Refractory organic matter content in sewage sludge: inaccessibility for hydrolysis or/and chemical resistance?

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Abstract
Sludge valorization through methane production is highly limited by the biodegradability of the organic matter. This may be related to the physical and chemical properties of the sludge organic matter that define its bioavailability, its bioaccessibility and its biodegradability. The objective is here to analyze the relationship between the physical state (floc) and the refractory content of a sludge. As depending on the sludge origin, experiments were made for sludge samples coming from plants running at very different sludge retention time. The range of the unbiodegradable COD content (COD_U) is between 42 and 73%. The COD_U remains mainly in the particulate form with a size distribution unchanged compared to the raw sludge before anaerobic digestion. Soft heating tests show that the major part of the biodegradable COD is easily solubilized whereas the refractory materials remain particulate. That means that the COD solubilisation potential of a given sludge can be used to indirectly get a fingerprint of its unbiodegradable COD content. Finally, the refractory particulate organic matter ensures the aggregated structure of flocculated sludge. Their components form a strongly cohesive porous matrix whose function could be assimilated to a skeleton entrapping the biodegradable matter.

Keywords
Anaerobic biodegradability; activated sludge; COD solubilisation; thermal desorption; refractory particulate fraction.

INTRODUCTION

Methane production from sludge is an appealing solution to combine sludge stabilisation and energy production. However, the bioavailability of the sludge COD must be improved to optimize methane production. Thus a better knowledge of the mechanisms limiting the COD anaerobic biodegradation is required. The sludge unbiodegradable COD (COD_U) comes from both the wastewater unbiodegradable organic matter, $X_{U,inf}$, and the refractory material produced by cell metabolism, $X_{U,E}$. Besides chemical resistances, the unbiodegradable character could result also from the aggregation that would limit the anaerobic biodegradation. Consequently, various disintegration strategies based on mechanical, electrical, thermal, thermo chemical and oxidative treatments were widely studied to force the organic matter hydrolysis and thus provide a bioavailable carbon source (Weemaes and Verstraete, 1998, Liu and Tay, 2001, Paul and Liu, 2012). Nevertheless only few works associate biodegradability analysis and characterization of the residual refractory material (Ramdani, 2012, Park, 2008).

In the current work, the impact of the mesophilic anaerobic biodegradation of sludge on the physical fractionation of the unbiodegradable COD (COD_U) is studied in batch. Firstly, the range of the refractory COD content is assessed for sludges sampled at a same plant but at different times or sampled at various plants running under different sludge retention times (SRT). Then, disintegration of the flocculated structure was attempted by heating the sludge at a rather low temperature (65±2°C). COD desorption and solubilisation were analyzed. The unbiodegradable COD content in both the remaining particulate and the solubilized COD fractions were followed to link the refractory character to the physical properties of the COD.

MATERIALS AND METHODS

Characterization of secondary or mixed sludge analyzed in the present work is presented in table 1.

Quantification of the anaerobic unbiodegradable COD fraction in mesophilic conditions

For a given sludge sample, the refractory COD fraction, COD_U, is determined as the complementary fraction of the biodegradable COD fraction, COD_B. COD_U is determined from the long term biochemical methane potential (BMP) assay (in duplicate) and is calculated from the following equation: COD_U = total COD_{sample} – COD_B (where $COD_B = (V_{CH4}/COD_{sample})/350$). Experimental conditions of BMP followed in this work are described in Dumas, 2010.

Sludge disintegration by heating at low temperature

Sludge placed in a jacketed stirred glass reactors were heated at 65±2°C during 150h. Soluble and particulate COD were measured along the assays and COD mass balances revealed that no COD was lost for all the experiments. The solubilisation yields are calculated in term of soluble COD per gram of total initial COD. The soluble fractions were obtained by centrifugation at 4000 g for 15 min.

Analytical methods

Measurements realised on the raw and the thermally treated sludge were: COD concentrations by using the NFT 90-101 from the Standard Methods (1995); the particle size distribution, expressed in terms of volume, with a laser granulometer (Microsizer 2000 Malvern) whose the measurement range is 0.02-2,000 µm. The samples were diluted to reach less than 0.5 g/l of suspended solids to avoid reflocculation process.

RESULTS AND DISCUSSION

The sludge COD_U content results from the accumulation of the unbiodegradable wastewater organic matter and of the refractory microbial metabolism products that depend highly on the operating parameters such as the SRT. In this way, the relationship between the flocculated state and the refractory character of the COD need to be analyzed for sludge for different plants. Firstly, COD_U was measured for five sludges whose the plants operate at a SRT ranging from 2 to 20 days (Table 1).

Figure 1 shows the evolution of the CODU fraction for a secondary sludge sampled five times over a period of eight months at a same urban WWTP (C in the table 1). Its CODU content fluctuates between 47 and 64 %. This difference is meaningful, since higher than the BMP test standard deviation (4 %).

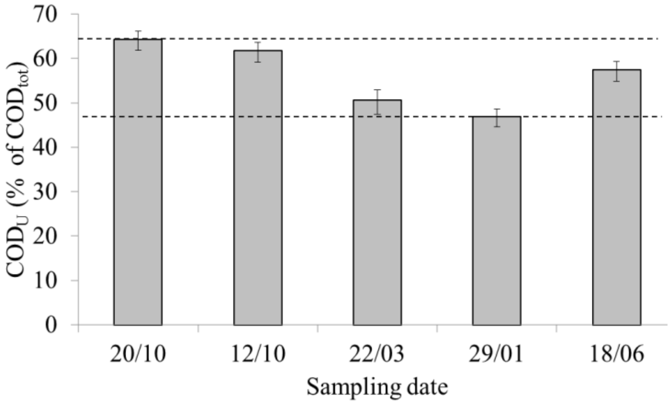

Figure 1. Evolution of the COD_U content for the secondary sludge originated from the plant C (table 1).

Table 1 gives the results for the different WWTP with increasing SRT. The variability of the content in COD_U observed for one given WWTP is as high as the variability observed for various plants. Despite this variability, the average COD_U increases from 49 to 70 % when the SRT increases from 2 to 20 days. The SRT parameter is indeed known as one of the most impacting operating parameter on the global sludge biodegradability.

Table 1. Characteristics of the different studied sludges

Plant	SRT	Refractory COD fraction		
	Days	Range (%)	Average ± SD (%)	Frequency of sampling and studied period
A(1)	2-3	41 - 56	49 ± 4	3 times over 7 months
B(2)	8	49 - 61	56 ± 4	8 times over 4 months
C(1)	10	47 - 64	56 ± 6	5 times over 8 months
D(3)	15	65	65	No data
E(1)	15-20	68 - 73	70 ± 3	2 times over 2 months

(1) Urban WWTP in the south of France; (2) Laboratory pilot supplied by reconstituted urban wastewater with primary sludge and biodegradable COD; (3) Ekama, 2007

These sludges with very different COD_U content were characterized once completely digested. Whatever the sludge, at the end of BMP tests, more than 90% of the total refractory COD are still particulate with a flocculated form. Figure 2 illustrates the size distribution measured before and after the BMP tests and highlights that the consumption of the biodegradable COD did not change the apparent physical structure of the raw sludge. Hence the organic materials that composed the COD_U may be seen as a skeleton that entrapped the biodegradable COD.

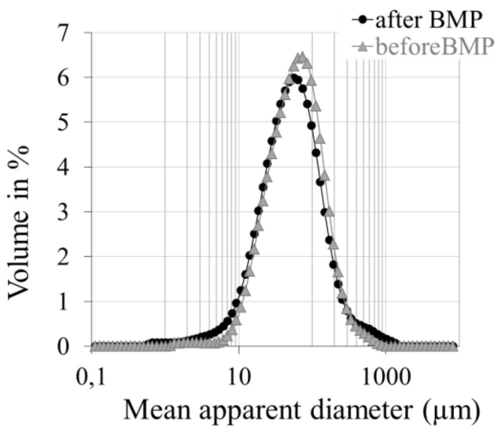

Figure 2. Comparison of the particle size distribution of the sludge before and after a long term BMP test (data for plant C).

The physical stability of the sludge refractory matrix was analyzed through soft disintegration tests (for sludges from plants A, C and E). For this, heating at 65°C was applied on sludge to desorb and solubilize the material weakly linked to the sludge skeleton. At this temperature, no chemical denaturation occurred (energy provided is too low to induce covalent bound rupture). For all the treated sludges, a rapid COD solubilisation is firstly observed lasting a few hours followed by a much slower solubilisation that continues up to 150h. The solubilisation yields measured at the end are comprised between 32 and 77 % in term of COD. Simultaneously, BMP tests on the whole sludge performed at different heating times revealed that no significant increase of the anaerobic biodegradability was achieved due to the heating, as is illustrated in figure 3-I for one of the treated sludge whose the biodegradable COD of the total fraction remain at 39 ± 3 %. Long term BMP tests on both the particulate and solubilized COD fractions were also performed in order to assess the quality of the solubilised COD in term of biodegradability. Figure 3-I shows that 80% of the total biodegradable COD shift to the soluble fraction after 150h. Therefore, heating at 65 °C improve the bioavailability of the biodegradable COD but let the refractory COD fraction unchanged, always mainly in a flocculated state. This residual matrix involves very stable bounds or/and interactions between the constitutive molecules. Its chemical composition must be more deeply characterized in order to overcome this chemical resistance to the biodegradation.

Finally, as plotted in Figure 3-II, the percentage of sludge refractory material is found inversely proportional to the maximum COD solubilisation yield obtained at 65°C. The COD solubilisation potential can be considered as a relevant sludge refractory fingerprint. The 65 °C heating test could be a relatively fast test, compared to long term BMP test, to assess both the biodegradable and refractory sludge contents.

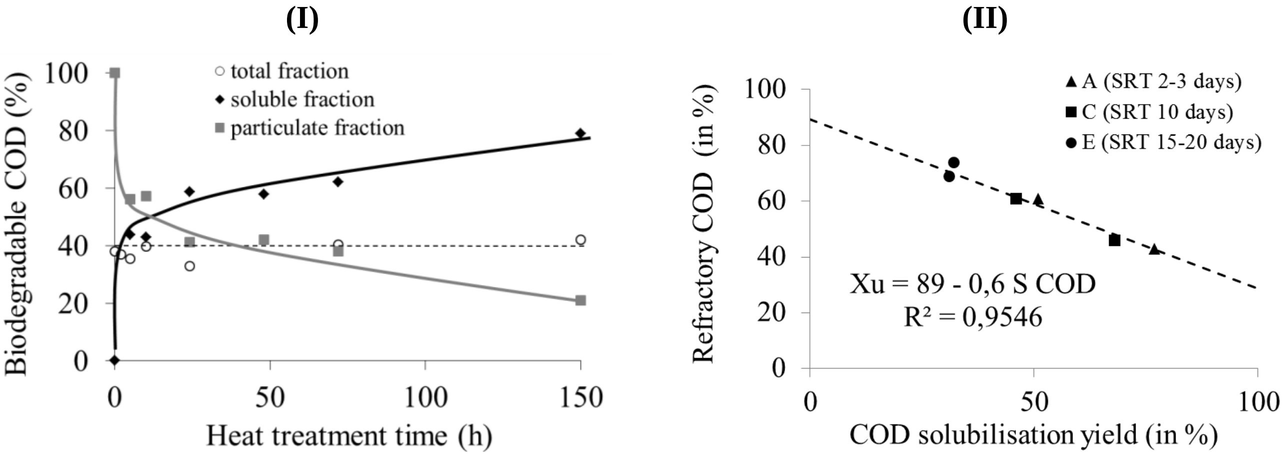

Figure 3. (I) Repartition of the biodegradable COD along the solubilisation at 65°C; (II) Relationship between the COD solubilisation yield and the unbiodegradable COD fraction for various sludges.

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