Size fractionation of COD in urban wastewater from a combined sewer system

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Abstract The objective of this work was to determine the partitioning of the pollutant load in urban wastewater in order to improve the conventional sewage treatment. In addition to settling tests, physical fractionation of COD in the degritted influent of Roma-Nord sewage treatment plant was performed via sequential filtration through sieves and membrane filters of the following pore size: 150–100–50–25–1–0.2 µm, and 100 kD (about 0.02 µm). Biodegradability studies were also performed on the different size fractions. Size fractionation showed that COD in Roma-Nord sewage is predominantly associated with settleable and supracolloidal (> 1 µm) particles, each size range including about 40% of total COD. Biodegradability tests indicated that the large fraction of COD associated with supracolloidal particles, which are not removed in the primary treatment, is characterised by slow degradability. This suggests that removal of these particles prior to biological treatment may greatly improve the overall treatment scheme. Preliminary pilot plant coagulation tests with lime at pH 9 showed that lime-enhanced primary treatment may increase COD removal efficiencies from typical 30–35% up to 65–70%, by inducing almost complete removal of the COD fraction associated with supracolloidal particles.

Keywords Coagulation; filtration; fractionation; particulate size; sewage; sieving

Introduction
Pollutants in municipal sewage include a complex mixture of soluble and insoluble constituents with highly heterogeneous chemical composition and size. A large part of the pollutant load is in the insoluble form, ranging in size from less than 0.001 µm up to over 100 µm (Levine et al., 1985). Pollutants are typically classified in four size ranges: settleable (>100 µm), supracolloidal (1–100 µm), colloidal (0.001–1 µm), and soluble (<0.001 µm). The limits of these operationally defined ranges may slightly change depending on the experimental technique used to separate the size fractions. Numerous works performed on size classification of organic pollutants in urban wastewater suggest that only a limited fraction of total COD in raw sewage may be considered truly soluble (Rickert and Hunter, 1971; Munck et al., 1980; Orhon et al., 1997; Vaillant et al., 1999). Typically, 30–35% of total COD is readily settleable. A considerable amount of insoluble COD is in the colloidal and supracolloidal fractions.

From the above considerations it can be deduced that total COD cannot be used as a valid process component in modelling carbon and nutrients removal, because it covers a large spectrum of organic compounds with different biodegradation characteristics. According to Morgenroth et al. (2002), the majority of slowly biodegradable organic matter entering the biological section of a wastewater treatment plant can be assumed to be in the range of 10³ amu to 100 µm. Whereas particles smaller than 10³ amu can be directly taken up by cells, the utilisation of slowly biodegradable COD requires a preliminary slow step of hydrolysis. Therefore, wastewater characterisation should include COD fractionation (Orhon et al., 1997). For example, guidelines for wastewater characterisation issued by the Dutch Foundation for Applied Water Research (STOWA) are based on direct filtration (0.45 or 0.1 µm) or flocculation and filtration to separate readily biodegradable COD
Particle size distribution may help to upgrade the primary treatment section in order to remove the slowly biodegradable fraction of COD. This can also result in more efficient removal of other contaminants, such as heavy metals, bacteria and viruses, and organic micropollutants (PCB, PAH), which are strongly associated with the suspended phase.

Methods for particle size distribution in wastewater are reviewed by Levine et al. (1991) and summarized by Morgenroth et al. (2002). In sewage characterisation indirect methods for particle size distribution are typically used, which imply quantification of particles after separating these particles in different size fractions. The indirect methods present the advantage that chemical or biological properties of particles can be associated to different size fractions.

In this work the total COD load of a sewage was fractionated into several size fractions by means of sequential screening and filtration. COD fractionation was complemented by biodegradability studies on the different size fractions. On the basis of this thorough sewage characterisation, potential improvements of the overall sewage treatment scheme were assessed by pilot plant studies on coagulation-enhanced primary treatment.

Methods

Wastewater and sludge source
The experimental work has been performed using wastewater and sludge from Roma-Nord sewage treatment plant (780,000 p.e; 354,000 m³/d). The plant consists of two parallel lines for sewage treatment, each one including preliminary treatment steps (screening, sand and grease removal), primary settling, secondary treatment by activated sludge, and final disinfection by chlorination. The sludge treatment line includes anaerobic digestion with pre- and post-thickening, and belt filter press dewatering.

Size fractionation of COD
In order to obtain the size distribution of COD in degritted influent sewage, settling tests and filtration tests through sieves and membrane filters, were performed. Grab samples (20 l) of degritted sewage were split in three portions: the first small aliquot (10 ml) was used for COD measurements; the second one (about 2 l) was immediately used to measure the easily settleable fraction; the third portion (about 17 l) underwent sequential sieving and filtration. Sieving was carried out by means of a sieve shaker and certified steel sieves. A specifically designed sieve holder permitted a continuous operation by feeding the sample with a pump. Micro and ultrafiltration tests were performed in a crossflow filtration mode to minimise cake formation on the filter. To avoid contamination, sieving and filtration apparatus was washed carefully between filtration steps. In addition, an initial aliquot of the filtrate sample (100 ml) was discarded. Then, the filtrate was divided in two aliquots. One small aliquot of the filtrate was used to measure COD and to perform respirometric tests. The remaining filtrate was used as a feed for the next filtration step. The whole sequence included 3 sieves and 4 filters of the following decreasing pore size: 150–100–50–25–1–0.2 µm, and 100 kD (about 0.02 µm).

Respirometric batch tests
In order to determine the amount of readily biodegradable COD (RBCOD) and slowly biodegradable COD (SBCOD) in raw and filtrate sewage, aerobic batch tests were performed under continuous stirring and at controlled temperature (25°C). For each test 1 l of biomass was withdrawn from Roma-Nord plant and aerated for 24 h in order to remove residual COD. Before starting the test, air bubbling was shut off and the biomass was
allowed to settle for one hour. After removing 500 ml of supernatant, the concentrated biomass was kept aerated for 30 min, wherein endogenous oxygen uptake rate (OUR) was repeatedly measured. Then 500 ml of raw or filtered sewage was added at once, and OUR measurements were continued at regular intervals until the substrate was completely removed. To perform OUR measurements air bubbling was stopped and the rate of decrease of dissolved oxygen with time was monitored. To take into account oxygen transfer through the air-medium interface during OUR measurements, the transfer coefficient of the apparatus was measured in blank tests after inactivation of the biomass with HgCl (80 mg/l). In order to characterise the sludge under well defined conditions, batch tests with acetate as the only carbon source were initially performed.

COD removal tests in a pilot primary treatment plant
Pilot coagulation-flocculation tests were performed using raw sewage withdrawn from the Roma-Nord plant after preliminary treatment by screening and degritting. The pilot plant included two separate reactors for coagulation and flocculation, with volumes of 170 and 520 l, respectively. Both tanks were split in two compartments. Mixing was induced by mechanical stirring (marine-type propellers for coagulation and anchor impellers for flocculation). The pilot plant did not include a settling tank, which was simulated through laboratory settling tests.

Degritted sewage was pumped to the coagulation tank using a screw pump. Part of the effluent from the coagulation tank was fed to the flocculation tank, using a second screw pump. Pump flowrates were set in order to establish sewage residence times of 10 minutes in the coagulation tank and of 40 minutes in the flocculation tank. Lime was added (as a 2% slurry) at the inlet of the coagulation tank, using two peristaltic pumps that were controlled by two pH meters. The pH probes were placed in the two compartments of the coagulation tank.

After steady state conditions (in terms of pH) were established in the pilot plant, couples of samples of the influent and effluent wastewater were withdrawn, as grab samples, from the feed of the coagulation tank and from the outlet of the flocculation tank, respectively. Sampling of the effluent wastewater was delayed, with respect to the corresponding influent sampling, by a time equal to the total residence time in the pilot plant. A portion of grab samples was used for pH and COD measurements, whereas the remaining portion was immediately used for a settling test.

Analytical methods
COD was measured using the Spectroquant COD cell test supplied by Merck (digestion with commercially available reagents followed by colorimetric measurement of excess dichromate). Replicate measurements of two potassium phthalate samples at COD levels of 160 and 275 mg/l showed variation coefficients of 1.7% and 1.4% respectively, and accuracy within 10%. In the highly heterogeneous samples of raw sewage higher coefficients of variation were found (around 8%), likely due to the use of small aliquots of sample (2 ml). To offset the lower precision of the method with commercial vials in samples containing suspended solids, in this work all the COD measurements were performed in three replicates.

Settling tests on the degritted sewage were performed according to Standard Methods (APHA, 1995). After one hour settling the residual COD in the supernatant liquor was measured. Oxygen concentration measurements for OUR determination were performed using a WTW oxygen probe.

Results and discussion
COD fractionation
A half year long survey of the degritted Roma-Nord sewage was devoted to the classifica-
tion of influent COD into the four conventional size ranges of settleable, supracolloidal, colloidal and soluble organic matter. To begin with, the hourly variability of grab samples of influent sewage was studied. As expected, the influent characteristics of Roma-Nord sewage treatment plant showed a quite large hourly variability. In particular, it was observed that sewage strength, in terms of COD, may more than double at the peak hours with respect to the minimum value (Figure 1a). In addition, Figure 1b shows that the hourly variability in sewage strength is accompanied by a significant change in the size distribution of COD. Thereafter, sewage sampling was performed at noon any time, to offset the hourly variability of sewage characteristics.

In Table 1 the results of the survey are compared with literature data. Because the operationally defined size intervals are not standardised, they are also reported (in parentheses) in the table. The settleable fraction determined in this work is in good agreement with data typically obtained in urban wastewaters. The supracolloidal fraction yields a contribution comparable with settleable COD. In contrast, the contribution of the colloidal fraction seems to be lower than those typically reported in the literature. This can be ascribed to the fact that in this survey colloidal and soluble fractions were separated via filtration through 0.2 µm, with the consequence that the so defined “soluble” fraction may include part of the colloidal COD. Similarly, the very high “soluble” fraction determined in Rickert and Hunter’s work is probably due to the fact these authors use centrifugation for physical separation between supracolloidal, colloidal, and soluble fractions. Centrifugation might have been less efficient than filtration for separation of the three fractions according to the nominal size intervals indicated.

To better understand the distribution of particulate COD in the influent sewage, the complete sequential procedure of screening, microfiltration, and ultrafiltration was used. A typical cumulative size distribution curve obtained in this way is reported in Figure 2. From

### Table 1 COD distribution in domestic wastewater

<table>
<thead>
<tr>
<th>Reference</th>
<th>Total COD (mg/l)</th>
<th>% of COD in size fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Settleable</td>
<td>Supracolloidal</td>
</tr>
<tr>
<td>Rickert and Hunter, 1971</td>
<td>418</td>
<td>29</td>
</tr>
<tr>
<td>Munk et al., 1980</td>
<td>498</td>
<td>43</td>
</tr>
<tr>
<td>(&lt;106 µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orhon et al., 1997</td>
<td>410</td>
<td>27</td>
</tr>
<tr>
<td>Vaillant et al., 1999</td>
<td>430</td>
<td>29</td>
</tr>
<tr>
<td>This work</td>
<td>162–392</td>
<td>34–49</td>
</tr>
</tbody>
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the cumulative distribution curve the histogram of Figure 3 showing COD distribution among the different size fractions may be easily derived. Figure 3 suggests that a very large fraction of COD is associated with particles larger than 150 µm. Among the supracolloidal fractions, particles in the size range 25–50 µm seem to be predominant. The colloidal and soluble fractions (< 1 µm) sum up to about 31% of the total COD. In this case a better separation between colloidal and soluble fractions suggests that the colloidal fractions predominate over the soluble one, which is only about 11% of total COD. This is in agreement with the results of Vaillant et al. (1999), who used similar ultrafiltration techniques to separate soluble from colloidal COD.

In parallel with the sequential screening and filtration procedure, an aliquot of sewage sample was submitted to the settling test. The easily settleable fraction measured with the settling test is reported in Figure 2 as the area above the dashed line. Considering the portion of the cumulative distribution curve included in this area, it can be argued that the conventional association of settleable COD with particles larger than 100 µm may be sometimes misleading. In this case the settleable fraction seems to include also smaller particles, down to about 50 µm. On the other hand it must be kept in mind that this fraction is
operationally defined with a settling test under quiescent conditions that may be poorly representative for the dynamic conditions of a primary settling tank.

**Biodegradability of different size fractions**

In order to characterise the biodegradability of different COD fractions, the Oxygen Uptake Rate (OUR) method was used. As reported by the literature, preliminary tests with acetate as the sole carbon source are necessary. The typical OUR profile for acetate, reported in Figure 4, shows a fast increase in the respiration rate soon after acetate addition, followed by a steady oxygen consumption, and finally by a slow decrease to reach the endogenous level. The observed yield ($Y_{obs}$) can be calculated as follow:

$$Y_{obs} = 1 - \frac{\Delta O_2}{S_i}$$  \hspace{1cm} (1)

where $\Delta O_2$ is the overall amount of oxygen consumed during the test and $S_i$ is the initial acetate concentration. Three replicate tests with acetate gave a mean yield value of 0.78 COD/COD, which is typical for respirometric tests performed using urban activated sludge spiked with acetate (Xu and Hasselblad, 1996).

The same experimental approach with raw sewage provided the results reported in Figure 5. The OUR profile can be easily divided into a high-OUR phase (phase I, corresponding to readily biodegradable COD depletion) and a low OUR phase (phase II, related to the consumption of slowly biodegradable COD). Using $Y_{obs}$ obtained with acetate tests, COD consumed in phase I and in phase II may be easily calculated. Preliminary results with raw and filtered sewage suggest that only about 36% of COD is readily biodegradable, and that size fractions below 0.2 µm do not contain slowly biodegradable COD. These results are in satisfactory agreement with the work of Levine et al. (1991), who found that for colloidal particles the rate constants for biodegradation were significantly higher than those calculated for supracolloidal particles. Below 1 µm the reaction rate constants did not change significantly, being always at the maximum value.

The results of the biodegradability studies suggest that eliminating the slowly degradable particles prior to aerobic biological treatment promotes more effective utilisation of the biological treatment capacity.

**Improving primary treatment**

Table 1 shows that over 30% of COD in Roma-Nord influent sewage is not easily settleable, even though it is still in suspended form. In addition, the biodegradability studies indicated that this large portion of COD entering the biological section is not easily biodegradable, requiring a preliminary hydrolysis step. These results suggest that the overall treatment system could be improved by aggregating the finely dispersed COD in order to remove it in the primary section. To investigate the potential removal of finely dispersed COD in the primary treatment, lime coagulation tests were carried out in a pilot plant as described in the experimental section. Lime was chosen as coagulant due to its relatively low cost and because lime dosage is very easy to control through a pH-stat system.

Previous process optimisation studies suggested to work at pH 9 to avoid excessive sludge formation due to precipitation of calcium carbonate (Marani et al., 2002). Therefore, in this work sewage coagulation tests at pH 9 were compared with plain settling of the Roma-Nord influent sewage. Figure 6 compares treatment efficiencies, in terms of percentage of COD removed, obtained in the pilot primary treatment plant with and without coagulation with lime. Plain settling may remove influent COD with an average efficiency of about 30%, in agreement with average efficiencies typically reported for the conventional primary treatment. In contrast, the lime-enhanced primary treatment shows an average
**Figure 4** OUR profile in a typical batch test with acetate

**Figure 5** Typical OUR profile in batch test with raw sewage

**Figure 6** Comparison between plain and lime-enhanced settling of suspended COD from Roma-Nord sewage in pilot plan
treatment efficiency of about 65%. This additional 30–35% efficiency of COD removal is consistent with the hypothesis that coagulation may induce the almost complete removal of the supracolloidal fraction in the primary treatment.

Potential advantages of enhancing the primary treatment of sewage by a coagulation-flocculation step include:

- lower load to the biological section, with lower energy demand for aeration
- lower space required for the biological plants, due to the higher biodegradability of the residual COD fraction
- energy recovery through the anaerobic digestion of primary sludge.

**Conclusions**

- The sequential procedure of sieving and micro and ultrafiltration is suitable for a thorough fractionation of COD in sewage, in a large size range including five orders of magnitude
- This procedure, complemented with settling tests, showed that COD in Roma-Nord sewage is predominantly associated with settleable and supracolloidal particles, each size range including about 40% of total COD
- The biodegradability tests indicated that the large fraction of COD associated with supracolloidal particles is characterised by slow degradability, therefore suggesting that removal of these particles prior to biological treatment may greatly improve the overall treatment scheme
- Preliminary pilot plant coagulation tests with lime at pH 9 showed that the lime-enhanced primary treatment may increase COD removal efficiencies from typical 30–35% up to 65–70%, by inducing the almost complete removal of the supracolloidal COD fraction.

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**References**


