Analysis of sludge aggregates produced during electrocoagulation of model wastewater
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ABSTRACT
This paper presents the results of the study of sludge aggregates produced during electrocoagulation of model wastewater of a composition corresponding to the effluents from the cellulose and paper industry. Wastewater was electrocoagulated statically using aluminium electrodes with a current density of 31.25 A m\(^{-2}\) and 62.50 A m\(^{-2}\). In subsequent stages of the treatment, sludge flocs were collected, their size was studied and their floc settling velocity (30–520 μm s\(^{-1}\)) and fractal dimension (D) were determined. The values of D ranged from 1.53 to 1.95 and were directly proportional to the degree of wastewater treatment. Higher values of D were determined for sludge with lower water content (after 24 hours’ settling). Fractal dimension can therefore be used as an additional parameter of wastewater treatment control.

Key words | aggregates, electrocoagulation, fractal dimension, model wastewater

INTRODUCTION
The progress of the modern world and modern science creates the demand for advanced methods to evaluate the complexity of images around us. Fractal geometry, which provides new quantitative parameters in the form of fractal dimension, offers an excellent tool for such assessments. The term ‘fractal’ was first defined by Mandelbrot (1982). Fractals (based on the Latin word fractus, meaning ‘broken’ or ‘fractured’) denote self-similar objects, or such objects that cannot be described by traditional Euclidean geometry, and their essential feature is a fractal dimension of a non-integral value. It describes the complexity of objects, and is applied in various fields of science to analyse surface irregularities, including to describe active sludge flocs (Chu et al. 2004).

Individual atoms or molecules can combine to form clusters (micromolecules), and the process is known as aggregation. Aggregation has been widely observed in various fields of science and technology, including materials engineering or polymer chemistry. This phenomenon is also encountered in the process of wastewater treatment by electrocoagulation. This method has been widely described in the literature: particularly for the waste from the textile industry (Aoudj et al. 2010), cellulose and paper industry (Shankar et al. 2013), and oil suspensions (El-Naas et al. 2009). Electrocoagulation was also used in theoretical models (Chen et al. 2002).

For many researchers, electrocoagulation of wastewater constitutes a problem for theoretical discussions, process modelling, and studies of aggregates of the formed sediments (Harif & Adin 2007; Smoczyński et al. 2014). The sludge produced by coagulation or electrocoagulation needs to be adequately managed. Minimized amounts of obtained sediments are produced in, among others, the dewatering process carried out using mechanical and thermal means. However, these methods are very expensive. Composition of the sediments depends on the type of wastewater and applied treatment methods. The electrocoagulation method is an alternative for chemical coagulation because of, among others, the produced sediment. The applied electro-chemical treatment technologies yield up to 50% less of sediments than conventional coagulation methods (Barrera-Diaz et al. 2011). Electrocoagulation is also favoured by the fact that the sediment formed contains flocs, which have less bound water, are more stable and more easily separated by filtration compared with sediment from chemical coagulation.

For this reason, continuous research is needed to determine new aggregate floc parameters. The value of fractal dimension D, described in the present study, determined in an analysis of sludge flocs produced during electrolytic treatment of wastewater, can serve as such a parameter.
MATERIALS AND METHODS

The analysed sludge was produced during the electrocoagulation of model wastewater of a composition similar to that of effluents from the cellulose and paper industry. Due to the nature of its production technology, the above-mentioned industry contributes significantly to environmental pollution, increasing the number of gaseous pollutants and industrial effluents. Wastewater produced under laboratory conditions was characterized by the following parameters (based on the properties of real wastewater): chemical oxygen demand (COD): 750 mgO₂ L⁻¹, turbidity: 240 FTU (formazine turbidity unit), suspended solids: 94 mg L⁻¹, and pH: 6.0. The applied wastewater production method provided a high reproducibility of wastewater parameters, and it was suitable for long-term experiments.

Wastewater was electrocoagulated in a static system (Figure 1). A pair of aluminium electrodes of dimensions of 16 x 1 x 0.1 cm and separated by a distance of 1 cm was immersed in a wastewater tank with a volume of 250 cm³. Constant current intensity of I₁ = 0.05 A and I₂ = 0.1 A was applied throughout the study. Electrocoagulation at constant current intensity improves the efficiency of wastewater treatment and reduces treatment costs, which determines its potential practical application. A self-designed control and supply system was used to provide adequate power supply and to stabilize current intensity (Załęska-Chróst et al. 2008).

Figure 1 | Diagram of electrocoagulation: 1—magnetic stirrer, 2—magnetic bar, 3—electrolytic cell, 4—aluminium electrodes, 5—power supply, 6—burette, 7—pH meter.

The following electrolytic reactions take place on the surface of electrodes during electrolytic wastewater treatment (Khemis et al. 2006; Koby & Delipinar 2008):

on the anode: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e \) \hspace{1cm} (1)

on the cathode: \( 3\text{H}_2\text{O} + 5e \rightarrow 3/2\text{H}_2 \uparrow + 3\text{OH}^- \) \hspace{1cm} (2)

At this stage, \( \text{Al}^{3+} \) ions formed on the anode capture \( \text{OH}^- \) ions to form various types of monomers such as \( \text{Al(OH)}^2^+ \), \( \text{Al(OH)}_2^+ \) and \( \text{Al}_2(\text{OH})_3^{3+} \), which are transformed and precipitated in the form of slightly soluble \( \text{Al(OH)}_3 \) hydroxide sludge. The coagulant is generated locally by electrolytic oxidation of anodic material, which under appropriate pH conditions leads to insoluble metal hydroxide, which is able to further remove pollutants. The newly formed amorphous hydroxide of a large surface area is a suitable material to adsorb organic compounds and capture dissolved particles of colloidal pollutants. When the load threshold is exceeded, the system quickly destabilizes and aggregation begins. Subsequently, flocs are separated by flotation under the influence of gas bubbles near electrodes, or due to an increase in density, and the resulting sludge undergoes sedimentation (Zodi et al. 2010).

When wastewater is treated, the system’s pH increases rapidly, as the resulting \( \text{OH}^- \) ions partially move to the solution. The highest efficiency of wastewater treatment using aluminium electrodes was reported during other electrocoagulation processes at pH maintained in the range of 4–6 (Bayramoglu et al. 2004). Amphoteric \( \text{Al(OH)}_3 \) is not precipitated at low pH, whereas other soluble forms of aluminium are produced at excessively high pH. A pH meter and a burette filled with 1 M HCl were installed to prevent significant pH variations during the process (Figure 1).

During the process, wastewater samples were collected at specific time intervals and they were analysed to determine their COD, turbidity and content of suspended solids by the standard spectrophotometric method using the Hach DR 2000 spectrophotometer. The results can be divided into two groups:

1. results of an analysis of the liquid phase of wastewater;
2. results of an analysis of sludge aggregates – the solid phase.

The present study focuses on the results of analysis of aggregates in electrocoagulated sludge.

Digital image analysis is the most popular method for determining fractal dimensions. Measuring techniques
based on digital image analysis can be applied only to structures whose fractal dimension is smaller than 2 (Bushell & Amal 2000).

Furthermore, the use of a microscope for the acquisition of digital images carries the risk of modifying the structure in the process of sample preparation for the analysis (Herman et al. 2004). Therefore, in this study, fractal dimensions were determined by photographic image analysis.

Sludge samples were collected at different stages of the wastewater treatment process. Fractal dimensions $D$ of aggregates were determined 1 hour after sampling. Fractal dimensions $D$ of aggregates were also determined 24 hours after sampling for comparative purposes, and the resulting data were used to describe structural changes during sludge ageing (maturation).

In this study, the parameters for 120 to 160 aggregates were determined for one type of process. The path travelled by aggregates during sedimentation in a column was obtained for every type of measurement. The pictures were lit by an electronically controlled system where light was flashed exactly every 5 seconds.

Ten flashes were registered per frame. An average of 15 frames was obtained for every type of measurement. The images were displayed on a screen to determine particle size $R$ and floc settling velocity $v$.

Geometric fractal dimension $D$ can be determined in various ways, depending on general conditions. For a one-dimensional condition, geometric fractal dimension $D_1$ describes the irregularity of the circumference formed by suspended particles. Additionally, it was proven that it is not correlated with the so-called roundness of suspended particles, but it is related to the irregularity of their boundaries. Two-dimensional fractal dimension $D_2$ defines the correlation between distance $l$ from the centre of the particle system forming suspensions and the increase in mass on a given surface at distance $l$. Radial distribution of mass may lead to the equality $l = R$ (Lee & Kramer 2004).

In this study, a possibility of describing aggregate particles using mass fractal dimension was employed (Liao et al. 2006). Mass fractal ($m$) is a mass aggregate composed of interconnected particles. Dimension $D$ of every fractal is described by the following formula:

$$m(R) \sim R^D$$  \hspace{1cm} (3)

where: $m(R)$ – mass of suspended particles, $R$ – linear size of a particle.

Mass fractal dimension takes on values in the range of $1 < D_m > \text{3}$.

The density of mass fractal ($d$) of $D_m$ dimension was presented as a function of a distance from its centre:

$$d(R) = \frac{m(R)}{V(R)} \approx R^{D_m} \approx R^{D_m-3}$$  \hspace{1cm} (4)

The results were used to determine the following logarithmic dependence:

$$\log d \sim f(\log R)$$  \hspace{1cm} (5)

and the slope of the plotted curves was used to determine the value of $D_m$ (referred to as $D$ in subsequent parts of the study).

Calculations were made using the self-designed Fractal 2 software based on the Microsoft Excel spreadsheet.

RESULTS AND DISCUSSION

The results related to aggregates obtained as a result of model wastewater treatment by electrocoagulation are presented in Tables 1 and 2. The level of wastewater treatment, expressed by percentage change in COD values, varied during the process.

Fractal dimension $D$ and floc settling velocity $v$ of sludge aggregates at different stages of the wastewater treatment process were determined 1 hour after sampling.

The results of the study of sludge produced by electrocoagulation at two current density values of $\rho_1 = 31.25 \text{ A m}^{-2}$ and $\rho_2 = 62.50 \text{ A m}^{-2}$ are presented in Tables 1 and 2, respectively. The electric charge ($q$) supplied to the solution depending on the time of electrolysis was calculated based on the formula $q = I \cdot t$ ($I$ – current, $t$ – time), and expressed as a charge per 1 L of wastewater. At current density $\rho_1$

<table>
<thead>
<tr>
<th>Electric charge C L$^{-1}$</th>
<th>COD removal %</th>
<th>Fractal dimension D</th>
<th>Settling velocity (v) $\mu$m s$^{-1}$</th>
<th>Coefficient of determination ($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>32.62</td>
<td>1.53</td>
<td>80–440</td>
<td>0.9405</td>
</tr>
<tr>
<td>144</td>
<td>50.65</td>
<td>1.75</td>
<td>70–460</td>
<td>0.9586</td>
</tr>
<tr>
<td>162</td>
<td>52.36</td>
<td>1.82</td>
<td>60–390</td>
<td>0.9214</td>
</tr>
<tr>
<td>243</td>
<td>57.90</td>
<td>1.88</td>
<td>60–330</td>
<td>0.9012</td>
</tr>
<tr>
<td>324</td>
<td>59.16</td>
<td>1.91</td>
<td>40–230</td>
<td>0.9660</td>
</tr>
</tbody>
</table>
(Table 1), the increase in electric charge from 0 to approximately 324 C L\(^{-1}\) led to nearly 60% removal of COD from electrocoagulated wastewater. Fractal dimensions \(D\) determined during the process were in the range of 1.53–1.91 and floc settling velocity \(v\) was in the range of 40–460 μm s\(^{-1}\). At current density \(\rho_1\), fractal dimensions \(D\) increased in samples with increasing purity, and the increase in \(D\) was accompanied by insignificantly different but progressively lower values of settling velocity \(v\).

The parameters obtained during the process at \(\rho_2 = 62.50\) A m\(^{-2}\) are presented in Table 2. The size of fractal dimension \(D\) of the obtained aggregates was in the range of 1.54–1.95, while their floc settling velocity was in the range of 70 to 420 μm s\(^{-1}\). Furthermore, a proportional relationship between the \(D\) value and wastewater treatment level was observed.

The application of electric charge of 144 to 1,440 C L\(^{-1}\) to the solution led to nearly 65% removal of COD in successive stages of the process, and the resulting sludge was characterized by higher values of \(D\), with maximum \(D = 1.95\), accompanied by better removal of pollutants. The determined floc settling velocity decreased with increasing \(D\) values.

The applied current density affected ‘coagulant dosing’ in successive stages of electrocoagulation, which probably exerted a further stimulating effect on wastewater treatment. Current density determines the speed of the process, the number and size of gas bubbles and subsequent floc formation. The application of a higher current density \((\rho)\) ultimately contributed to a better removal of contaminations (COD removal estimated at 65%), which could probably be attributed to increased production of aluminium, while the resulting sludge was characterized by higher values of \(D\). However, higher current density also involved a higher electric charge flowing through the solution (1,440 C L\(^{-1}\)) and at the same time, higher electricity consumption. At lower values of \(\rho\), wastewater treatment was estimated at over 50% with electric charge of as low as 162–243 C L\(^{-1}\), and fractal dimensions at this treatment level were in the range of 1.82–1.88. However, at higher values of \(\rho\), similar fractal dimensions of \(D = 1.83\) and comparable impurity removal were noted for an electric charge of as high as 648 C L\(^{-1}\).

A satisfactory level of wastewater treatment and lower electricity consumption were reported at a current density of \(\rho_1 = 31.25\) A m\(^{-2}\). The above-mentioned results indicate that current density, which can also be determined with the use of fractal dimension \(D\) is a very important parameter in electrolytic wastewater treatment. The value of \(\rho\) should be planned in a way that guarantees the maximum efficiency of current consumption.

Fractal dimension of treated sludge aggregates can be to a greater or lesser degree indicative of the water content in sludge. A lower \(D\) value describes sludge with higher water content. It could be observed that during the electrocoagulation process, a degree of wastewater treatment was directly proportional to the value of \(D\). The above could imply that an increase in the purity of the liquid phase of wastewater was accompanied by a decrease in the water content of sludge, and the resulting aggregates were characterized by lower settling velocity.

Logarithmic dependencies \(\lg d = f (\lg R)\) for selected aggregates are presented in Figures 2 and 3, and they were used to determine fractal dimensions \(D\). In successive
measurements, coefficients of determination are marked with the symbol $r^2$. Their values for all processes were $r^2 > 0.9$. The proposed method for determining the dimensions of all produced aggregates was thus statistically justified, at the same time indicating that the resulting aggregates were self-similar objects with fractal properties (Figures 2 and 3).

Generally, small and medium-sized flocs measuring 100–500 μm constituted the largest group of aggregates in the analysed sludge, and their settling velocity was 30–520 μm s$^{-1}$. Fractal dimension was correlated with the percentage content of flocs of a given size group. The percentage share of selected aggregates in sludge, based on their real dimensions, is presented in Figures 4 and 5. Higher values of $D$ (1.91) described sludge with a higher content of small flocs (150–300 μm). Such sludge was also characterized by a low floc settling velocity $v$ in the range of 40–230 μm s$^{-1}$, as observed during the sedimentation process. Sludge with smaller dimension (1.75) was characterized by larger flocs (250–400 μm) and slightly higher floc settling velocity (70–460 μm s$^{-1}$). A higher share of small flocs in coagulated sludge eliminates the number of free spaces in the sludge, increases its water content and usually improves the filling of sludge air spaces with solids.

In aggregates of wastewater samples characterized by the same treatment, fractal dimensions $D$ were higher 24 hours after sampling than 1 hour after sampling (Figures 6 and 7). Sludge ageing led to the increase in the $D$ value in aggregates obtained by electrocoagulation. Most probably the gravitational self-dewatering of flocs, which increased the share of the potential solid phase in aggregates, took place.

**CONCLUSIONS**

Aggregates produced during model wastewater electrocoagulation using a static method with aluminium electrodes have fractal properties and are statistically self-similar. The use of electrolysis in wastewater treatment produced sludge composed of small and medium-sized aggregates. Values of fractal dimensions were in the range of 1.55–1.91 at $\rho_1 = 31.25$ A m$^{-2}$, and in the range of 1.54–1.95 at $\rho_2 = 62.50$ A m$^{-2}$. The parameters which characterize the electrocoagulation treatment such as electrode

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**Figure 4** | Percentage content (%) of aggregates in sludge, based on their real dimensions $D = 1.75$, $v$: 70–460 μm s$^{-1}$.

**Figure 5** | Percentage content (%) of aggregates in sludge, based on their real dimensions $D = 1.91$, $v$: 40–230 μm s$^{-1}$.

**Figure 6** | Fractal dimension measured 1 h and 24 h after sampling, dependent on COD removal during electrocoagulation at $\rho_1 = 31.25$ A m$^{-2}$.

**Figure 7** | Fractal dimension measured 1 h and 24 h after sampling, dependent on COD removal during electrocoagulation at $\rho_2 = 62.50$ A m$^{-2}$.
current density and electric charge flowing through the solution also influence the structure and size of aggregates, determining fractal dimension $D$ of the resulting flocs. A satisfactory level of wastewater treatment was reported at a lower current density of $\rho_l = 31.25 \, \text{A m}^{-2}$, and sludge ageing contributed to an increase in the value of $D$. This was a positive effect, as it was related to a decrease in the amount and water content of sludge, and thus to a reduction in the storage and transport cost.

The fractal dimension of wastewater sludge is practically the only method for quantitative descriptions of irregularities or the degree of folding of the analysed objects, whereas the coefficient of determination ($r^2$), obtained for the $\lg d \sim (\lg R)$ relationship describes the self-similarity of the study group of aggregates. Fractal dimension $D$ may be an additional tool to evaluate sewage sludge, as well as a supporting parameter for the monitoring and control of wastewater treatment processes.

REFERENCES


