were somewhat less than at alkaline coagulation pHs.

Considering the initial turbidity and UV_{254} of humic acid solution, the residual turbidities at coagulation pH = 5.0 ± 0.05 and most PFC dosages except for 8.08×10^{-4} mol/L (Fe^{3+}) were higher than 1.40 NTU; however, the corresponding UV_{254} values were much lower than 0.33 cm^{-1} . These findings demonstrated that there were some residual fine flocs suspended in the water after 30 min of sedimentation that could be removed once the water samples were filtered through the $0.45\text{-}\mu\text{m}$ membrane. The UV_{254} values of the filtered water then decreased to less than that of the original HA solution. Furthermore, when increasing the coagulation pHs from 5.0 ± 0.05 , all of the residual turbidities were lower than those of the original humic solutions. Comparing Fig. 2a with Fig. 2b, revealed that these variations in the residual turbidities as functions of pH were not in accordance with those of their UV_{254} absorbance, indicating that sometimes both good performance on the dissolved humic acid removal and the suspending flocs removal may not occur concurrently.

Fig. 2a and b also shows that there are different particles or dissolved humic acid removal results among these coagulation pHs, but that these differences were gradually reduced with increasing PFC dosages, especially with respect to the elimination of dissolved humic acid from solutions.

Polyferric chloride (PFC) is a type of inorganic polymeric flocculant (IPF) that contains many types of pre-formed Fe(III) enhanced-hydrolysis species with different molecular and positive charges. In general, basicity (B) was used to characterize the PFC quality related to molecular weight and positive charges, which can give some information regarding PFC preparation. However, Tang and Stumm [36,37] proposed that a new characteristic param-

eter, hydrolysis degree (B^*), could be used to characterize the hydrolysis–polymerization–gelation–precipitation process for the preparation of PFC. The B^* value can be calculated according to Eq. (7):

$$B^* = \frac{10^{14-\text{pH}}}{\text{Fe}_T} - \frac{10^{-\text{pH}}}{\text{Fe}_T} + \frac{[\text{OH}^-]_{\text{add}}}{\text{Fe}_T} - \frac{[\text{H}^+]_{\text{add}}}{\text{Fe}_T} \quad (7)$$

where $[\text{Fe}_T]$ is the total concentration of Fe(III) in solution, $[\text{OH}^-]_{\text{add}}$ and $[\text{H}^+]_{\text{add}}$ represent the concentration of hydroxyl ions and hydrogen ions added into solution, respectively. It is obvious that the $[\text{OH}^-]_{\text{add}}/[\text{Fe}_T]$ equals to the basicity (B) of PFC. Since B^* value presents more correct quantities of hydroxyl ions included in the enhanced-hydrolysis species of PFC than B , the former could give better information regarding the Fe(III) hydrolysis species distribution during PFC preparation than the latter. According to their research, the corresponding solution of Fe(III) flocculant is mainly composed of multicore polymers with high positive charge when the B^* value is in the range of 0.5–1.0 [38]. In this study, the B^* value of the original PFC solution was 0.7063, while that of the diluted solution (working solution) was 0.6027. Therefore, the B^* value of PFC working solution indicates that medium polymeric species from Fe(III) hydrolysis–polymerization with high positive charges are the main components in it [36–38]. These medium polymeric species with high positive charges can play a charge neutralization and adsorption-bridge role in coagulation process [36–38].

Fig. 3 illustrates the influence of PFC dosages on the zeta potentials of PFC–HA micro-flocs. It is obvious that each pH of the original HA solution employed had to be different to maintain constant pHs during coagulation and flocculation, and their negative zeta potentials showed a linear decrease from acidic pHs to alkaline pHs as well. This behavior is consistent with the electrostatic and configuration characteristics of HAs that are dependent on pH, specifically, the high intramolecular electrostatic repulsion and stretched configuration at alkaline pHs versus the formation of small aggregates below pH 5.00 [10,39,40]. As PFC was added to the

Fig. 2. Jar-test results at different coagulated pHs: (a) residual turbidity and (b) UV absorbance at 254 nm.

Fig. 3. Evolution of zeta potential of HA or PFC–HA flocs versus pH before or after PFC dosing.

HA solutions, the zeta potentials of PFC–HA micro-flocs decreased from positive to negative as the coagulation pHs increased at all PFC doses, and almost all zeta potentials of PFC–HA micro-flocs were much higher than those of the original HA solutions. A gradual reduction of the above differences was observed, and was accompanied by an increase in coagulation pHs, whereas a gradual enlargement was also observed in Fig. 3 as the PFC doses increased under most conditions. It is obvious that complete charge neutralization occurred at almost all acidic coagulation pHs because the positive charges of dosed PFC were greater than the negative charges of the HA molecules and some alkalinity substance in each original HA solution. When the coagulation pHs change to neutral and alkaline, only partial charge neutralization can happen, the negative zeta potentials for coagulated HA solutions were observed.

At coagulation $\text{pH} = 5.00 \pm 0.05$, the zeta potentials of the PFC–HA micro-flocs were above 0 mV and they reached the maximum value (12.10 mV) at a PFC dose of $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}). In addition, the zeta potential was slightly higher than 2.00 mV at a dose of $1.01 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}). However, the zeta potentials of the PFC–HA micro-flocs gradually decreased as the doses increased above $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), showing a close constant difference with that of the corresponding original HA values, which implies that the increased amount of positive charges possessed by PFC

species as its doses rose from $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}) was approximately equal to that of negative charges owned by both HA and some alkalinity substances in each corresponding original HA solution. For PFC–HA flocs formed at coagulation $\text{pH} = 6.00 \pm 0.05$, their zeta potential was zero when the PFC dose was $1.01 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), while the other zeta potentials at higher PFC dosages were close to 2.20 mV, which seem to indicate that the increased amount of positive charges possessed by PFC species as its doses rose from $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}) was higher than that of the negative charges of HA molecular and some alkaline substances in each corresponding original HA solution.

However, at neutral and alkaline coagulation pHs, charge reversal was not attained. Under these conditions, once PFC was injected into HA solution the remaining alkaline substances after neutralization by hydrogen ions from PFC diluted solution initially reacted with PFC species containing high positive charges and fresh precipitate with low or zero charges were produced, after which the residual PFC polymeric species with positive charges began to neutralize more negative charges of other alkaline substances and HA molecules in these original HA solutions than in the above acidic ones [10,39,40]. Therefore, only a portion of the PFC species with positive charges played a charge neutralization role in HA solutions at neutral and alkaline coagulation pHs. Moving from neutral to alkaline coagulation pHs results in more and more fresh pre-

a. Coagulated pH=7.00 , PFC= 1.01×10^{-4} mol/L(Fe^{3+})

b. Coagulated pH=7.00 , PFC= 2.02×10^{-4} mol/L(Fe^{3+})

c. Coagulated pH=7.00 , PFC= 4.04×10^{-4} mol/L(Fe^{3+})

d. Coagulated pH=7.00 , PFC= 5.65×10^{-4} mol/L(Fe^{3+})

e. Coagulated pH=7.00 , PFC= 8.08×10^{-4} mol/L(Fe^{3+})

Fig. 4. CCD images of PFC–HA flocs.

precipitate being formed and more negative charges on the PFC–HA flocs.

These zeta potential results indicate that the charge neutralization mechanism preferentially apply at acidic coagulation pHs,

while from neutral to alkaline conditions both adsorption-bridge and charge neutralization mechanisms play a partial role in HA elimination. Perhaps the physical enmeshment and/or adsorption onto freshly formed precipitate also has more and more effect on

Fig. 5. Variation in median diameters of PFC–HA flocs as a function of PFC dosages at different coagulated pHs.

the HA removal under conditions favoring PFC species precipitation.

3.2. PFC–HA morphology and size distribution

The images of PFC–HA flocs formed after the slow-stir phase were acquired by a CCD image recording system. As shown in Fig. 4, all of the PFC–HA flocs at coagulation pH = 7.00 ± 0.05 had an irregular shape and different compactness and sizes. In addition, as the PFC dosage increased, the sizes of flocs formed decreased. Under other coagulation pHs, irregular flocs were also observed, implying that they had a fractal characteristic.

Fig. 5 provides the median diameter results of PFC–HA flocs under different coagulation pHs and PFC doses. All data were obtained by calculation of the size distribution of about 120 PFC–HA flocs. As shown in Fig. 5, the median diameter of PFC–HA flocs sharply decreased with the addition of PFC coagulant at acidic and neutral coagulation pHs, but as the coagulation pHs converted to the alkaline phase, the PFC–HA floc sizes increased at first, after which they gradually decreased or fluctuated only slightly at further dosages, and most of their median diameters were close to 1.5 mm. At PFC doses less than $4.04 \times 10^{-4} \text{ mol/L} (\text{Fe}^{3+})$, much larger flocs with median diameters greater than 1.8 mm were observed at acidic and neutral coagulation pHs, while the flocs formed at coagulation pH 5.00 ± 0.05 and 6.00 ± 0.05 had similar sizes and maximum median diameters of about 2.75 mm. Upon further PFC addition, the flocs formed at neutral and alkaline pHs had a median diameter of about 1.5 mm, which was somewhat larger than those formed at acidic coagulation pHs, while the smallest size of less than 1.2 mm was observed at coagulation pH = 5.00 ± 0.05 . These results

could be attributed to the different species of PFC existed under the corresponding coagulation pH conditions. At acidic coagulation pHs, the charge neutralization mechanism involved by medium polymeric species of PFC diluted solution can lead to very large flocs at low PFC doses, while the flocs size decreased sharply with PFC dose increasing. When the coagulation pHs moved to neutral and alkaline conditions, more and more physical enmeshment and/or fresh precipitate adsorption mechanisms can happen during PFC–HA coagulation process, and the fresh precipitate formed through above medium polymeric species hydrolysis was becoming the main component of the corresponding flocs. A little change in size was observed for these precipitate-based flocs formed at most PFC doses and alkaline coagulation pHs, while sharp variation still appeared in the size of flocs formed at neutral coagulation conditions, at which both the charge neutralization and physical enmeshment and/or fresh precipitate adsorption mechanisms may play important roles in flocs production. In addition, the flocs formed mainly under physical enmeshment and/or fresh precipitate adsorption mechanisms were much smaller than those formed under charge neutralization mechanisms when PFC doses were less than $4.04 \times 10^{-4} \text{ mol/L} (\text{Fe}^{3+})$, while at higher PFC doses, above trend reversed.

3.3. Fractal dimensions in different topological spaces of PFC–HA flocs

The fractal dimensions of PFC–HA flocs in different topological spaces were calculated by the corresponding regression method based on the image geometrical parameters of 120 flocs. All of these results are listed in Fig. 6. Fig. 6a shows the evolution of one-dimensional fractal dimension (D_1) versus PFC doses at different coagulation pHs. At acidic coagulation pHs, D_1 values decreased initially, after which they increased to about 1.10. Some values of D_1 less than 1.00 were observed at low PFC doses and coagulation pH = 6.00 ± 0.05 , which is not agreement with the definition of D_1 . In general, values of D_1 cannot be less than 1.00, a higher D_1 is associated with a more irregular boundary or surface of the particles [19] and therefore indicates that PFC–HA flocs with a more irregular boundary and surface are obtained at acidic coagulation pHs and higher doses. At neutral or alkaline coagulation pHs, all of the PFC–HA flocs showed D_1 values above 1.0. Especially, the highest D_1 values were observed at a PFC dose of $2.02 \times 10^{-4} \text{ mol/L} (\text{Fe}^{3+})$, which is equal to 1.17 at coagulation pH = 9.00 ± 0.05 . These findings demonstrate that PFC–HA flocs formed at coagulation pH = 9.00 ± 0.05 and a PFC dose of less than $2.02 \times 10^{-4} \text{ mol/L} (\text{Fe}^{3+})$ possess the most irregular boundaries or surfaces, while the corresponding flocs formed at coagulation pH = 6.00 ± 0.05 and a PFC dose of less than $5.65 \times 10^{-4} \text{ mol/L} (\text{Fe}^{3+})$

Fig. 6. Evolution as a function of PFC dosages of fractal dimensions in different topological spaces for PFC–HA flocs.

Fig. 7. SEM images of cryofixation–vacuum–freeze-dried powder for PFC–HA flocs formed at a PFC dose of 1.01×10^{-4} mol/L (Fe^{3+}).

display the least irregularity in their boundaries or surfaces. At PFC doses greater than 5.65×10^{-4} mol/L (Fe^{3+}) the flocs formed at acidic and neutral coagulation pHs present more irregular boundaries or surfaces than those formed at alkaline coagulation pHs. On the basis of these observations, it seems that the change of one-fractal dimension for PFC–HA flocs did not totally depend on the coagulation pHs mentioned above, while PFC doses also had an important effect on D_1 . When PFC doses are less than 5.65×10^{-4} mol/L (Fe^{3+}), the flocs mainly produced through physical enmeshment and/or fresh precipitate adsorption mechanism (alkaline coagulation pHs) presented more irregular boundaries or surfaces than those primarily caused by charge neutralization mechanism (acidic coagulation pHs), while at PFC doses greater than 5.65×10^{-4} mol/L (Fe^{3+}), these trend reversed. And at coagulation pH equals to 7.00 ± 0.05 , the D_1 values of the corresponding flocs showed the similar trend to alkaline coagulation pHs when PFC doses were less than 5.65×10^{-4} mol/L (Fe^{3+}), but as PFC doses increased from it, another similar trend to acidic coagulation pHs was observed for the D_1 values of these flocs.

The effects of PFC doses on the two-dimensional fractal dimension, D_2 , estimated from the regression results of the projected area and perimeter of the floc image are shown in Fig. 6b. In general, high D_2 values indicate a compact structure while low ones indicate a loose structure. Evaluation of the PFC–HA flocs revealed that there were no D_2 values higher than 1.8. Under acidic coagulation pH conditions, D_2 values of PFC–HA flocs initially increased with the addition of PFC and reach the maxima at a PFC dose of 4.04×10^{-4} mol/L (Fe^{3+}), while they continuously decreased or fluctuated with further PFC dosing. However, the D_2 values of PFC–HA flocs at alkaline coagulation pHs initially decreased as the PFC doses increased and reach the minima at specific doses, while they continuously increased with further PFC dosing. When compared with the above conditions, the two-dimensional fractal dimensions of PFC–HA flocs formed at neutral coagulation pH showed an increasing trend at all PFC doses. In addition, more compact PFC–HA flocs were formed at acidic coagulation pHs and PFC doses between 2.02×10^{-4} mol/L (Fe^{3+}) and 5.65×10^{-4} mol/L (Fe^{3+}), while the

PFC doses increased, the PFC–HA flocs formed at neutral and alkaline coagulation pHs gradually became more compact than those formed at acidic coagulation pHs. The D_2 values demonstrate that the most compact PFC–HA flocs were formed at coagulation pH = 6.00 ± 0.05 and a PFC dosage of 4.04×10^{-4} mol/L (Fe^{3+}). The loosest PFC–HA flocs were formed at coagulation pH = 7.00 ± 0.05 and a PFC dose of 1.01×10^{-4} mol/L (Fe^{3+}).

The variation in D_1 and D_2 values of the flocs implied that when coagulation mechanisms change from charge neutralization (acidic coagulation pHs) to physical enmeshment and/or fresh precipitate adsorption (alkaline coagulation pHs), PFC–HA flocs formed at PFC doses lower than 5.65×10^{-4} mol/L (Fe^{3+}) usually had more irregular boundaries or surface and looser structures, while flocs formed at PFC doses higher than 5.65×10^{-4} mol/L (Fe^{3+}) gradually showed less irregular boundaries and surfaces and a more compact structures. Moreover, Fig. 6b revealed that the different compositions of charge neutralization mechanism and physical enmeshment and/or fresh precipitate adsorption mechanisms that occurred at neutral and alkaline coagulation pHs had important effects on the structure of PFC–HA flocs.

3.4. Microstructure and pore surface fractal dimensions of cryofixation–vacuum–freeze-dried powder of PFC–HA flocs

The surface morphology of cryofixation–vacuum–freeze-dried powders is shown in Fig. 7. The surface of the powders was obviously irregular and rough when observed by SEM at 30,000 times magnification. While the surface became looser as the coagulation pHs increased, the highest space occupation ability was observed at the surface of dried powders prepared at coagulation pH = 6.00 ± 0.05 when the PFC dosage was 1.01×10^{-4} mol/L (Fe^{3+}).

The nitrogen adsorption–desorption isotherms of different dried flocs were used to analyze their microstructure characteristics. Fig. 8 shows the change in the specific surface area, pore volume, diameter and surface fractal dimensions with the coagulation pHs and PFC doses. These pore surface fractal dimensions (D_s) were calculated with nitrogen adsorption data based on fractal

Fig. 8. Variation in the microstructure of cryo-freezing–vacuum-dried powder for dried PFC–HA flocs as a function of PFC doses at different coagulated pHs.

FHH equations. However, the D_s values of greater than three were observed based on nitrogen adsorption data and thermodynamic equation, and exceeded the range of surface fractal dimensions [18,20,21–27].

For most cases, the dried powders prepared at higher coagulation pHs, at which the charge neutralization mechanism had a tapered partial effect on the PFC–HA coagulation process, showed higher specific surface areas, pore volumes and diameters. When PFC–HA flocs are formed at PFC doses ranging from $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}) to $5.65 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), the specific surface areas of their dried powders begin to decrease gradually, but above that dose only the specific surface areas of the dried powders prepared at coagulation pH 5.00 ± 0.05 continue to decrease. In addition, both pore volumes and diameters of these dried powders primarily increased with the addition of more PFC in HA water, while for the dried powder prepared at acidic coagulation pHs, such an increase was slow or ended at a PFC dose of $5.65 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}). For the dried powder prepared at neutral and alkaline coagulation pHs, the increase rate became slow at a PFC dose of $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}).

As shown in Fig. 8d, the pore surface fractal dimensions (D_s) of the dried powders prepared at acidic and neutral coagulation pHs decreased rapidly before a PFC dose of $4.04 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}) was

reached, after which the D_s values began to increase. The D_s values of the dried powders prepared at coagulation pH = 5.00 ± 0.05 or pH = 6.00 ± 0.05 were much higher than those at pH = 7.00 ± 0.05 , and the highest D_s value obtained was about 2.70. For the dried powders prepared at alkaline coagulation pHs, their pore surface fractal dimensions (D_s) continued to increase from about 2.47 to 2.55 at all tested PFC doses, and little differences were observed in the D_s values between the dried powders prepared under these two alkaline coagulation pHs. The D_s values of the dried powders prepared at acidic coagulation pHs were higher than those of powders prepared at neutral and alkaline coagulation pHs when the PFC doses were lower than $2.02 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), which indicates that the dried powders prepared from PFC–HA flocs under the charge neutralization mechanism could result in more irregularity in the pore surface or pore size distribution than flocs produced under physical enmeshment and/or fresh precipitate adsorption mechanisms. Above this dose, with the exception of $8.08 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), the D_s values of the dried powders remained close, presenting similar irregularities in the pore surface or pore size distribution. This trend was demonstrated in part in Fig. 7. When the PFC dose was $8.08 \times 10^{-4} \text{ mol/L}$ (Fe^{3+}), differences between these D_s values increased again. In addition, the pore surface fractal dimensions showed a general opposite varia-

Table 2

Fractal scale for pore surface fractal dimensions of cryofixation–vacuum-freeze-dried PFC–HA flocs powder.

PFC doses ($\times 10^{-4} \text{ mg/L}$ as Fe^{3+})	Fractal scale (nm)				
	Coagulation pH 5.00 ± 0.05	Coagulation pH 6.00 ± 0.05	Coagulation pH 7.00 ± 0.05	Coagulation pH 8.00 ± 0.05	Coagulation pH 9.00 ± 0.05
1.01	0.97–5.69	1.11–6.50	0.83–4.91	0.74–4.47	0.72–4.39
2.02	0.82–4.91	0.81–4.79	0.75–4.53	0.76–4.64	0.76–4.65
4.04	0.76–4.62	0.76–4.67	0.76–4.60	0.77–4.70	0.78–4.73
5.65	0.81–4.96	0.79–4.84	0.78–4.78	0.78–4.81	0.79–4.85
8.08	0.79–4.87	0.90–5.58	0.79–4.81	0.80–4.87	0.83–5.05

tions to other surface parameters, such as specific surface areas, pore volumes and diameters, especially at PFC doses less than 4.04×10^{-4} mol/L (Fe^{3+}), this result indicted that the higher values in the latter three parameters did not ensure increase in both D_s and irregularities in the pore surface or pore size distribution. Indeed, the flocs with higher specific surface areas, pore volumes and diameters were observed at neutral or alkaline coagulation pHs, while their D_s values were lower than those flocs formed at acidic coagulation pHs and lower PFC doses.

The length scales for fractal behavior observed in these fractal FHH equation plots are shown in Table 2. There was no large difference in the fractal scale data for pore surface fractal behavior of these dried powders at each PFC dose and the coagulation pH. Most of the fractal scales were in the range of 0.75–5.00 nm.

4. Conclusions

In general, both the residual turbidity and $\text{UV}_{254\text{nm}}$ for coagulated HA solution decreased as the PFC doses increased up to 8.08×10^{-4} mol/L (Fe^{3+}). The differences in turbidity and dissolved HA removal among different coagulation pHs were also gradually reduced when raising the PFC dosages. Occasionally, both good performances on the dissolved humic acid and suspending flocs removal may not occur concurrently.

For HA solutions coagulated by PFC, charge neutralization mechanisms preferentially occur at acidic coagulation pHs, while under the conditions of neutral and alkaline coagulation pHs, charge neutralization mechanisms play a partial role in HA elimination, while with the increase in coagulation pHs physical enmeshment and/or fresh precipitate adsorption mechanisms gradually have a major effect on the HA removal.

PFC–HA flocs formed under the charge neutralization mechanism were much bigger than those formed primarily under physical enmeshment and/or fresh precipitate adsorption mechanisms when PFC doses increased by up to 4.04×10^{-4} mol/L (Fe^{3+}). This trend was gradually reversed at higher PFC doses.

When coagulation mechanisms changed from charge neutralization to physical enmeshment and/or fresh precipitate adsorption, PFC–HA flocs with more irregular boundaries or surfaces (higher D_1 value) and looser structures (lower D_2 value) were observed at PFC doses lower than 5.65×10^{-4} mol/L (Fe^{3+}), while flocs with less irregularity in the boundary or surface (lower D_1 value) and more compact structures (high D_2 value) gradually appeared at PFC doses higher than 5.65×10^{-4} mol/L (Fe^{3+}).

The dried powders prepared from PFC–HA flocs under a charge neutralization mechanism could lead to a more irregular pore surface or pore size distribution than flocs produced under physical enmeshment and/or fresh precipitate adsorption mechanisms at PFC doses lower than 2.02×10^{-4} mol/L (Fe^{3+}). Above this dose, except for 8.08×10^{-4} mol/L (Fe^{3+}), the dried powders showed similar irregularities in pore surface or pore size distribution. Moreover, the pore surface fractal dimensions (D_s) of the dried powders prepared from PFC–HA flocs under different coagulation pHs showed different variations with PFC doses. Finally, the dried powders of PFC–HA flocs formed at neutral and alkaline coagulation pHs had high specific surface areas, large pore volumes and average pore diameters in most cases.

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