Sizes of particles formed during municipal wastewater treatment
Smoczynski Lech, Kosobucka Marta, Smoczynski Michal, Ratnaweera Harsha and Pieczulis-Smoczynska Krystyna

ABSTRACT

Volumetric diameters $D_v$ and specific surface area $SpS$ of sludge particles formed during chemical coagulation and electrocoagulation of sewage were determined. The obtained aggregate-flocs differed substantially in both $D_v$ and $SpS$ values. The differences in $D_v$ and $SpS$ values of the analyzed particles were interpreted based on theoretical models for expanding aggregates. The most uniform particles were formed under exposure to: (a) optimal and maximal doses of PIX, (b) optimal doses of PAX, (c) maximal doses of the Al electro-coagulant. The lowest PIX dose produced the least uniform particles. Sludge aggregates-particles produced under exposure to minimal doses of PIX and the Al electro-coagulant were characterized by the lowest $SpS$ values. Sludge particles coagulated by PAX and the particles formed at higher doses of PIX and the Al electro-coagulant had higher $SpS$ values. The particles formed at all doses of the applied coagulants and electro-coagulants were generally classified into two size ranges: the main range and the secondary range. Most particles belonged to the main size range. An increase in the percentage of colloidal hydroxide particles in sewage sludge increased $SpS$.

Key words | chemical coagulation, electrocoagulation, particles, sewage

INTRODUCTION

In Poland, municipal wastewater is generally subjected to preliminary chemical coagulation before it undergoes the main and final biological purification. Under certain conditions, electrocoagulation (Groterud & Smoczynski 1986; Holt et al. 2002; Smoczynski et al. 2015) provides a valid alternative to coagulation-flocculation of wastewater. Sewage flocs produced during latent hetero-flocculation (Duan & Gregory 2005; Smoczynski et al. 2009a, 2009b) differ considerably from the agglomerates that are formed during sweep flocculation. The composition (Mikkelsen & Keiding 2002), properties (Jin et al. 2004) and structure (Jarvis et al. 2005; Wang et al. 2009; Smoczynski et al. 2014a, 2014b) of various sewage sludges have been widely researched, but problems relating to sludge management have not yet been fully resolved (Fytili & Zabaniotou 2008).

Aggregation, agglomeration and flocculation are important from the theoretical and practical point of view in many industries, including food production (Konieczny et al. 2005) and the chemical industry (Verna et al. 2010). Sludge aggregates, agglomerates, particles, clusters and flocs play a significant role in many life processes (Stradner et al. 2004), therefore, studies examining their size and structure expand our theoretical and practical knowledge. The size of sludge particles often determines the main properties of the analyzed material, and it provides valuable information about the conditions in which it was formed. The course of coagulation-flocculation processes and electrocoagulation parameters leave an ‘imprint’ on the structure of sludge particles (Smoczynski et al. 2014a, 2014b). The nature and shape of sludge aggregates can be described by volumetric diameters $D_v$ and their specific surface area $SpS$ (Malvern 2012). Particles with wrinkled and folding surface (high $SpS$)
increase the sorption potential of sewage sludge during sweep flocculation, whereas compact flocs (small SpS) are easily dehydrated and separated after leaving the wastewater treatment plant.

This study analyzes sludge produced by coagulation and electrocoagulation of municipal wastewater. The size and specific surface area of sludge particles were significantly affected by the sewage treatment method.

**EXPERIMENTAL**

Samples of municipal sewage from Reszel (Poland, 5000pe) were collected from a tank after preliminary mechanical treatment. They were refrigerated overnight and heated to room temperature before analysis. In the examined samples, the content of suspended solids ranged from 500 to 1,000, and turbidity was determined at 250–500 mg·dm⁻³. The values of pH₀, Colour₀, COD₀ and P₀ for raw wastewater are given in the captions of Figures 1–3.

Sludge samples for particle size analyses were obtained by: (a) coagulation with Kemira PIX-113 Fe-coagulant (the most commonly used coagulant in Poland; total Fe = 11.8 ± 0.4%, density = 1,500–1,570 kg·m⁻³, pH < 1), (b) coagulation with Kemira PAX-18 (total Al = 9.0 ± 0.3%, density = 1,360 ± 10 kg·m⁻³, basicity = 41.0 ± 3%, pH = 1.0 ± 0.2), a preliminarily hydrolyzed Al-coagulant (as an alternative to PIX), (c) 1 h of electrocoagulation in a recirculation system at I = 0.1 or/and 0.3 A on aluminum electrodes (Groterud & Smoczynski 1986; Butler et al. 2011). The pH of coagulated wastewater was registered but not adjusted because chemical coagulation is more effective at low pH. The pH of electro-coagulated wastewater was kept constant at 6.0 by adding HCl during the process. The effectiveness of coagulation decreases with a rise in pH, and final pH can be as high as 11.

The protocols for jar tests, electrocoagulation, physicochemical analyses and measurements were described previously (Smoczynski et al. 2014a, 2014b), and the results of wastewater treatment are presented in Tables 1–3. Each sample of separated sludge was obtained after 30 min of sedimentation.

Particle size distribution in the examined wastewater sludge was determined by measuring laser light dispersion with the Mastersizer 3000 analyzer (Malvern 2012). Five drops of the sludge were added to the measurement cell to

![Figure 1](https://iwaponline.com/wst/article-pdf/75/4/971/455330/wst075040971.pdf)

**Figure 1** | Coagulation of sewage with PAX (Δ – Turbidity, x – Suspended Solids). pH₀ = 7.80 → pHᵢ = 7.14; Colour₀ = 3,590 → Colourᵢ = 110; COD₀ = 1,190 → CODᵢ = 313; P₀ = 9.75 → Pᵢ = 0.22.

![Figure 2](https://iwaponline.com/wst/article-pdf/75/4/971/455330/wst075040971.pdf)

**Figure 2** | Coagulation of sewage with PIX (Δ – Turbidity, x – Suspended Solids). pH₀ = 7.53 → pHᵢ = 6.84; Colour₀ = 5,610 → Colourᵢ = 422; COD₀ = 1,690 → CODᵢ = 360; P₀ = 11.40 → Pᵢ = 0.64.

![Figure 3](https://iwaponline.com/wst/article-pdf/75/4/971/455330/wst075040971.pdf)

**Figure 3** | 1 h of electrocoagulation of sewage at I = 0.1 A (Δ – Turbidity, x – Suspended Solids). Colour₀ = 3,160 → Colourᵢ = 185; P₀ = 16.2 → Pᵢ = 0.80; COD₀ = 527 → CODᵢ = 279.

![Table 1](https://iwaponline.com/wst/article-pdf/75/4/971/455330/wst075040971.pdf)

**Table 1** | Volumetric parameters for the size distribution of sludge aggregate-flocs formed during chemical coagulation with three different doses of PAX

<table>
<thead>
<tr>
<th>Parameter</th>
<th>min dose Al dm⁻³</th>
<th>opt dose Al dm⁻³</th>
<th>max dose Al dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dv10 (μm)</td>
<td>7.60</td>
<td>11.28</td>
<td>9.33</td>
</tr>
<tr>
<td>Dv50 (μm)</td>
<td>67.92</td>
<td>30.30</td>
<td>34.54</td>
</tr>
<tr>
<td>Dv90 (μm)</td>
<td>411.0</td>
<td>280.8</td>
<td>431.6</td>
</tr>
<tr>
<td>SpS (m²·g⁻¹)</td>
<td>359.54</td>
<td>323.12</td>
<td>329.76</td>
</tr>
</tbody>
</table>
produce laser obscuration values of 5–15%. The refractive index was determined at 1.33 for water and 3.8 for wastewater. All measurements were performed in accordance with the manufacturer’s protocol. The results were presented as means of five replications for every type of evaluated sewage sludge. Volumetric diameters \( D_{v10} \), \( D_{v50} \) and \( D_{v90} \) denote the maximum particle diameter in a given population of sludge aggregates, which accounts for 10%, 50% and 90% of particle volume, respectively.

### RESULTS AND DISCUSSION

Sludge samples were obtained after chemical coagulation and electrocoagulation of municipal wastewater. The conditions in which sewage sludge were formed are presented in Figures 1–3.

Even the lowest doses of PAX (6.2 and 12.4 mg Al·dm\(^{-3}\)) removed more than 80% of colour, turbidity and suspended solids (Figure 1). A dose of 101.5 mg Al·dm\(^{-3}\) removed 90–100% of colour, turbidity and suspended solids from the coagulated wastewater. Under such conditions, the chemical oxygen demand (COD) of coagulated wastewater decreased from 1,190 to 313, and phosphorus levels decreased from 11.4 to 0.64 mg·dm\(^{-3}\). This process was accompanied by a decrease in the pH of the treated wastewater from 7.53 to 6.84. PAX was somewhat less efficient in purifying treated sewage than PAC (Figure 1).

Consecutive 10-minute stages of electrocoagulation (Figure 3) were conducted at constant \( I = 0.1 \) A. According to Faraday’s law \( (m = k \cdot i \cdot t) \), this was equivalent to doses of the aluminum electro-coagulant from 2.7 to 33.5 mg Al·dm\(^{-3}\), although higher doses are used in practice (Smoczynski et al. 2015). When the sedimentation of wastewater treated with 33.5 mg Al·dm\(^{-3}\) was prolonged by 30 minutes (1,800 s), colour, turbidity, suspended solids and phosphorus were removed in nearly 100% from the liquid phase of electro-coagulated wastewater. COD decreased from 527 to 279 mg·dm\(^{-3}\), i.e. by 47%.

The size distribution of sludge particles produced by chemical coagulation with various doses of PAX is presented in Figure 4. Unlike synthetic wastewater sludge particles (Smoczynski et al. 2016), the particles analyzed in this study were characterized by a significantly broader size range from approximately 2 \( \mu \)m to 1,000 \( \mu \)m. At low coagulant doses, the predominant particle size is difficult to identify, whereas two size ranges are generally observed at optimal and excessive coagulant doses: (a) the main size range of approximately 2 \( \mu \)m to 70 \( \mu \)m and (b) the secondary size range of approximately 70 \( \mu \)m to 1,000 \( \mu \)m.

The aggregate-flocs produced during coagulation of municipal wastewater with various doses of PAC are presented in Table 1.

The data in Table 1 indicate that the analyzed aggregate-flocs were characterized by similar \( SpS \) regardless of the applied dose of inorganic coagulant. \( Dv \) varied across particles, where \( Dv_{\text{min}} \) was similar to \( Dv_{\text{max}} \) and higher than the \( Dv_{\text{opt}} \). These results may indicate that the optimal dose of PAX led to the formation of the most uniform aggregates. This implies that the size distribution of the resulting particles was most similar to normal distribution, therefore, the variations in particle structure were lowest. It is known that uniform particles are formed under stoichiometric conditions. Therefore, both insufficient (a) and excessive doses of PAX (b) can lead to the formation of products that are ‘contaminated’ with other structures, such as: (a) residues

### Table 2 | Volumetric parameters for the size distribution of sludge aggregates-flocs formed during chemical coagulation with three different doses of PAX

<table>
<thead>
<tr>
<th>Parameter ((\mu m))</th>
<th>(33.5 \text{ mg Al·dm}^{-3})</th>
<th>(54.20 \text{ mg Fe·dm}^{-3})</th>
<th>(121.95 \text{ mg Fe·dm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{v10})</td>
<td>10.53</td>
<td>7.98</td>
<td>10.5</td>
</tr>
<tr>
<td>(D_{v50})</td>
<td>116.82</td>
<td>46.02</td>
<td>24.48</td>
</tr>
<tr>
<td>(D_{v90})</td>
<td>915.6</td>
<td>165.8</td>
<td>200.8</td>
</tr>
<tr>
<td>(SpS) ( (m^2·g^{-1}))</td>
<td>260.5</td>
<td>355.52</td>
<td>328.5</td>
</tr>
</tbody>
</table>

### Table 3 | Volumetric parameters for the size distribution of sludge particles formed during electrocoagulation of municipal wastewater at \( I = 0.1 \) A and \( I = 0.3 \) A

<table>
<thead>
<tr>
<th>Parameter ((\mu m))</th>
<th>(33.5 \text{ mg Al·dm}^{-3} (I = 0.1 ) A)</th>
<th>(105.5 \text{ mg Al·dm}^{-3} (I = 0.3 ) A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{v10})</td>
<td>11.76</td>
<td>9.54</td>
</tr>
<tr>
<td>(D_{v50})</td>
<td>38.56</td>
<td>24.28</td>
</tr>
<tr>
<td>(D_{v90})</td>
<td>356.6</td>
<td>227.1</td>
</tr>
<tr>
<td>(SpS) ( (m^2·g^{-1}))</td>
<td>269.2</td>
<td>372.0</td>
</tr>
</tbody>
</table>
of non-coagulated pollutants and (b) residues of ‘unused’ stable micelles \( \{ \text{Al(OH)}_3 \}_n \) or their destabilization products. In both cases, the size distribution of sludge particles will be less uniform than under stoichiometric or near-stoichiometric conditions.

The structures presented in Figure 5 should be characterized by relatively constant \( \text{SpS} \) values. It seems obvious that colloidal particles which are responsible for COD and are adsorbed on the surface of the colloidal sorbent \( \{ \text{Al(OH)}_3 \}_n \) (Figure 5(a)) are significantly larger than the particles of dye D, for instance (Smoczynski et al. 2016). When the PAX dose was increased in municipal wastewater, the cross-linking of micelles \( \{ \text{Al(OH)}_3 \}_n \) with COD bridges (Figure 5(b)) significantly larger than D bridges had a less pronounced effect on \( \text{SpS} \) than in synthetic wastewater. The folding (wrinkling) of aggregate surfaces described quantitatively with \( \text{SpS} \) values was also significantly smaller in comparison with synthetic wastewater aggregates.

The size distribution of aggregate-flocs produced by chemical coagulation of wastewater with various PIX doses is presented in Figure 6. Similar to wastewater treated with PAX (Figure 4), sludge particles were characterized by a much broader size range from approximately 1.5 \( \mu \text{m} \) to 1,100 \( \mu \text{m} \). Similar to PAX, at low doses of PIX, the predominant particle size was difficult to identify, which could indicate that coagulated sewage was not completely treated. At optimal and excessive doses of the coagulant, two particle size ranges were generally noted: (a) the main size range of approximately 0.5 \( \mu \text{m} \) to 80 \( \mu \text{m} \) and (b) the secondary size range of approximately 90 \( \mu \text{m} \) to 1,000 \( \mu \text{m} \). The second peak could represent residual particles in the treated material.

The size of aggregate-flocs produced during wastewater coagulation with various doses of PIX is presented in Table 2.

The minimal dose of 13.55 mg Fe dm\(^{-3} \) (PIX) contributed to the formation of less uniform aggregates in sludge (Table 2). The greatest difference was noted in the value of \( D_{v90} \) which was nearly three-fold higher under exposure to the minimal PIX dose \( (D_{v90} = 915) \) than the minimal PAC dose \( (D_{v90} = 360) \) (Table 1). The high value of \( D_{v90} = 915 \) under exposure to the smallest PIX dose could point to the presence of larger (in diameter) structures such as \( \{ \text{Fe(OH)}_3 \}_n - \text{COD} \) rather than \( \{ \text{Al(OH)}_3 \}_n - \text{COD} \). Both optimal and maximal doses of PIX created much more uniform particles with the lowest values of \( D_v \), which are characteristic of uniform and compact structures. The differences in the compaction and uniformity of \( \{ \text{Fe(OH)}_3 \}_n - \text{COD} \) structures formed under stoichiometric conditions and \( \{ \text{Fe(OH)}_3 \}_n - \text{COD} + \{ \text{Fe(OH)}_3 \}_n \) structures formed under exposure to excessive coagulant doses, in comparison with PAX, could be attributed to structural variations in the corresponding micelles: rod-shaped micelles \( \{ \text{Fe(OH)}_3 \}_n \) and spherical micelles \( \{ \text{Al(OH)}_3 \}_n \). The vast

![Figure 5](Image)

**Figure 5** Stages of aggregate-flocs formation under exposure to (a) minimal, (b) optimal and/or maximal doses of the coagulant.

![Figure 4](Image)

**Figure 4** Size of sludge aggregate-flocs formed during chemical coagulation with three different doses of PAX: minimal – 2.45 mg Al · dm\(^{-3} \), optimal – 17.14 mg Al · dm\(^{-3} \), and maximal – 40.06 mg Al · dm\(^{-3} \).
The majority of large particles formed in response to the minimal PIX dose significantly contributed to a decrease in SpS to 260.5 μm. The values in Table 2 point to minor variations in SpS values, and similar results were noted for PAX. The SpS values of sludge aggregates in municipal wastewater coagulated with PIX were also significantly lower in comparison with synthetic sewage aggregates, which was also observed for PAX.

The aggregates-flocs presented in Figure 7 should be characterized by relatively constant SpS values. Similar to PAX, when the PIX dose was increased in municipal wastewater, the cross-linking of cylindrical micelles \( \text{Fe(OH)}_3 \) with COD bridges – much larger than D bridges – had a less significant effect on SpS than in synthetic wastewater (Smoczynski et al. 2016).

The size distribution of sludge particles formed during electrocoagulation of municipal wastewater at two coagulant doses, 33.5 Al·dm\(^{-3}\) and 105.5 mg Al·dm\(^{-3}\), is presented in Figure 8. Unlike in synthetic wastewater, the analyzed particles were characterized by a much broader size range of approximately 2 μm to 1,000 μm. Similar to the results noted for PAX (Figure 4 – optimal and maximal doses of Al), two particle size ranges were generally formed in response to both doses of the electro-coagulant: (a) the main size range of approximately 2 μm to 70 μm and (b) the secondary size range of approximately 70 μm to 1,000 μm. The high similarity in the size of particles formed by optimal and excessive doses of PAX and particles...
formed by electrocoagulation could point to similarities in their formation processes, i.e. sweep-floculation.

The aggregate-flocs formed in response to two electro-coagulant doses are described in Table 3.

The lower dose of the Al electro-coagulant (33.5) was somewhat lower than the maximal dose of Al in PAX (40.0 mg Al dm$^{-3}$, Figure 4). An increase in current from 0.1 A to 0.3 A decreased $Dv_{10}$, $Dv_{50}$ and $Dv_{90}$. The values of $Dv$ described in Table 3 could indicate that a higher dose of the Al electro-coagulant ($I = 0.5 A$) contributed to the formation of more uniform aggregates than the lower dose ($I = 0.1 A$). This implies that the size distribution of particles produced at $I = 0.5 A$ was most similar to normal distribution, and the resulting structures were less varied than those obtained at $I = 0.1 A$. Unlike in chemical coagulation, during electrocoagulation, impurities are removed from wastewater mainly by sweep-floculation. Sweep-floculation can produce a similar situation to that observed under exposure to PIX: excessive coagulant doses support the formation of more uniform sludge particles. This phenomenon must have been accompanied by an increase in $SpS$ values, in this case from approximately 270 to 364. When the electro-coagulant dose was tripled ($I = 0.3 A$), the quantity of colloidal [Al(OH)$_3$] in the structure of aggregate-flocs increased significantly, which contributed to the observed rise in $SpS$ values.

In this study, the most uniform particles were formed under exposure to: (a) optimal and maximal doses of PIX, (b) optimal doses of PAX, (c) maximal doses of the Al electro-coagulant. The lowest PIX dose produced the least uniform particles. Sewage sludge particles formed in response to minimal doses of PIX and the AI electro-coagulant were characterized by smaller specific surface area $SpS$ than particles produced by coagulation with PAX as well as particles formed in response to higher doses of PIX and the Al electro-coagulant. The particles produced by all evaluated doses of coagulants and electro-coagulants were generally grouped in two size ranges: the main size range and the secondary size range. The vast majority of particles were classified in the main size range. An increase in the percentage of colloidal hydroxide particles in sewage sludge particles increased $SpS$ values. Volumetric diameters of sludge particles ($Dv_{10}$, $Dv_{50}$ and $Dv_{90}$) formed in natural municipal wastewater and their $SpS$ values differed significantly from the parameters of sludge particles noted in synthetic wastewater. Those variations could be attributed to differences in the structure of sludge obtained from municipal wastewater and synthetic wastewater.

CONCLUSIONS

The most uniform particles were formed under exposure to: (a) optimal and maximal doses of PIX, (b) optimal doses of PAX, (c) maximal doses of the Al electro-coagulant. The lowest PIX dose produced the least uniform particles. Sewage sludge particles formed in response to minimal doses of PIX and the AI electro-coagulant were characterized by smaller specific surface area $SpS$ than particles produced by coagulation with PAX as well as particles formed in response to higher doses of PIX and the AI electro-coagulant. The particles produced by all evaluated doses of coagulants and electro-coagulants were generally grouped in two size ranges: the main size range and the secondary size range. The vast majority of particles were classified in the main size range. An increase in the percentage of colloidal hydroxide particles in sewage sludge particles increased $SpS$ values. Volumetric diameters of sludge particles ($Dv_{10}$, $Dv_{50}$ and $Dv_{90}$) formed in natural municipal wastewater and their $SpS$ values differed significantly from the parameters of sludge particles noted in synthetic wastewater. Those variations could be attributed to differences in the structure of sludge obtained from municipal wastewater and synthetic wastewater.

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