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FRACTAL CHARACTERISTICS OF POST-COAGULATION SLUDGE FROM SEWAGE

Aggregates obtained as a result of chemical coagulation of municipal sewage were studied. Fractal dimension D ranging from 1.71 to 1.92 of 1300 measured aggregates at mean determination coefficient r^2 = 0.949 was calculated. An effect of the type of coagulant, dose and "age" of the aggregates on D was examined and explained. Fractal dimension has appeared a powerful tool in the investigation of the structure and composition of sludge aggregates. This tool was sensitive enough to indicate even such subtle changes as sludge ageing or coagulant overdosing.

1. INTRODUCTION

The methods of sewage treatment and sludge utilization should be continuously improved. This improvement by means of more and more popular inorganic coagulants increases the amount of sewage sludge, especially at municipal sewage treatment plants. Sludge characteristics are important for optimizing a sewage treatment. The use of fractal geometry [1] for describing aggregates/flocs may provide information (unavailable in the case of other methods) about the morphological properties of sludge and the mechanism of aggregation. Fractal structure of aggregates was observed in numerous experiments [2] as well as during computer simulation. Computer technology allowed us also to simulate aggregation, which resulted in developing several models of this process. The first one, proposed by Witten and Sander, is the so-called particle–cluster model. Aggregation is here described as a series of random collection of particles into expanding aggregates. The process starts with a single immovable particle, which is joined by a moving particle to form an irreversible combination. Then there appear other particles, etc. In the simulation conducted in three-dimensional space, the value D of the aggregate obtained was 2.5. Another model of aggregation formulated in-

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dependently by Meakin and by Kolb is referred to as the cluster–cluster model. According to this model identical particles are evenly distributed in space and move at random. When two particles come into contact, they start to move together. Such particles are bonded irreversibly and maintain their orientation. Dimer may stick to another dimmer or a single particle. The product of such aggregation is characterized by more open structure, with D = 1.75 in three-dimensional space.

This paper presents the fractal characteristics of sludge aggregates obtained as a result of chemical coagulation of municipal sewage.

2. METHODS

The experiments were conducted on clarified samples of municipal sewage collected at the municipal sewage treatment plant in Olsztyn. The main parameters of the sewage were as follows: pH, 8.0; phosphates, 1.6 g P/m^3 and COD, 180 g/m^3. At the laboratory they were enriched with phosphorus in the form of a solution of KH_2PO_4.

A dose of 4–16 mg of aluminum or iron from $FeCl_3$, $Fe_2(SO_4)_3$, PAC and $Al_2(SO_4)_3$ per 1 dm^3 of sewage was used for the coagulation [3]. A standard coagulation procedure was applied, i.e., 1 min of rapid stirring (ca. 200 rpm), 15 min of slow stirring (ca. 10 rpm) and 15 min of sedimentation. pH and phosphate ion concentration were determined in the solution, above the sludge. Then the fractal dimensions of post-coagulation sludge were determined. The sample of ca 2 cm^3 of sludge was taken with a pipette and put into a column filled with distilled water. Floc settling was photographed in a dark-room. The settling flocs were illuminated with a photo-flash-lamp controlled by an electronic system ensuring flashes every 3 s. With an opened shutter, the image of 10 flashes was caught in each frame. The time between successive shots was 2–5 min, which allowed us to "grasp" flocs characterized by various dimensions and different rates of sedimentation. There were on average 15 shots per experiment. The negative was magnified by means of a projector Diapol. The diameter R and the velocity V of a floc settling were measured on the screen. The fractal dimension D of aggregates/flocs was determined using Stoke's law:

- $d = V/R^2(V9\eta/2g)$, therefore $d \sim V/R^2$,
- for fractal objects $M \sim R^D$,
- $M = Vd$ where $V = 4/3\ (\pi R^3)$, provided that the flock is spherical,
- then $4/3(\pi R^3 d) \sim R^D$, hence $d \sim R^{D-3}$ and $\log d \sim (D-3)\log R$,
- $(D-3)$ means the slope of lg–lg line,
- therefore $D = 3 + \Delta\log d/\Delta\log R$,

where: V – velocity of settling flocs, d – real density of a floc, R – aggregate size, M – object mass, D – fractal dimension.

3. RESULTS AND DISCUSSION

One of the most important indicators of municipal sewage pollution is the concentration of phosphorous compounds. Removal of phosphates from sewage by biological methods has not been fully investigated yet. Such process is unstable and susceptible to disturbances. Therefore, to increase the effectiveness of phosphate removal, biological methods are combined with chemical ones, i.e., chemical coagulation, enabling the formation of the desired kind of sludge. This process is unstable and susceptible to disturbances. Therefore, in order to increase the effectiveness of phosphate removal, biological methods are combined with chemical ones. Phosphate removal from sewage may take place either as a result of precipitation, according to the reaction: $Me^{3+} + H_nPO_4^{n-3} \rightarrow MePO_4 + nH^+$, where Me is Al or Fe, or as a result of classical coagulation, where the phases of destabilization and flocculation can be distinguished. Destabilization is caused by ions and colloidal hydroxides formed due to coagulant hydrolysis, which is described by a general formula $Me_n(OH)_y^{3n-y}$. Phosphate adsorption on metal hydroxide flocs dominates during flocculation. Chemical composition of settling flocs proves that they are mixed hydroxide-phosphate forms of metals characterized by amorphous structure. The degree of sewage purification and sludge structure depend on coagulation conditions, i.e., the kind of coagulant, its dose, pH, etc. The results of previous investigations [4] indicate that determination of the fractal dimension of aggregates/flocs can provide information about changes in the conditions of coagulation–flocculation.

Average fractal dimension D of flocs was determined by measuring the parameters of ca. 1 300 of them. Their sizes R and rates of sedimentation V varied from 0.04 to 3.03 mm and from 0.03 to 1.79 mm/s, respectively. The average coefficient of determination, indicating the suitability of the mathematical model used for describing the experimental data, was $r^2 = 0.939$.

Figure 1 presents the characteristics of aggregates/flocs (including D) obtained as a result of municipal sewage coagulation with ferric salts. The graphs in figure 1 present:

a) the relationship $V = f(R)$,

b) $\log d = f(\log R)$,

c) the "distribution", i.e., percentage of aggregates of a given size in sludge.

The dependence $V = f(R)$ (upper graph) shows the rate of floc settling and its size. The values of the coefficient of determination for the relationship $V = aR + b$ were $r^2 = 0.454$ and 0.789, so they turned out to be much lower than for $\log d = f(\log R)$, where $r^2 = 0.955$ and 0.900. Anyway the values of $r^2 > 0.9$ may confirm a fractal nature of the aggregates investigated.

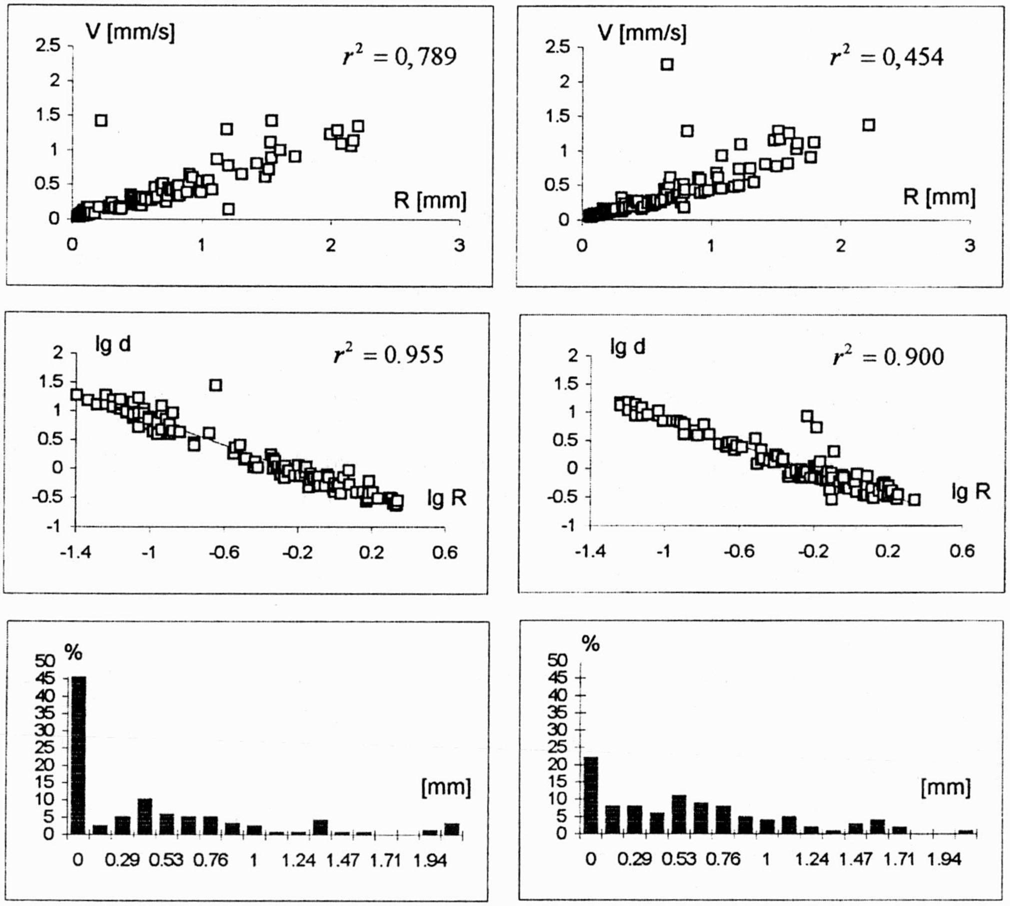

Fig. 1. Characteristics of aggregates obtained as a result of municipal sewage coagulation.
Left side: 16 mg/dm^3 $FeCl_3$, pH = 6.8, 124 aggregates, R = 0.04–2.21 mm, V = 0.03–1.34 mm/s.
Right side: 16 mg/dm^3 $Fe_2(SO_4)_3$, pH = 6.8, 104 aggregates, R = 0.06–2.21 mm, V = 0.05–1.37 mm/s

Table 1 presents the fractal dimensions of aggregates obtained as a result of municipal sewage coagulation by selected coagulants [5]. In the sewage being coagulated, the dose of iron equivalent to the dose of aluminum (1 mole of Fe ≈ 2 moles of Al) produced aggregates characterized by bigger fractal dimensions, since D_3 and $D_4 > D_1$ and D_2. However, the efficiency of P–PO_4 removal by ferric ions was lower than that by aluminum ions. As expected [6], "loose" and more "rugose" structure of "Al–OH–PO_4" aggregates (D_1 and D_2) enabled more effective P–PO_4 removal than more compact structure of "Fe–OH–PO_4" aggregates (D_3 and D_4). The results obtained are satisfactory taking into account purification of the liquid phase of coagulated sewage. On the other hand, the "loose" and "rugose" structures of aggregates (low values D) are responsible for unsatisfactory filling of aggregate spaces with the solid phase. This may cause certain problems in the process of dewatering of post-coagulation sludge found on presses, filters or in centrifuges. The determination of the optimum value of D seems very important for practical reasons. This kind of optimization allows us to combine and correlate the results of treatment of the sewage liquid phase with the quality of post-coagulation sludge [7].

Table 1

Selected parameters of municipal sewage coagulation ($[P–PO_4]_0 = 4.9$ mg/dm^3, $pH_0 = 8$)

Kind of coagulant	Al or Fe dose (mg/dm^3)	$P–PO_{4\,rem.}$ (%)	pH_f	D	r^2
PAC	8	94	7.0	$D_1 = 1.79$	0.978
$Al_2(SO_4)_3$	8	90	6.9	$D_2 = 1.80$	0.956
$FeCl_3$	16	88	6.8	$D_3 = 1.87$	0.956
$Fe_2(SO_4)_3$	16	87	6.8	$D_4 = 1.90$	0.900

Table 2

Effect of coagulant dose and "age" of flocs on the fractal dimension of sludge aggregates from municipal sewage

PAC/Al dose (mg/dm^3)	"Age" of sludge (h)	D	r^2	$P–PO_{4\,rem.}$ (%)
4	0	$D_5 = 1.71$	0.970	67
4	46	$D_6 = 1.84$	0.935	67
6	0	$D_7 = 1.79$	0.948	92
6	46	$D_8 = 1.92$	0.946	92
8	0	$D_9 = 1.80$	0.936	99
8	46	$D_{10} = 1.83$	0.907	99

Table 2 presents the fractal dimensions of aggregates, "fresh" and after 46 h. They were obtained as a result of municipal sewage coagulation with PAC (4–8 mg of Al/dm^3). A correlation was observed between the dose of a coagulant, the degree of sewage purification and the value D. A higher dose of the coagulant caused an increase in D, whose maximum value was 1.80 for 8 mg of Al/dm^3 of sewage. An increase in the aluminum dose would probably cause a decrease in D of the flocs obtained. A low value of the fractal size (D = 1.71) at a dose of 4 mg of Al/dm^3 of sewage may indicate an uncontrolled hydrolysis of PAC, including the formation of various polymeric aluminum forms, which do not determine the structure and shape of products [8].

As expected, the fractal dimensions of aggregates increased after 46 hours. This was connected with "sludge aging", which consists in ordered arrangement of the sludge structure. However, this process concerns mainly crystalline sludge. In the case of amorphous sludge, the process of "self-dewatering" (hydrostatic pressing out of water from post-coagulation sludge) may be observed. This process results in a higher share of potential solid phase of $Al\text{-}PO_4$ in aggregates reflected by higher *D*. This is consistent with previous investigations by SMOCZYŃSKI [9], in which "statistical, fresh" aggregates contained almost 20 times less of the solid phase than "old" ones.

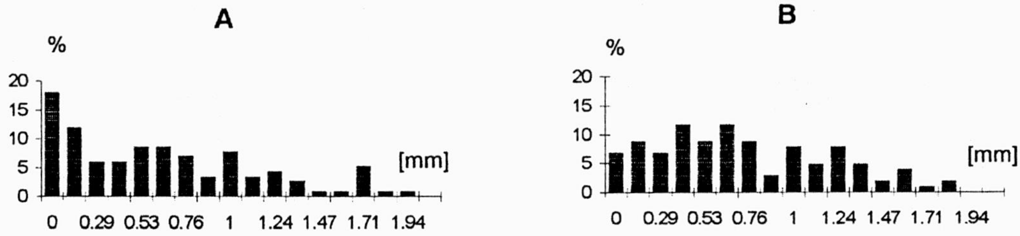

Fig. 2. Percentage of aggregates, depending on their actual dimensions;
A – "fresh" aggregates, $D = 1.71$; B – aggregates after 46 h, $D = 1.84$ (PAC, 4 mg Al/dm^3)

The distribution of dimensions of "fresh" aggregates differs from the distribution of their dimensions after 46 h (figure 2). It was found that the percentage of aggregates whose diameter ranged from 0 to 0.17 mm decreased with sludge aging and their fractal size increased. This seems to be a logical consequence of the process of aggregate aging (smaller and open clusters form bigger and more compact ones).

The process of aggregation was very slow. The first aggregates appeared after 5–6 minutes. In colloidal systems, particles usually must get through a repulsive barrier before they are systematically affected by short-range Van der Waals forces. According to the hypothesis proposed by JULLIEN and BOTET [10], this barrier makes that particles bounce many times before they stick. This can be connected with the lenghty process of aggregation. Therefore, under the conditions discussed and at low reagent concentration (within critical values), the "cluster–cluster" aggregation model seems to represent the reality better than the "particle–cluster" model. The most significant consequence of the "cluster–cluster" model is the fact that aggregates formed in this way are in most cases characterized by open structure, i.e. low values *D*. According to JULLIEN and BOTET [10], in "cluster–cluster" aggregation, with clusters of the same size, cluster (aggregate) interpenetration is at a much lower level than in the "particle–cluster" model, where small particles cannot interpenetrate into large clusters.

4. CONCLUSIONS

The application of fractal geometry in the description of coagulation, aggregation and flocculation, and the structure of post-coagulation aggregates/flocs is still considered innovative. Knowing the fractal dimensions *D* of sludge we can determine the degree of "loosing" and "rugosing" the objects studied and the degree of space filling with their irregular structure. It follows that the determination of *D* should be of great practical significance. Post-coagulation sludge characterized by low values *D* has loose and open structure, which means that it can "adsorb" large quantities of pollutants. On the other hand, sludge of high values *D*, with its compact structure, is easier to dewater, by e.g. pressurised filtration, in an expensive and technologically valid process.

1. Aggregates obtained during municipal sewage coagulation are characterized by fractal features and statistical self-similarity, i.e. each subunit of a given aggregate shows the same features as this aggregate.
2. The determination of the fractal dimension *D* enables a quantitative description of the structure of aggregates/flocs formed during coagulation.
3. The fractal dimension *D* depends on the dose and kind of coagulant as well as on the "age" of aggregates, so it can be a factor facilitating control of the process of purification.
4. The value *D* may also help to determine the mechanism of aggregation.

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FRAKTALNA CHARAKTERYSTYKA OSADÓW POKOAGULACYJNYCH ŚCIEKÓW KOMUNALNYCH

Badano agregaty otrzymane w wyniku chemicznej koagulacji ścieków komunalnych. Rozmiar fraktalny otrzymanych agregatów mieścił się w granicach D = 1,71–1,92 przy średnim współczynniku determinacji r^2 = 0,949. Rozmiar fraktalny okazał się ważnym kryterium oceny struktury osadu pokoagulacyjnego, zależnym od dawki, rodzaju koagulanta oraz „wieku" agregatów.