A Comparison of Fractal Dimensions of Clay and Humic Acid Flocs under Optimum Coagulation Conditions

Hira Amjad and Zahiruddin Khan

Abstract—The fractal dimension of floc provides the basic information on the structure and origin of the flocs. The removal efficiency of several drinking water contaminants depends upon the floc characteristics especially in their fractal dimension in the conventional (coagulation/flocculation) water treatment process. In this study two synthetic feed suspensions (humic acid and clay suspension) were prepared and coagulated under optimum coagulation conditions. Aluminum sulfate (alum, $Al_2(SO_4)_3.18H_2O$) was used as a principal coagulant for both humic acid and clay suspensions. The flocs so produced were measured for their size and fractal dimension distribution as a function of flocculation time using small angle light scattering (SALS) technique. Results showed that floc size increases with an increase in the flocculation time both for humic acid and clay flocs. Same is true for fractal dimensions of humic acid and clay flocs. Fractal dimensions of humic acid flocs were somewhat higher than the fractal dimension of clay flocs due to the difference in coagulation mechanism involved for the formation of humic acid and clay flocs.

Index Terms—Fractal dimension distribution, floc size distribution, small angle light scattering, velocity gradient.

I. INTRODUCTION

Usually groundwater has been considered to be a safe source of drinking water but with everyday rising population and demands for potable water, have forced authorities to consider surface water as alternate source of potable water for public supply [1]. Suspended colloidal particles in surface water resources are one of the main obstacles of its utilization as potable water. Turbidity up to certain level does not harm human health but it can provide refuge to pathogens from disinfection. These pathogens are responsible for adverse health effects amongst consumers.

Humic acid is a natural organic matter and sources of humic acid contamination in drinking water are weathering of rocks and/or biodegradation of animals and plants [2]. The yellowish to brown color of water most of the times indicates the presence of humic acid in water. Humic acid has very high affinity to form complexes with various pollutants for example pesticides and heavy metals. These complexes cause the ground and surface water contamination. Further, during chlorination step in drinking water treatment humic acid will produce toxic disinfection (chlorinated organic compounds such as trihalomethanes) by-products which exhibit mutagenic properties [3]. For this reason, removing humic acid from drinking water resources is a serious issue.

Coagulation is one of the very effective and ancient methods to remove the humic acid and clay contamination from drinking water [4]. Other technologies such as oxidative and absorptive processes can also be employed to remove the humic acid from the drinking water resources [5].

For effective coagulation process, optimum coagulation conditions (coagulant dose, pH, velocity gradient, temperature) are very essential [6]. Floc characteristics such as size, shape and density are greatly influenced by flocculation conditions and have direct influence on floc filterability [7]. Optimal flocculation conditions are required to agglomerate small particles into large flocs and to reduce their breakup. Floc size produced by flocculation varies over a wide range [8].

Floc strength is one of the basic characteristics of floc nature and it determines the efficiency of solid-liquid separation process in water treatment system. Flocs that are once formed during coagulation process tend to break-up due to irregular shear rate distribution throughout the flocculation mechanism. In field systems flocs must be strong enough (Reaction-Limited Aggregation, RLA) to withstand the shear rates fluctuations in slow mix basin for efficient removal of solid particles from water. Otherwise the loose clusters of flocs (Diffusion-Limited Aggregation, DLA) will reduce the removal efficiency of solid particles. Colloidal particles form bonds when they come close to each other and the strength of flocs formed depends on these bonds [9].

The fractal dimension of flocs has great influence on packing density and settling of flocs which is an important tool in water treatment systems [10]. Fractal dimension of flocs is significantly related to the rate of aggregation of particles i.e., reaction-limited aggregation and diffusion-limited aggregation. In diffusion-limited aggregation particles are very sticky and repulsive forces between them are very weak so the only limiting factor for aggregation is time taken for these to come close and aggregate by the process of diffusion. While in reaction-limited aggregation particles have relatively strong repulsive forces and aggregation is limited by time taken by particles to overcome that repulsive barrier by thermal activation [11], [12].

With direct filtration and membrane filtration gaining momentum, the effect of variations in coagulant mixing conditions and settling of flocs on filtration effectiveness and flux decline needs exploration.

II. MATERIALS AND METHODS

A. Synthetic Feed Water I-Humic Acid Suspension

Humic acid synthetic feed water was prepared using ultrapure water (~18 MΩ cm^{-1}) that was supplied by Barnstead E-pure system. Aluminum sulfate (alum, $Al_2(SO_4)_3.18H_2O$, reagent grade, Sigma Aldrich) was used as a principal coagulant. 1 g of sodium humate (MW 4,000 to 23,000 Da, Sigma-Aldrich) was mixed in 1 L of ultrapure water for three days to prepare the stock solution of humic acid. To adjust the pH of that stock solution to 8.0, 0.1M HCl was used. Then the stock solution was filtered through a 0.45 µm nitrocellulose membrane (Millipore) and stored in the dark at 4°C. A TOC analyzer was used to measure the concentration of humic acid in the stock solution and the concentration of stock solution was in range of 240 to 280mg (TOC)/L. This stock solution was diluted to 10 mg(TOC)/L (as confirmed by TOC measurements) for the coagulation flocculation experiments. To provide the sufficient carbonate alkalinity 1mL of 2mM solution of $NaHCO_3$ was added per 5L of diluted stock solution of humic acid.

B. Synthetic Feed Water II — Clay Suspension

To prepare the stock suspension of clay deionized water and kaolin clay (Spectrum Chemicals) was used. For this purpose, 3 g of kaolin clay was suspended in 1L of deionized water and mixed it at 300 rpm for 30 min. After mixing the suspension was allowed to settle for 24 hr on room temperature. After settling the top 800 mL of stock suspension was decanted in a separate jar and further diluted using deionized water to maintain the turbidity in range of 30-35 NTU. A turbiditimeter of Hach 2100N was used to measure the turbidity of clay suspension. A 0.1 M NaOH solution was used to adjust the pH of synthetic feed water around 8.7 ± 0.1. The particle size distribution of clay synthetic water was characterized by using Malvern Mastersizer 2000 and it was $d_{90} = 0.98$ µm.

C. Coagulation and Flocculation

For coagulation of humic acid suspension, stock solution of aluminum sulfate was prepared by dissolving 10 g of aluminum sulfate in 1 L of ultrapure water. A jar test apparatus (Model 7790-400, Phipps & Bird) with 2 L cylindrical beakers was used for coagulation experiments. For coagulant dose determination various amounts of the coagulant were added into 1 L of the synthetic feed water. The rapid mixing was provided for 1 min at 200 rpm. Flocculation was done at 40 rpm for 20 min (Table I). Using the impeller diameter of 7.5 cm, the G value for flocculation was 42 s^{-1}. For coagulant dose determination, before coagulant addition, the pH of the solution was adjusted to 5.5 for flocculation. After flocculation the floc suspension was allowed to settle for 30 min, and then 40 mL of supernatant sample was collected approximately 2 cm below the water surface using a micropipette and tested for humic acid concentration using a TOC analyzer. In all coagulation and flocculation experiments the temperature of feed water was kept constant in range of 25 ± 0.5 °C.

For clay suspension coagulation, stock solution of aluminum sulfate was prepared by mixing 1 g of aluminum sulfate in 1 L of deionized water. The coagulation/flocculation apparatus and conditions for clay flocs were the same as for humic acid flocs. Turbidity of clay suspension was measured using turbiditimeter (Model Hach 2100N).

D. Determination of Floc Fractal Dimension

To determine the fractal dimension of flocs by small angle light scattering technique, Malvern Mastersizer 2000 instrument was used. The dependence of the intensity I of scattered light on the scattering vector Q was recorded using a manufacturer's provided soft module for this instrument.

$$Q = \frac{4\pi n}{\lambda} \sin\left(\frac{\varphi}{2}\right) \tag{1}$$

where λ is the wavelength of the incident light, the scattering angle is ϕ, and the refractive index of solvent (water) is n. A linear fit to the double logarithmic plot of the power law dependence of intensity on the scattering vector was used to determine the fractal dimension of aggregates:

$$I(Q) \propto Q^{-Df} \tag{2}$$

E. Measurements of Floc Size and Fractal Dimension Distribution

A light scattering instrument (Malvern Mastersizer 2000, Malvern) was used to measure the floc size and fractal dimension distribution as a function of flocculation time [13]. A peristaltic pump (Model no. 7520-00, Masterflux, Cole-Palmer) was used to circulate the humic acid floc suspension continuously between jar test beaker and optical unit of Mastersizer (Fig. 1). This pump was operated at flow rate of 25 mL/min and installed downstream of the Mastersizer to reduce the floc breakup. To measure the floc size and their fractal dimension as a function of flocculation time the Mastersizer was programmed to take the reading after every 30 s during the entire duration of flocculation process.

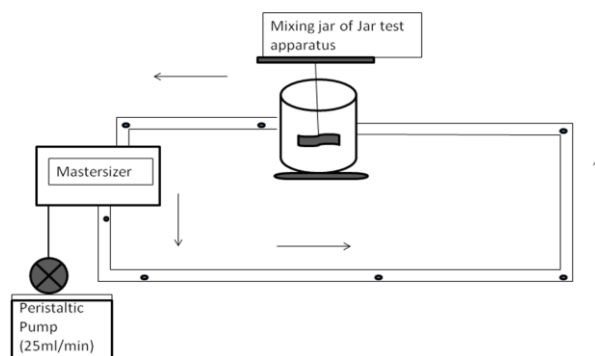Same procedure is used to measure the floc size and fractal dimension of clay flocs.

Fig. 1. Experimental set up for floc size and fractal dimension measurement.

III. RESULTS AND DISCUSSIONS

A. Dose Optimization

Alum dose required for the maximum removal of humic

acid and clay was determined by coagulant dose optimization tests. Coagulant dose optimization tests included coagulation, flocculation and settling process. The maximum humic acid removal was achieved for the alum dose of 70 mg/L approximately which corresponded to pH 5.5 [14]. Fig. 2 showed the removal of humic acid from synthetic feed water as a function of alum dose variations.

The turbidity of synthetic feed water of kaoline was 30-35 NTU. Fig. 3 showed the turbidity removal from synthetic clay solution as a function of alum dose. At alum dose of 5 to 5.5 mg/L maximum turbidity removal was achieved. Therefore 5.5 mg/L alum was selected as the optimum coagulant dose for synthetic feed water of kaoline.

TABLE I: COAGULATION AND FLOCCULATION CONDITIONS AND FLOC CHARACTERISTICS FORMED BY THESE CONDITIONS

Synthetic soln.	Conc. of soln.	Coagulation		Flocculation	Floc characteristics	
		Alum dose, mg/L	pH	Mixing rate, G	Floc size[a], µm	Fractal dimension[b], D_f
Humic acid	30 mg/L	70	5.5	42	303	2.667
Clay	33.4 NTU	5.5	7.5	42	125	2.149

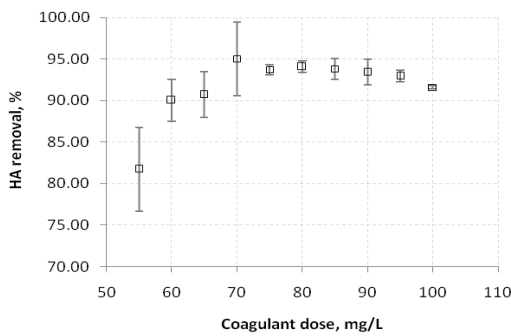[a, b] At the end of flocculation process

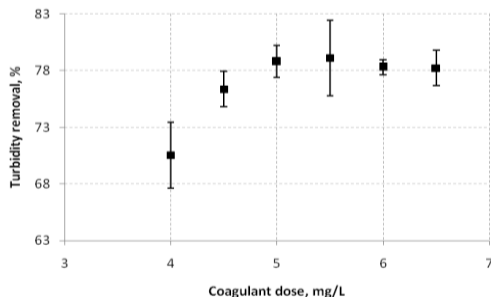Fig. 2. Humic acid percent removal as a function of alum coagulant dose.

Fig. 3. Turbidity removal as a function of alum coagulant dose.

B. Floc Size Distribution

Floc size is one of the important floc characteristic that directly affects removal of solids from water by settling and indirectly the efficiency of filtration process. Average diameter and percent changes in floc volume of humic acid flocs as a function of flocculation time are shown in Fig. 2. These flocs are prepared at a G value of 42 s^{-1}, alum dose 70 mg/L and pH of 5.5. The maximum floc size of humic acid flocs was ~303 µm that was achieved at 20 min of flocculation time.

Fig. 3 represents the volume average diameter of clay flocs formed at G value of 42 s^{-1}, 5.5 mg/L of alum dose and a pH of 7.5. During the flocculation stage flocs started to grow in size at 3 min of flocculation time and reached to maximum size ~125 µm at flocculation time of 20 min. Fig. 4 shows that 20 min of flocculation time gives the maximum volume percentage of larger flocs. In flocculation process aggregation and breakage of flocs occur simultaneously. Finally a steady-state achieved when floc growth overcomes the floc breakage [10].
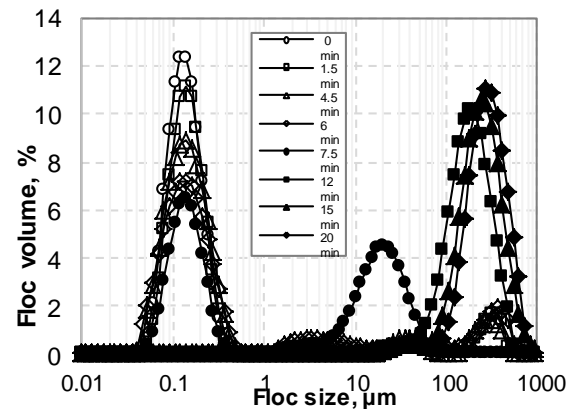

Fig. 4. Humic acid floc size distribution as a function of flocculation time. Conditions: G=42 s-1; 70 mg(alum)/L; pH 5.5.
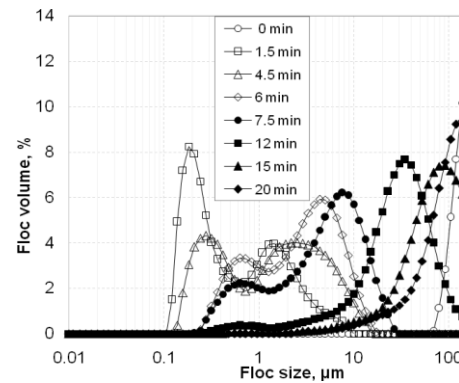

Fig. 5. Clay floc size distribution as a function of flocculation time. Conditions: G=42 s-1; 5.5 mg(alum)/L; pH 7.5.

C. Fractal Dimension Distribution

Fractal dimension distribution of humic acid and clay flocs as a function of flocculation time is shown in Fig. 5. These results were obtained from light scattering of humic acid and clay flocs using approach adopted by [13], [15]. As the flocculation of humic acid and clay flocs is dependent upon flocculation time, the fractal dimension of flocs also vary with flocculation time. At start of the flocculation time the flocs formed were fragile, porous and small in size. As the flocculation time increases flocs under the effect of shear force grow in size, compactness and density. The colloidal aggregates fit in the small pores in the flocs. As a result the flocs formed are more solid, tightly packed and having higher fractal dimensions [16].

Fig. 6 shows that fractal dimension of humic acids flocs is higher than those of clay flocs at their respective optimum coagulant doses. The possible reason for the lower fractal dimension of clay flocs is the coagulation conditions on which the flocs are produced. In clay coagulation/flocculation the dominant phenomenon was sweep flocculation. So the flocs produced were relatively weak and exhibited low fractal dimensions. Whereas humic acid flocs produced were developed under adsorption and charge neutralization conditions. For charge neutralization, the suspended particles go through several collisions and attachment cycles before stabilization. As a result, the humic acid flocs obtained were stronger and compact in shape and exhibit higher fractal dimensions.
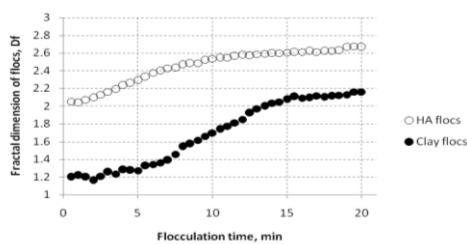

Fig. 6. Fractal dimension distribution of humic acid (HA) and clay flocs as a function of flocculation time.

IV. CONCLUSIONS

Two synthetic feed suspensions were prepared to study the effect of coagulation conditions on humic acid and clay floc characteristics. Aluminum sulfate was used for the coagulation/flocculation of both suspensions. Optimum coagulant dose was measured for both synthetic feed suspensions using jar test apparatus. The mixing speed and time was same for both synthetic feed suspensions. Somehow the pH and coagulant dose were different for the two different synthetic feed suspensions. Floc growth in size with the flocculation time was observed in both suspensions using small angle light scattering (SALS) technique. For both humic acid and clay flocs the floc size produced was maximum at the end of flocculation process. Fractal dimensions of humic acid and clay flocs were also increased with the flocculation time under the effect of shear force applied to them in flocculation. The fractal dimensions of humic acid flocs were higher than the fractal dimensions of clay flocs. The reason for this difference is coagulation mechanism of these two flocs. As in case of humic acid charge neutralization was the reason for flocculation while sweep flocculation was found to be dominant in case of clay flocs. As a result the humic acid flocs were more strong and compact when compared with the clay flocs. These results can be applied to field conditions to see the effect of floc size and fractal dimension on membrane fouling.

REFERENCES

[1] Z. Khan and R. Farooqi, "Roughing filtration as an effective pretreatment system for high turbidity water," *Water Science & Technology*, vol. 64, pp. 1419-1427, Oct. 2011.
[2] P. MacCarthy, *Aquatic Humic Substances: Influence of Fate and Treatment of Pollutants*, Advances in Chemistry Series 219, American Chemical Society, Washington, DC, 1989.
[3] S. Wang and Z. H. Zhu, "Humic acid adsorption on fly ash and its derived unburned carbon," *Journal of. Colloid & Interface Science*, vol. 315, pp. 41-46, June 2007.
[4] Y. Wang, B. Y. Gao, X. M. Xu, and W. Y. Xu, "The effect of total hardness and ionic strength on the coagulation performance and kinetics of aluminum salts to remove humic acid," *Chemical Engineering Journal,* vol. 160, pp. 150-156, May 2010.
[5] R. Fabris, E. K. Lee, C. W. K. Chow, V. Chen, and M. Drikas, "Pre-treatment to reduce fouling of low pressure micro-filtration (MF) membranes," *Journal of Membrane Science*, vol. 289, pp. 231-240, Feb. 2007.
[6] T. Li, Z. Zhu, D. Wang, C. Yao, and H. Tang, "Characterization of floc size, strength and structure under various coagulation mechanisms," *Powder Technology*, vol. 168, pp. 104-110, Oct. 2006.
[7] M. H. Cho, C. H. Lee, and S. Lee, "Influence of floc structure on membrane permeability in the coagulation-MF process," *Water Science & Technology*, vol. 51, pp. 143-150, June 2005.
[8] T. Serra, J. Colomer, and B. E. Logan, "Efficiency of different shear devices on flocculation," *Water Research,* vol. 42, pp. 1113-1121, Feb. 2008.
[9] D. H. Bache, E. Rasool, D. Moffat, and F. J. McGilligan, "On the strength and character of alumino-humic flocs," *Water Science and Technology*, vol. 40, pp. 81-88, Jan. 1999.
[10] P. Jarvis, B. Jefferson, J. Gregory, and S. A. Parsons, "A review of floc strength and breakage," *Water Research*, vol. 39, pp. 3121-3137 Sep. 2005.
[11] G. C. Bushell, R. Amal, and J. A. Raper, "The effect of a bimodal primary particle size distribution on scattering from hematite aggregates," *Physica A: Statistical Mechanics and its Applications*, vol. 233, no. 3-4, pp. 859-866, Dec. 1996.
[12] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, "Universality in colloid aggregation," *Nature*, vol. 339, pp. 360-362, June 1989.
[13] T. D. Waite, "Measurement and implications of floc structure in water and wastewater treatment," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 151, pp. 27-41, June 1999.
[14] X. Zhan, B. Gao, Y. Wang, and Q. Yue, "Influence of velocity gradient on aluminum and iron floc property for NOM removal from organic matter surface water by coagulation," *Chemical Engineering Journal*, vol. 166, pp. 116-121, Jan. 2011.
[15] G. Bushell and R. Amal, "Measurement of fractal aggregates of polydisperse particles using small angle light scattering," *Journal of Colloid and Interface Science*, vol. 221, vol. 186-194, Jan. 2000.
[16] D. Wang, R. Wu, Y. Jiang, and C. W. K. Chow, "Characterization of floc structure and strength: Role of changing shear rates under various coagulation mechanism," *Colloids and Surfaces A: Physicochemical Engineering Aspects*, vol. 379, pp. 36-42, Apr. 2011.

Hira Amjad was born in October 10, 1985 at District Layyah, Punjab, Pakistan. She has done her undergrad from the Department of Zoology, University of the Punjab, Lahore in 2007 and completed her MS environmental engineering from Institute of Environmental Sciences and Engineering (IESE), National University of Sciences and Technology (NUST), Islamabad, Pakistan in 2009. She is currently doing her PhD in environmental engineering from the same institute.

She provided her services as a consultant in a private organization named "Green development". She taught an engineering course in National University of Sciences and Technology titled "Water Supply and Wastewater Engineering". She published some articles.

Hira Amjad has got a Mega S&T scholarship from National University of Sciences and Technology for her MS leading to PhD study. She was also awarded by International Research Support Initiative Program (IRSIP) scholarship from HEC for her PhD foreign research work.