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Morphological characteristics and fractal approach of the flocs obtained from the natural organic matter extracts of water of the Keddara dam (Algeria)

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Abstract

A technique of analysis of images coupled with a data processing system using VISILOG software was used to determine the morphological characteristics of flocs obtained in natural organic matter (NOM) extracted from the waters of Keddara dam (supplying partially Algiers city, Algeria) and from synthetic fulvic acids. Slower sedimentation speeds (≈ 0.7 mm.s^{-1}) as well as the small effective volumic masses (≈ 3 kg.m^{-3}) of the flocs of NOM extracts from Keddara dam show poor sedimentation capacity. The fractal approach, involving natural extracts, showed that fractal dimensions obtained from two proposed relations are close (D_{f2}= 1.55–1.51 and D_{f3} = 1.99–1.91). Results reveal that, from an applied point of view, in spite of the optimization of the conditions of coagulation–flocculation, the NOM of Keddara dam can partially remove the advantage of optimisation.

Keywords: NOM; Flocculation; Fractal approach; Dam water

1. Introduction

Drinking water for the city of Algiers is partly supplied by the drinking water factory of Boudouaou supplied from the Keddara dam. The results of the data processing sequence show that in spite of the treatment carried out, the percentages of total organic carbon (COT) and organohalogen compound (AOX) remain important.

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This work deals in its first phase with the extraction and the fractionation of the natural organic matter (NOM) of water of the Keddara dam. The implementation of adsorption on macroporous resins XAD-8 and XAD-4 in series made it possible to split the organic matter into humic acid (11.4%), fulvic acid (33.9%) and hydrophilic acid (19.1%), for a total extraction yield of 64.4%. There is prevalence of hydrophilic acids (55%) compared to hydrophobic acids (45%) [1,2]. The characterizations carried out showed that the extracts obtained had a relatively weak aromaticity and molecular masses.

The analysis by pyrolysis CG/SM showed that the extracted fractions possess both aliphatic and aromatic character. In the humic acid structure proteins prevail, with a higher polyhydroxyaromatic (PHA) content. Fulvic acid, with the same percentage of PHA, is richer in polysaccharides. Lastly, hydrophilic acid, which is low in PHA, presents more important proportions of aromatic species and aminosaccharides [1,2].

The study with the jar test made it possible to show that humic and fulvic acids represent the fractions that coagulate and flocculate in the presence of aluminium. The abatement close to 40% in COT is primarily due to a relatively low absorbance of the extracts of the Keddara dam [3].

This paper will outline the performance of the various morphological parameters (diameter, factor of form, surface, perimeter) of flocs formed in optimum conditions for coagulation–flocculation. Morphological experiments of characterization of the flocs were carried out with flocs formed in an installation made up of a coagulation–flocculation reactor of the Actiflo® type. A column of decantation was directly connected to the flocculator. A technique of image analysis coupled to a data processing system using VISILOG 5.2 software was used. The sedimentation test as well as the density of the flocs was determined in order to judge the aptitude of the flocs for sedimentation. The fractal dimension of the aggregates was deduced.

2. Experiment

2.1. Experimental system

The morphological experiments for characterization of the flocs were carried out in an installation which was designed for this purpose (Fig. 1). It is made up of a reactor for coagulation–flocculation of the Actiflo® type whose dimensions are standardized so as to be able to reach the different hydrodynamic sizes (dissipated power, average gradient speed). A column for decantation is

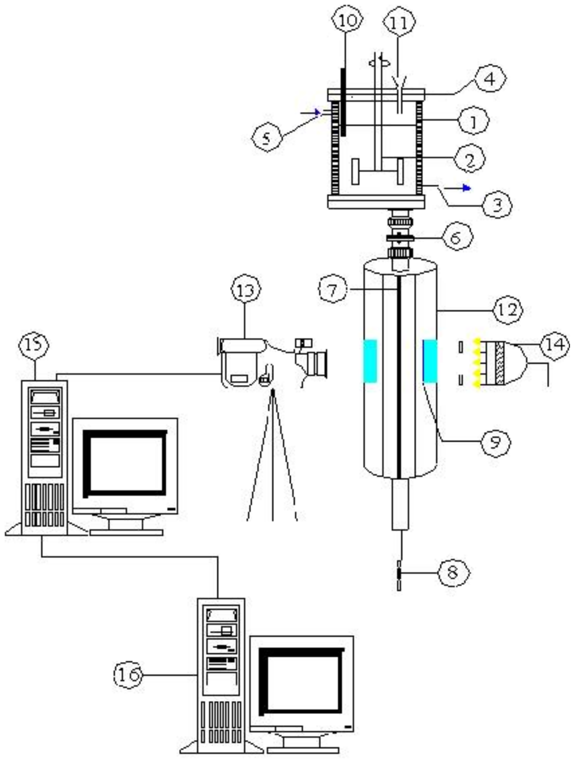

Fig. 1. Experimental device for measurement of floc dimensions by image analysis.1) Reactor with double envelopes; 2) Agitation system; 3) Thermostated water exit; 4) Joint; 5) Water in at 20°C; 6) Sluice; 7) Wire of fishing (0.33 mm); 8) Mohr clip; 9) Dioptre; 10) pH meter; 11) Reactive input; 12) Thermostated cell of decantation; 13) Camera; 14) Lighting (optical fibre); 15) Computer (image acquisition station); 16) Computer (image treatment station).

directly connected to the floculator thanks by a pipe equipped with a valve. A diopter is installed in this column, which is 400 mm long and with internal diameter of 50 mm, to allow the observation of the flocs using a video camera. The images of the flocs are captured by a Sony colour camera DXC 930P 3CCD, connected to a Nikon microscope SMZ-U. These images are visualized via a chart of frame grabbing Matrox Meteor, on the station of acquisition, using Visilog 5.2 (Noesis) software. Image acquisitions are done in situ, by placing the microscope vertical of the column of decantation. The lighting of the decantation cell is carried out by optical fibre. During the tests carried out with natural organic matter extracts the image of the flocs was not sufficiently contrasted and this required the use of a laser source to increase the contrast. The calibration was carried out by fishing wire with a diameter of 330 µm.

The image processing was thus carried out using Visilog 5.2 software. A program in C^{++} was developed for the image processing. The last stage of the image processing was the analysis of flocs identified on the treated image. The direct measurement of following characteristics of the flocs was made:

1. The surface of the projected surface of the floc (S),
2. The perimeter of the projected image of the floc (P),
3. The equivalent diameter of the floc (d_f):

$$d_f = \left(\frac{4 \times S}{\pi}\right)^{\frac{1}{2}} \tag{1}$$

4. The factor of form (circularity) was defined by the relation:

$$\mathrm{FF} = \frac{4\pi \times S}{P^2} \tag{2}$$

This factor measure the variation was compared to the circle.

2.2. Experimental procedure

The Actiflo® pilot was filled with 2.65 L of water to be treated and the sample was mixed at high speed (150 rpm) for 1 min, with an amount of aluminium sulphate predetermined beforehand by the jar test. The pH was maintained constant by adding a base (0.1 N NaOH) or an acid (0.1 N HCl). This stage was followed by slow agitation (flocculation) carried out at 60 rpm for 20 min. At the end of this period, the valve connecting the Actiflo® to the decantation column was opened. The flocs in the Actiflo® reactor formed a deposit in the decantation column. Well contrasted images of the flocs were taken. Four experiments of the image analysis were carried out on the flocs obtained from:

- Fractions extracted from water of the Keddara dam (fulvic acids and hydrophilic acids). The concentrations of fulvic and hydrophilic acids were 9–10 mg/L corresponding to COT = 4.5 mg.L^{-1} and pH range between 7 and 7.5. The concentration of aluminium sulphate was 1 mg of Al/mg of COT.
- Commercial fulvic acids with pH = 5 and pH = 7 with a concentration of 10 mg/L corresponding to COT = 4.65 mg.L^{-1}. With the pH equal to 5, the concentration of aluminium sulphate was 0.346 mg of Al/mg of COT. When the pH was equal to 7, the concentration of aluminium sulphate was 1.05 mg of Al/mg of COT.

3. Results

3.1. Dimensional and morphological parameters

The results obtained for the natural extracts of Keddara and the commercial acids fulvic are represented in Table 1.

Flocs obtained for AF and AHy's natural extracts, for the same pH = 7 and the same concentration of Al equal to 1 mg from COT's, presented dimensional characteristics which were very close. The diameter of the flocs of AF was slightly big-

Table 1
Summary of the dimensional and morphological parameters of the four tests

Extracts used	Surface (mm^2)	Perimeter (mm)	Diameter (mm)	Factor of form
Natural fulvic acid	$m = 0.75$	$m = 8.55$	$m = 0.93$	$m = 0.14$
	$\sigma = 0.57$	$\sigma = 3.85$	$\sigma = 0.34$	$\sigma = 0.083$
Natural hydrophilic acid	$m = 0.66$	$m = 8.06$	$m = 0.86$	$m = 0.12$
	$\sigma = 0.389$	$\sigma = 2.89$	$\sigma = 0.27$	$\sigma = 0.04$
Fulvic acid pH=5 (Canada)	$m = 0.05$	$m = 1.33$	$m = 0.22$	$m = 0.34$
	$\sigma = 0.06$	$\sigma = 0.946$	$\sigma = 0.108$	$\sigma = 0.05$
Fulvic acid pH=7 (Canada)	$m = 0.37$	$m = 4.32$	$m = 0.52$	$m = 0.21$
	$\sigma = 0.47$	$\sigma = 4.00$	$\sigma = 0.383$	$\sigma = 0.101$

m and σ are respectively the average and the standard deviation of the sample

ger than that of the AHy. They were respectively 930 μm and 860 μm. The values of the factors of form (FF) were slightly different (0.14 for the AF and 0.12 for the AHy).

Flocs obtained for commercial fulvic acids at pH = 5 (concentration of 20 mg/L of Al) and at pH = 7 (concentration of 60 mg/L of Al) presented different dimensional characteristics. The diameter of the AF flocs at pH = 7 was bigger than that of the AF at pH = 5. They were respectively 520 μm and 220 μm. The FF were superior to those obtained for the natural extracts. One can notice that FF for AF at pH = 5 was the highest (0.34) but remained far from spherical (Table 1).

The values obtained for the FF were lower than 0.34. This value is smaller than that used by Tambo et al. [4] (FF = 0.8) to represent the non-sphericity of flocs and that determined by Kellil [5] (FF = 0.6) during experiments with kaolinite and the sulphate of aluminium.

Our values are comparable to those obtained by Franscesci [6] (FF = 0.24) during attempts on a clay suspension of bentonite and to those of Gorcyca et al. [7] (FF = 0.26–0.36) who worked on mineral suspensions (illite, montmorillonite, and calcite) coagulated with the sulphate of aluminium.

All these authors used the same definition for the FF [Eq. (2)] except for Tambo et al. [4] who considered FF equal to 0.8 without justifying this value.

These values of FF indicate that the flocs have a stretched out shape and are not close the spherical value which is equal to 1. This departure from the sphericity was confirmed recently by Chakraborti [8] during experiments with a mineral suspension (montmorillonite) flocculated in the sulphate of aluminium.

3.2. Determination of floc sedimentation speed

Sedimentation speed was calculated from the distance crossed by a floc during a defined period of time. The Visilog software allows five images of flocs obtained by coagulation and flocculation to be taken spaced out by an interval of time Δt. In our case $\Delta t = 300$ ms.

Fig. 2 shows the sedimentation speed according to the equivalent diameter of the floc on a log–log scale for the experiment with natural fulvic acid.

The speed of fall of aggregates is very often expressed with an empirical law of the shape:

$$V = k_s \times d^{n_s} \qquad (3)$$

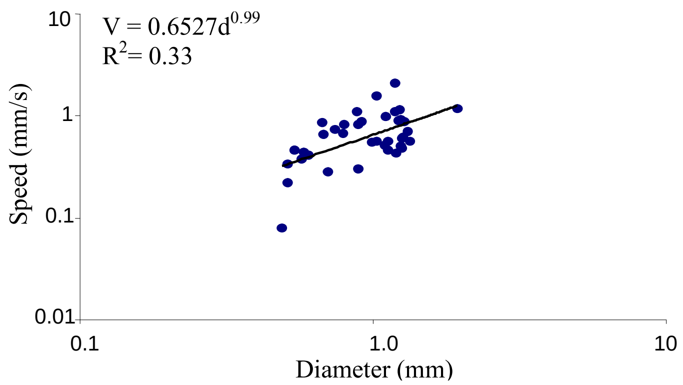

Fig. 2. Sedimentation speed vs. flocs equivalent diameter (natural fulvic acid).

Fig. 2 also shows the correlation of the data with this equation.

The empirical law of the shape relating the sedimentation speed with the diameter of the floc is shown in Table 2 for all types of samples studied. The value of n (see Eq. (3) and Table 2) is close to 1 for Keddara natural extracts and a value close to 0.5 for commercial fulvic acids.

Several works indicate that the sedimentation speed of flocs does not increase according to the square of the diameter as predicted by Stokes law, and that aggregates fall slower than predicted by this law [9]. This is probably due to the porosity of the aggregates and to the possibility of drainage through the floc.

3.3. Volumetric mass determination

The effective volumetric mass was determined by using the modified Stokes law, introducing a factor of sphericity equal to 0.8 as recommended by Tambo et al. [4]. The mean values of the effective volumetric masses were calculated and they are represented in Table 3. Fig. 3 shows the variation of the effective volumetric masses of the floc with its diameter on the log–log scale. The diameter of the floc increases when the effective volumetric mass decreases. According to Tambo et al. [4] the relationship between the diameter and the volumetric mass can be expressed by the following equation:

$$\rho_e = \rho_f - \rho_w = \frac{a}{d_f^{K_p}}$$

or (4)

$$\log \rho_e = \log \rho a - K_p \log d_f$$

with ρ_e — effective volumetric mass (kg.m^{-3}), d_f — floc diameter (m), a and K_p are constants de-

Table 2
Average speed and equations for studied samples

	Natural fulvic acid	Natural hydrophilic acid	Commercial fulvic acid (pH 5)	Commercial fulvic acid (pH 7)
Average speed (mm/s)	0.706	0.705	0.450	2.278
Equation	$V = 0.653 \times d^{0.99}$	$V = 0.707 \times d^{0.91}$	$V = 1.209 \times d^{0.60}$	$V = 0.466 \times d^{0.40}$

Table 3
Mean volumetric mass, equations and coefficients of correlation for four extracts

	Acid			
	Natural fulvic	Hydrophilic	Commercial fulvic	
			pH 5	pH 7
ρ_e (kg.m^{-3})	2.857	3.199	79.61	21.934
Equation	$\rho = 0.0021 \times d^{-1.01}$	$\rho = 0.0013 \times d^{-1.094}$	$\rho = 0.0003 \times d^{-1.40}$	$\rho = 0.0002 \times d^{-1.55}$
R^2	0.34	0.39	0.73	0.76

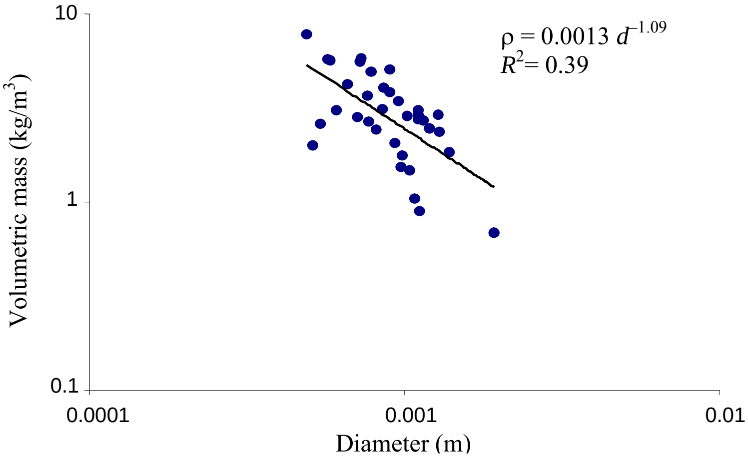

Fig. 3. Variation of the effective volumetric mass with the equivalent diameter (natural hydrophilic acid).

pending on aluminium mass introduced/colloid mass [4].

Fig. 3 gives the variation of the effective volumetric mass according to the diameter in the log–log scale for the experiments with natural hydrophilic acid. The equations for other types of samples studied as well as the coefficients of correlation are summarized in Table 3.

The effective volumetric masses of fulvic and hydrophilic acids are very close (2.857 and 3.199 kg/m^3) and they are also very weak indicating that the obtained flocs had a density close to that of water.

Commercial fulvic acids have larger effective volumetric masses (79.61 kg/m^3 at pH = 5 and 21.93 kg/m^3 at pH = 7). Besides, AF and AHy's natural extracts are characterized by large diameters (860–930 µm) but they have smaller sedimentation speed as well as smaller effective volumetric masses. This is contrary to floc diameters of commercial fulvic acids which are smaller (220–520 µm) but have larger sedimentation speeds and volumetric masses. The volumetric masses vary inversely with diameters. The correlations coefficients are better for commercial fulvic acids.

3.4. Fractal dimension determination

We determined the fractal dimensions by using two types of relations which apply to a population of aggregates. One supposes that the principle of auto-similarity is verified.

The relation between the size of flocs and their thrown surface [10,11] is:

$$S = d_p^{D_{f2}} \quad (5)$$

log S is plotted against log d assuming a constant value of the fractal dimension D_{f2} (Fig. 4). The diameter used during our experiments was in fact obtained by considering a circular floc. Then $d_p = P_m / \Pi$, where d_p is the diameter obtained from the perimeter and P_m is the perimeter of the thrown floc measured with the analyzer of images. In that case, the maximum value of D_{f2} is 2.

The relationship of the fractal dimension of formed aggregates is given by:

$$D_{f3} = 3 - K_p \quad (6)$$

By representing the effective volumetric mass according to the diameter on a plan log–log scale, the diameter d_f used here corresponds to the diameter of the sphere which has the same thrown surface as the floc.

Values obtained by the two relationships as well as FF are obtained with the values of K_p from Table 2 and the relationship $D_{f3} = 3 - K_p$.

Fractal dimensions obtained by two relationships follow the same logic. They are very close for the natural extracts (1.55–1.51 and 1.99–1.91)

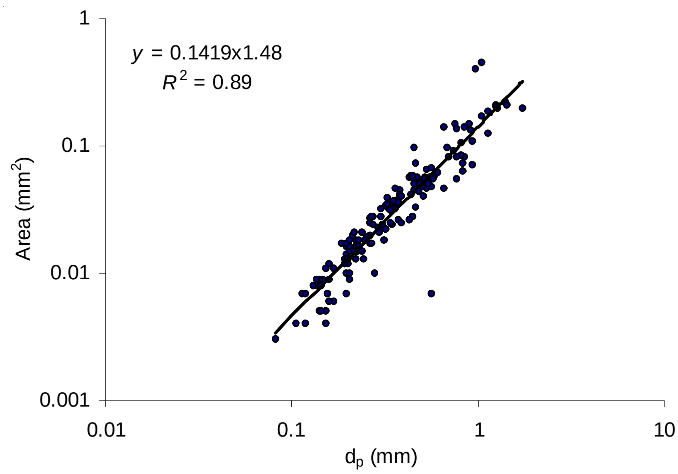

Fig. 4. Diameter d_p vs. floc area.

Table 4
Fractal dimensions for four samples

	Acid			
	Natural fulvic	Hydrophilic	Commercial fulvic	
			pH 5	pH 7
D_{f2}	1.55	1.51	1.48	1.33
D_{f3}	1.99	1.91	1.60	1.45
FF	0.14	0.12	0.34	0.21

but slightly different for commercial fulvic acids at the two different pH values (1.49–1.33 and 1.60–1.45).

In the ideal case, if the projection of the floc was circular, the value of D_{f2} would be equal to 2, which is not case for our samples.

For the natural extracts, the values of D_{f2} very closely reflect the FF, while departing from the sphericity. They show, for fulvic acids and hydrophilic extracted from Keddara's dam, that there is no important difference in the structure of the flocs obtained.

With commercial fulvic acids, the differences obtained for the fractal dimension are in good agreement with the factors of shape. Indeed, small values obtained at pH = 5 (D_{f2}= 1.33) correspond to wide flocs having an irregular structure entailing weak factors of shape. At pH = 7, D_{f2} has a higher value entailing a better structure of the floc corresponding to a higher FF. Nevertheless, in every case our FFs are relatively departing from the sphericity.

A decrease of the fractal dimension can be attributed to the increase of the pH as shown by Vilgé-Ritter et al. [12] and Chakraborti et al. [8].

The results we obtained show that the volumetric masses obtained at pH = 7 are small (3 kg/m^3 for the natural extracts and 22 kg/m^3 for the commercial AF). This result is important as most of the researchers [12] have obtained fractal dimension from flocs by diffusion of the radiation, obtained values of D_f which are high (> 2). They concluded that the formed flocs are dense without having measured the density.

The measurement technique with sedimentation that we used show the opposite result because of the flocs which are voluminous, porous and established essentially with hydroxide of aluminium for the values of pH used.

4. Conclusions

This study concerns the morphological characteristics of flocs obtained from the extracts of fulvic acids and from hydrophilic acids of the waters of the Keddara dam. This study showed that two extracts present very close dimensional characteristics. The diameter of the flocs of fulvic acids was 930 µm while that of the hydrophilic acids was 860 µm. Their factors of shape are appreciably similar (0.15 and 0.12).

This study also confirmed weak dejections obtained in coagulation–flocculation for Keddara extracts. Indeed, small sedimentation speeds (≈ 0.7 mm.s^{-1}) as well as small effective volumetric masses (≈ 3 kg.m^{-3}) indicate a poor capacity for sedimentation of flocs (extracts of fulvic and hydrophilic acids) of the Keddara dam.

Flocs obtained from commercial fulvic acids at pH = 5 and 7 present different dimensional characteristics.

Indeed, at pH = 7 flocs are characterized by a large diameter (520 µm), a large sedimentation speed equal to 2.28 mm.s^{-1} and a relatively small volumetric mass (21.93 kg.m^{-3}) compared with flocs formed at pH = 5 where the volumetric mass was larger (79.61 kg.m^{-3}), but the diameter was smaller (220 µm) and the sedimentation speed was lower (0.450 mm.s^{-1}).

The fractal analysis involving natural extracts showed that the fractal dimensions obtained from two proposed relationships were very close (D_{f2} = 1.55–1.51 and D_{f3} = 1.99–1.91). This is also reflected in the factors of shape being very close but departing from the sphericity. These dimensions show that there was no significant difference in the structure of flocs obtained from fulvic acids and hydrophilic acids extracted from the Keddara dam.

The fractal dimensions obtained were slightly different for commercial fulvic acids at pH = 5 and 7 respectively (1.49–1.33 and 1.60–1.45). These differences are consistent with the factors of shape. Indeed, small D_f values obtained at pH 7 correspond to wide flocs having a loose and irregular structure entailing weak factors of shape. At pH = 5, the highest value of D_f was obtained from the best structure of the floc corresponding to a higher factor of shape. However, in every case, the obtained factors of shape were relatively weak and departing from the sphericity.

There was a decrease of the fractal dimension with the increase in the pH using commercial fulvic acids. This allowed us to form a hypothesis on the mechanisms contributing to the formation of the floc. These are complexation and precipitation mechanisms.

The results show that from an applied point of view, in spite of the optimization of the conditions of coagulation–flocculation, NOM of the Keddara dam can be partially eliminated at the level of the Boudouaou drinking water factory.

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