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Surface analysis of cryofixation-vacuum-freeze-dried polyaluminum chloride–humic acid (PACl–HA) flocs

Yili Wang [a,*], Baiyu Du [a], Jie Liu [a], Jia Lu [a], Baoyou Shi [b], Hongxiao Tang [b]

[a] *Environmental Science, College of Environmental Science and Engineering, The Key Laboratory for Silviculture and Conservation of Ministry of Education, Beijing Forestry University, Beijing 100083, PR China*

[b] *State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China*

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Abstract

The powder of polyaluminum chloride–humic acid (PACl–HA) flocs was prepared by cryofixation-vacuum-freeze-drying method. The FTIR spectra show that some characteristic functional groups in polyaluminum chloride (PACl), humic acid (HA), and kaolin still existed in the dried flocs. X-ray diffractometry (XRD) patterns indicate that these flocs are amorphous. Nitrogen adsorption–desorption isotherms were obtained for different samples of the dried PACl–HA flocs. The BET specific surface area, BJH cumulative absorbed volume and BJH desorption average pore diameter of them were determined. The peak values of 8.4–11.2 nm (pore diameter) for pore size distribution (PSD) curves indicate that the pores of the dried flocs are mostly mesopores. The surface fractal dimensions D_S and the corresponding fractal scales determined from both SEM images and nitrogen adsorption–desorption data sets reveal the multi-scale surface fractal properties of the dried PACl–HA flocs, which exhibited two distinct fractal regimes: a regime of low fractal dimensions (2.07–2.26) at higher scales (23–387 nm), mainly belonging to exterior surface scales, and a higher fractal dimensions (2.24–2.37) at lower scales (0.80–7.81 nm), falling in pore surface scales. Both HA addition and kaolin reduction in dried floc can decrease the irregularity and roughness of external surface. However, for the irregularity and roughness of pore surface, the addition of HA or kaolin in dried floc can increase them. Furthermore, some difference was found between the pore surface fractal dimensions D_S calculated from nitrogen adsorption and desorption data. The pore surface D_S values calculated through thermodynamic model were much greater than three.

Keywords: Cryofixation-vacuum-freeze-drying; Polyaluminum chloride (PACl); Humic acid; Floc structure; Surface fractal analysis

1. Introduction

Humic acids (HAs) are one of the main constituents of natural organic matter (NOM) in most surface waters [1–3]. The removal of NOM has become increasingly important in light of the potential for carcinogenic disinfection-byproducts (DBPs), such as trihalomathanes (THMs), haloacetic acids (HAAs), to form if organic carbon is insufficiently removed [1–3]. The United States Environmental Protection Agency has proposed that enhanced coagulation is a best available technology (BAT) for NOM removal [1,2,4]. Extensive enhanced coagulation studies have been devoted to the coagulation of humic acids by traditional coagulants (e.g., aluminum and iron salts) [1,2,4], but fewer studies have focused on the humic acids removal by polyaluminum chloride (PACl)—one of the most widely used inorganic polymer flocculants (IPFs) with extraordinary performance being related to the high charge neutralization ability of some partially neutralized aluminum species [5]. Therefore, the NOM removal by PACl coagulation is also becoming an increasing important work in water treatment, and the corresponding flocs formed by them and their morphology have important effects on the NOM removal.

Abbreviations: PACl–HA, polyaluminum chloride–humic acid; PACl, polyaluminum chloride; HA, humic acid; XRD, X-ray diffractometry; PSD, pore size distribution; SEM, scanning electron microscope; D_S, surface fractal dimensions; NOM, natural organic matter; DBPs, disinfection by-products; THMs, trihalomathanes; HAAs, haloacetic acids; BAT, best available technology; IPFs, inorganic polymer flocculants; FHH, Frenkel–Halsey–Hill; DAF, dissolved air flotation; JMS, jet mixed separator; HRT, hydraulic retention time.

* Corresponding author.
E-mail address: wangyilimail@126.com (Y. Wang).

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A review of previous work shows floc fractal properties, such as mass fractal or fractal characteristics under different dimensions, could give some hints on the formation dynamics and the microstructure of flocs induced by coagulants [6–11]. Generally, a mass fractal may have some influence on bulk physical structural characteristics, such as floc density, settling rates and floc strength [8–10]. In fact, the physical and chemical properties of floc surface have an important effect on the kinetic growing process of flocs, and more irregular and rough surfaces will imply more collision and attachment rates between different flocs in flocculation/flotation and filtration. However, the surface fractal dimension as an indication on the irregularity and roughness of surfaces [12–20] has rarely been reported in above coagulation process. In order to calculate the surface fractal dimension of floc, we must get the data matrix of surface irregularity from fine floc images or of micro-pore structure. Then how to prepare the floc samples for surface image and micro-pore structure detection is becoming a big problem.

The first objective of this work is to prepare an PACl–HA flocs by cryofixation-vacuum drying technique. Recently, cryofixation is becoming a promising technique in many research and industrial fields. Plunging sample into a liquid with high thermal conductivity can result in ultrarapid freezing of sample and transform the water into micro-ice crystals with dimensions of a few nanometers to a few tens of nanometers, and thus distortion to the morphology of the sample could be minimized [21–23]. After floc cryofixation, vacuum-drying technique has been used to sublimate the micro-ice crystals from sample. Cryofixation-vacuum-drying has been proved to a reliable technique in the studies of the micro-morphologies of microbial soil crusts, clay-or sand-polysaccharide associations [24]. Cryofixation has also been applied to characterize humic substances and their binary and ternary associations with clay minerals, ferrihydrite and smectite. With the aid of this technique, better understanding of the role of organic soil polymers in the aggregation processes of soil components is obtained [22].

The further objective of this work is to analysis the surface morphology of PACl–HA flocs prepared by cryofixation-vacuum drying technique. The SEM images and adsorption–desorption isotherms of N_2 (77 K) were analyzed, aiming to investigate the external and internal surface fractal dimensions of dried PACl–HAs flocs, specific surface area, and pore structure. The application of three image analysis methods and two isotherm equations, mainly, FHH (Frenkel–Halsey–Hill) and Neimark's, for this purpose were discussed. The dried flocs were also characterized by XRD analysis and FTIR spectroscopy. Then the investigation on the dried PACl–HA flocs will give some knowledge of their surface fractal.

2. Materials and methods

2.1. Generation of PACl–HA flocs

In order to remove HA from resource water, the micro-eddy flocculation-DAF (dissolved air flotation) process was employed. In micro-eddy flocculation-DAF experiments, a synthetic matrix was used, which included four test water samples synthesized by adding humic acid (Beijing Yanqing humic acid plant, China) and/or kaolin (Beijing Chaoyang chemical plant, China) into tap water. The humic acid and kaolin concentrations of the test waters are listed in Table 1.

Table 1
Humic acid and kaolin concentration of raw water and corresponding PACl dosage

Test water	1	2	3	4
Humic acid ($mg\,L^{-1}$)	5.0	10.0	5.0	5.0
Kaolin ($mg\,L^{-1}$)	0	0	5.0	10.0
PACl dosage (10^{-3} $mol\,L^{-1}$, Al^{3+})	0.60	0.60	0.69	0.69

Commercial PACl product (Beijing Wanshui Co., China) was used as coagulant. The basicity (OH/Al molar percentage) and Al_2O_3 content of the PACl was 55 and 10% (w/w), respectively. Before use, the PACl was diluted to 0.241 $mol\,L^{-1}$ (as Al^{3+}) with ultra-purified water.

When using PACl as a coagulant, different doses were added to test water for detecting the HA removal effect by this process. The PACl–HA flocs were formed in a micro-eddy flocculator, which included a tube mixer and a jet mixed separator (JMS, invented by Watanabe et al.) [25]. In JMS, with porous plates perpendicular to the flow, flocculation and sedimentation could occur simultaneously. The hydraulic retention time (HRT) was 10–13 min. When PACl was added, strong tube mixing dispersed the PACl in a very short time. Then the water passed through the holes in the plates, and jets were developed. With the gentle agitation under micro-eddy condition, strong and compact flocs were formed. Some flocs could be precipitated along the bottom of JMS, and other flocs were transferred to the next unit process (sedimentation, flotation, or filtration) for separation [5]. Through comparing HA removal ratios under different PACl doses, the optimum dosage was selected for different test water samples in Table 1. The flocs formed at optimum dosage were sampled at the end of JMS for the following analysis.

2.2. Cryofixation and vacuum drying of PACl–HA flocs

Cryofixation of PACl–HA flocs samples were carried out by plunge-freezing in liquid nitrogen at 77 K. A 15-ml plastic tube containing 10 ml of flocculated water (with flocs in the water) was plunged in a liquid-nitrogen tank for 30 min. After cryofixation, the samples were put in a vacuum-freeze dryer (FD-1A, BoYikang, China) for 24–48 h. Sublimation of the ice (formed from void or interstitial water in the samples) was achieved through the vacuum-freeze drying process. The dried floc samples were stored in a desiccator for later use.

2.3. Analytical methods

SEM images of 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). The crystallinity of dried samples was characterized by X-ray diffraction (XRD) analysis (D/max-RB, Japan). The instrument settings were: