Rethinking wastewater characterisation methods for activated sludge systems – a position paper

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ABSTRACT

Increasingly stringent effluent limits and an expanding scope of model system boundaries beyond activated sludge has led to new modelling objectives and consequently to new and often more detailed modelling concepts. Nearly three decades after the publication of Activated Sludge Model No1 (ASM1), the authors believe it is time to re-evaluate wastewater characterisation procedures and targets. The present position paper gives a brief overview of state-of-the-art methods and discusses newly developed measurement techniques on a conceptual level. Potential future paths are presented including on-line instrumentation, promising measuring techniques, and mathematical solutions to fractionation problems. This is accompanied by a discussion on standardisation needs to increase modelling efficiency in our industry.

Key words | activated sludge, ASM, chemical oxygen demand fractionation, modelling, wastewater characterisation

INTRODUCTION

Wastewater characterisation has been an ongoing topic of research (Spanjers et al. 1998; Henze et al. 2000) and is still a major challenge for model application in engineering practice (Copp et al. 2009; Phillips et al. 2009). Fractionating the variables that are traditionally measured by practitioners (chemical oxygen demand (COD), nitrogen and phosphorus) into model variables (different classes of biodegradability) is an important input to the model. Calibration of the model parameters by adopting an incorrect fractionation of the wastewater composition may lead to compensation of the
fractionation errors by introducing errors in the parameter estimates (Rieger et al. 2012). Moreover, combined expertise of modellers (Phillips et al. 2009) and sensitivity analysis (Petersen et al. 2002) have shown profound effects of wastewater characterisation on modelling outputs (Henze et al. 2000):

- Sludge production is influenced by the estimated inert particulate COD.
- Oxygen demand is influenced by the estimated total biodegradable COD.
- Anoxic denitrification rate and anaerobic phosphorus release are influenced by the estimated readily biodegradable COD.
- Effluent COD is influenced by the estimated inert soluble COD.

Although some milestone research has been published (STOWA: Roeleveld & van Loosdrecht 2002; WERF: Melcer et al. 2003; BIOMATH: Vanrolleghem et al. 2003), and a recent attempt at guidelines has been proposed (Lu et al. 2010), there is a lack of standardisation. Gillot & Choubert (2010) and Fall et al. (2011) compared different experimental COD fractionation approaches and found significant differences in the results.

New measurement techniques allow for a more detailed evaluation of the wastewater, but the techniques published decades ago can provide significant insight into a particular wastewater when performed properly and the results are analysed appropriately. In practice, questionable results are commonplace due to a lack of standardisation and method complexity (Rieger et al. 2012). In this context, this paper gives a brief overview of state-of-the-art methods for wastewater characterisation and discusses gaps in research. It presents recently developed measurement techniques on a conceptual level, and explains new insights into wastewater characteristics and involved components. Potential future paths are presented including on-line instrumentation, promising measuring techniques, and mathematical solutions to fractionation problems. This is accompanied by a discussion on standardisation needs to increase modelling efficiency in the wastewater treatment field. The paper focuses on wastewater characterisation methods for activated sludge systems and does not intend to cover all aspects of wastewater characterisation. Links are made to membrane systems, biofilm systems and anaerobic digestion processes as they can either provide ideas for improving, or taking advantage of developments in, activated sludge wastewater characterisation methods.

**EXISTING WASTEWATER CHARACTERISATION METHODS**

In the Activated Sludge Model (ASM) framework (Henze et al. 2000), the influent COD of a wastewater is split into different fractions. For Activated Sludge Model No1 (ASM1), six fractions are considered (slowly biodegradable, readily biodegradable, inert soluble and inert particulate, heterotrophic and autotrophic biomass). In ASM No2d (ASM2d), the readily biodegradable fraction was divided into fermentable organic matter and fermentation products (volatile fatty acids, VFA); moreover, storage compounds in biomass and an additional biomass were considered. In ASM No3 (ASM3), similar fractions to ASM1 are considered with additional organics stored by heterotrophic biomass. In the literature, most of the fractionation methods are dedicated to the differentiation between inert and biodegradable fractions, readily or slowly biodegradable variables, initially defined for ASM1; however, most of the following protocols and statements are valid by extension for ASM2 and ASM3. This approach assumes the wastewater is devoid of biomass, has no inert endogenous products and includes inert soluble material. Although not ideal or detailed enough to account for all constituents, these assumptions have proven to be effective in the past and are linked to the model structures.

Comparison of the most relevant protocols showed only slight methodological differences for the characterisation of the nitrogen and phosphorus fractions. However, for the characterisation of the wastewater COD, there are different approaches. Table 1 presents the methods and concepts. The following discussion briefly presents the limitations caused by the differences between conceptual meaning and experimental results.

The existing methods of fractionating COD into the different fractions of a given wastewater generally combined the determination of the total biodegradable COD fraction (COD_{tot,B}) and the determination of the readily biodegradable COD (noted S_B).

Two types of biological assay have been proposed to determine the total biodegradable COD fraction of a given wastewater:

- Direct monitoring using the oxygen uptake versus time in batch experiments. Various protocols exist, but typically methodologies include respirometry monitoring the modification of the oxygen uptake rate for a few hours with a low substrate to biomass ratio (S/X) (Spérandio et al. 2001; Vanrolleghem et al. 2003), ultimate biochemical oxygen demand (BOD) tests monitoring the
total oxygen uptake for 10 days with a high S/X ratio (Roeleveld & van Loosdrecht 2002), or monitoring the COD uptake versus time (total and soluble) for 30 days with a high S/X ratio (Lesouef et al. 1992; Orhon et al. 1997; Stricker et al. 2005).

- Indirect assessment of COD_{tot,B} by determination of the particulate unbiodegradable COD (X_{U,Inf}) of the wastewater. This fraction is deduced by using a simulation model to match experimental sludge production in a bioreactor (Melcer et al. 2005).

Three distinct principles have been used to determine the readily biodegradable COD (noted S_B):

- Bioassay tests that are based on respirometric characterisation methods where oxygen or nitrate utilisation rates (OUR and NUR, respectively) are recorded (Ekama et al. 1986; Naidoo et al. 1998; Spanjers et al. 1999).
- Physical-chemical methods that assume a direct link between the size of organic molecules and their biodegradability. Filtrations with different pore sizes (Roeleveld & van Loosdrecht 2002; Lu et al. 2010), and with or without a flocculation step (Mamais et al. 1993) have been proposed.
- VFAs are typically measured directly using gas chromatography method (Martin-Ruel et al. 2005).

COD fractions (and particularly readily biodegradable COD) are measured (or estimated) with batch experiments and first used for plant model set-up. Although wastewater characterisation is considered as part of the data collection
step by the IWA Good Modelling Practice Task Group (Rieger et al. 2012), there is a possibility to modify the obtained fractions during one of the three main steps that compose the calibration procedure. The latter starts with fixing the parameters that represent hydrodynamics (number of tanks, flow distribution), then continues with modifying the influent wastewater or recycle streams’ characteristics, and finishes with parameters’ estimation: settling parameters, aeration parameters (oxygen mass transfer over time description) and biokinetic parameters (stoichiometric, kinetic). Influent wastewater characterisation and parameter assignment (also called ‘calibration’ stricto sensu) are therefore related stages when adjustments of the fractions are required (at least to take into account measurement errors), for example modifying the inert particulate COD (i.e. $X_{U,\text{Inf}}$) to match the sludge production. To avoid this fine-tuning, the industry would have to develop methods to better represent the inert particulate COD (i.e. $X_{U,\text{Inf}}$).

ADAPTATION OF EXISTING METHODS

Changes to the influent fractions (i.e. percentage of total COD) are not uncommon under wet-weather conditions or due to temperature variations (Henze 1992). In plants with long hydraulic buffering capacity (like those applied in conventional activated sludge, 6–24 h) it is often sufficient to separate the COD into biodegradable/unbiodegradable fractions. However, with the migration to more stringent effluent requirements, and the development of short hydraulic retention time (HRT) processes (few tens of minutes), this assumption may need to be revisited.

The following discussion briefly presents the limitations caused by the differences between conceptual meaning and experimental results, and suggests some recommendations.

Impact of the experimental protocol on the fractionation results

Even with defined approaches, the experimental methods and resulting output still remain sensitive to practical inaccuracies due to the complex ecosystem biology, the biodegradable fractions that depend on protocol length (few hours to a couple of days) and substrate to biomass ratio (Gillot & Choubert 2010), or physical limitations such as filter pore size (Fall et al. 2011). The wide variety of possible experimental conditions in the methods further complicates the interpretation of results.

Even for apparently simple methods (e.g. physical-chemical separation), differences are obtained (e.g. due to differences in filter pore size 0.7, 0.45 or 0.1 μm according to Fall et al. (2011)). Coagulation/flocculation prior to filtration reduces the importance of the filter pore size; however, if not standardised or reported it may lead to further ambiguity in determining results.

A change in model structure or the introduction of another state variable makes it necessary to adapt the experimental methods also. It is important to use a fractionation method that fits the model concepts. ASM1 is based on the biodegradability of the fractions, but for practical reasons the profession has turned to physical–chemical methods (Roeleveld & van Loosdrecht 2002). Thus, several concerns have been raised about the comparability of the methods and how to link the physical–chemical methods with the biodegradability of the different fractions.

The obtained fractionation based on measurements is sometimes adapted during model calibration to be consistent with other data collected on the plants (Rieger et al. 2012). During the calibration step, certain fractions can be changed until simulation results match observed data; for example, it is not unusual to modify the inert COD fraction to fit the simulated sludge production to the observed values. However, this indicates problems with the link between what the modeller requires and what these experimental procedures actually measure. As a result, the value of expensive wastewater characterisation studies – which are essential for good predictions – might be questioned if the results cannot be applied in all cases, and might be critical for the application of modelling in today’s engineering practice. Other sources of information about plant behaviour are nevertheless always required and can minimise the probability of a deficient wastewater characterisation.

Changing COD fractions for long sludge retention time processes

The plant type to which a wastewater is introduced determines how the wastewater should be characterised. Haider et al. (2000) and Spérandio et al. (2013) clearly identified a larger biodegradable fraction when the same wastewater was subjected to a longer sludge age process. The definition of specific fractions can be process specific. For example, material considered inert in a short sludge retention time (SRT) system (e.g. those applied in conventional activated sludge) may not be inert in long SRT systems (e.g. membrane bioreactor (MBR), sludge reduction techniques, constructed
wetlands). New model concepts that improve the understanding and models incorporating hydrolysis are suggested below.

**Changing COD fractions versus time**

Under dry-weather conditions, a basic assumption in today’s modelling practice is that influent fractions are stable over time during a 24 h period (Henze 1992). However, it may change with temperature (Henze 1992). Also in the case of wet-weather treatment, significant changes in the fraction of \(X_{U,\text{Inf}}\) and \(X_{C_B}\) due to rain may have to be considered. Improving the determination of the colloidal COD fraction is important for a better prediction of sludge production and optimisation studies (Petersen et al. 2002; Rönner-Holm et al. 2009). Variations in the estimated COD fractions through the day are another potential concern as clearly shown in Figures 1(a) and 1(b). These results were obtained with the STOWA protocol on 2 h composite samples (Barry et al. 2012; Morvannou 2012). One would expect more stable ratios but the measurements of lumped COD show that the \(\text{COD}_{\text{filtered}}/\text{COD}_{\text{tot}}\) ratio varied between 20 and 60% (Figure 2(a)) and the \(S_B\) fraction varied between 5 and 25% of the total COD over a period of a few hours (Figure 2(b)) (Hess 2001). Large variations in the COD fractions over the course of a single day were also noted in Germany (Hintermaier & Thiele 2005; Affeld 2006; Roog 2005).

Assuming that the previous variations are not plant specific and are not due to measurement artefacts, it is clear that the plant behaviour may well vary throughout the day as a direct result of the variability in wastewater fractions. The impact of these fraction variations is even more critical when modelling systems with HRTs of only a few tens of minutes (e.g. of A-stage of an A/B plant, moving-bed biofilm bioreactor (MBBR)), so it is reasoned that a higher temporal resolution of the fractionation would then improve simulation results (Haider et al. 2000). Future research needs to address the magnitude and the impact of the variations. However, in the short term, it would seem prudent to estimate the variations in the COD fractions using a time series of total, filtered and flocculated-filtered COD, instead of using incorrectly measured \(S_B\) and \(X_{C_B}\) values.

**NEW AND ALTERNATIVE METHODS**

The development of new treatment processes and the need to predict very low nutrient effluent concentrations requires model extensions and consequently adapted influent characterisation methods. Still, models and fractionation methods have to be complementary, and the model objective should be taken into consideration when selecting a fractionation method. To meet this next challenge, and to meet the needs of different modelling objectives, modellers will have to consider new measurements, experiments/procedures, checks, data resolution and also model changes. Table 2 provides expected adaptations of fractionation concepts published in the literature that are then explained in the subsequent paragraphs.

**Biomass determination**

Most characterisation protocols assume that wastewater is devoid of biomass \((X_{\text{OHO}} \approx 0)\), including the related COD in \(X_{U,\text{Inf}}\) and \(X_{C_B}\). These assumptions have proven to be effective in the past as it did not impact model predictions in activated sludge systems (Melcer et al. 2005) and the assumptions were linked to the model structure. However, active heterotrophic biomass has been estimated to be up to 25% of the raw wastewater COD (Henze 1992; Spérandio et al. 2001). Compensating for this assumption (i.e. considering this COD to be slowly biodegradable \(X_{C_B}\)) may require
that the yield coefficient be increased by approximately 10% (Henze 1992).

This is observed when modelling systems operated at high loading rates, or when modelling downstream of a preliminary stage of biological treatment, as the influent biomass should not be incorrectly assumed to be zero, otherwise the behaviour of the models may have to be incorrectly altered (by changing parameters) to compensate. Thus a more systematic measurement of active biomass content in influents might reduce calibration efforts. Respirometry can be used for active biomass determination and it is still the recommended method for modelling application. Progress towards biomass determination is expected with the development of quantitative biomolecular techniques (e.g. quantitative real-time polymerase chain reaction) but until now these methods have not demonstrated their superiority for model validation or calibration.

**Standardisation of biological tests**

Respirometric biological tests are subjected to uncertainty (Gatti et al. 2010), for example the endogenous state can be confounded by slow hydrolysis, or sludge that is not adapted (unacclimatised) to the wastewater. Two suggestions are made to improve the results: the first one is to standardise the conditions that define when a respirometric test enters the endogenous respiration phase (i.e. when all substrate is consumed). Experience indicates that most of the error is introduced because of the uncertainty in identifying this transition.

The second option is to improve our understanding of biomass development inside the bioreactors (e.g. compliance to biomass growth and decay concepts used to model OUR), and to develop ways to grow the biological inoculums for seeding bioreactors, so that the results are not dependent on the level of acclimation of the biomass.

**New probes**

On-line sensors for measuring COD, NH₄, PO₄, NOₓ and total suspended solids (TSS) have shown the potential for on-line analysis and control of biological systems. Newer types of probes offer even more potential for collecting more detailed wastewater characterisation data. The data from on-line respirometer or UV-vis probes (with appropriate correlations) allow for a continuous estimation of wastewater fractions. It is expected that significant strides towards ensuring the quality of these data will have to be made in the future. However, the benefits gained with respect to parameter uncertainty and model predictive power have been shown by Cierkens et al. (2012).

**Inorganic compounds**

The use of inorganic suspended solids (ISS) (Melcer et al. 1998; Ekama & Wentzel 2004) has improved the predictions of sludge production in terms of suspended solids (total, TSS). As the requirement for more detailed models increases, there is a clear need for an improvement in the prediction of inorganics, and especially those involved in precipitation/dissolution (sulphide, magnesium, calcium, iron, aluminium, phosphates and nitrogen). This requirement may include a procedure to distinguish between different fractions of mineral suspended solids in raw wastewater and in biological sludge (e.g. inert, bound to organic matter, etc.). There will be a requirement for more detailed influent information including pH, and salt/metal concentrations. It is also possible that the use of models for warm climate applications may require sulphur modelling, and the measurement of the different sulphur fractions (Sharma et al. 2008).
Mathematical estimation/verification

With more and often contradictory data, new methods would be helpful to facilitate data reconciliation in wastewater fractionation analysis. Automated techniques based on statistical analyses could improve fractionation quality and consequently reduce calibration needs of kinetic parameters in biological reactors. Grau et al. (2007) proposed a relationship between the model component and the most common analytical measurements in the wastewater, combining a priori knowledge of the expected wastewater composition and experimental information. An optimisation algorithm uses an extended list of non-redundant model components with definition of their elemental mass balance fractions in
terms of C, H, N, O, P and charge. This approach might be applied more systematically to improve the estimation of COD fractions.

**HOW MODEL EXTENSIONS INFLUENCE FUTURE WASTEWATER CHARACTERISATION**

The need to account for other processes is obvious when dealing with the modelling of sulphur production (Sharma et al. 2008), modelling of the fate of micropollutants (Plósz et al. 2013; Pomiès et al. 2013), modelling of MBR clogging (Naessens et al. 2012) or modelling the emission of greenhouse gas (Ni et al. 2011).

Future wastewater characterisation may need to account for new model components such as a very slowly biodegradable COD fraction, detailed organic matter characterisation (e.g. molecular level variables and/or particle size distribution), or fractionation for nutrients.

**Very slowly biodegradable COD fraction**

Recent analyses (e.g. Menniti et al. 2012; Spérandio et al. 2013) has demonstrated that hydrolysis of particulate undegradable endogenous products (X_{U,E}) and particulate undegradable organics from the influent (X_{U,in}) – using a slow hydrolysis rate (Ramdani et al. 2010) – might be suitable to deal with measured behaviour in long SRT systems such as processes operated under very low organic loading rate (AS or MBR plants designed with long time capacity). This approach might also be introduced to model sludge reduction where a portion of the inert particulate COD might become biodegradable (e.g. Cannibal process, mycelium hydrolysing). A state variable for ‘very slowly biodegradable matter’ might increase the range of applicable SRTs. However, a dedicated procedure is still needed to accurately assess this fraction in the wastewater.

**Molecular level variables/particle size distribution**

The hydrolysis rate is a function of the influent characterisation. Simulations of biological nutrient removal (BNR) plants with ASM1 suppose a conversion of X_{C_B} into S_{B}, and use the instantaneous X_{C_B}/X_{OH_2} ratio in a bioreactor to predict the hydrolysis rate (Henze et al. 2002). However, in some cases, more detailed organic matter characterisation (e.g. molecular level variables, particle size distribution) will benefit description of hydrolysis phenomena. More accurately predicted hydrolysis rates would then be obtained for denitrification or anaerobic phosphorus release (Drewnowski & Makinia 2011). Also, the assumption that compounds of a certain class (colloidal or particulate) are hydrolysed at an equal rate irrespective of their source (i.e. centrate or influent) is potentially problematic for modelling. More detailed organic matter characterisation becomes also relevant for wastewater characterisation when wastewater contains industrial discharges, whereas it is probably not necessary for standard applications and objectives for domestic wastewater.

Besides using substrate availability, a few protocols have been proposed to help with the calibration of hydrolysis at macro-scale (Naidoo et al. 1998; Martin-Ruel et al. 2005). Recently, papers reported that a deeper characterisation of the organic matter should be considered to improve the hydrolysis prediction:

- Fractionating the influent at a molecular level (i.e. lipids, proteins and carbohydrates) because hydrolysis rates are likely to be component specific. Indeed, systematic measurements of these components may provide added clarity (Gorini et al. 2011). The correlation between these components and the COD fractions is still insufficiently investigated. In comparison, those components were included in Anaerobic Digestion Model No 1 (ADM1) for the prediction of gas production with wasted sludge (Batstone et al. 2002; Henze et al. 2002) and were shown to be essential for the prediction of the behaviour of some micropollutants (Barret et al. 2010).
- Particle size distribution, in association with a surface-based kinetics, may lead to a better description of hydrolysis, assuming that particles breaking up into smaller ones will allow for an increasing hydrolysis rate over time (Dimock & Morgenroth 2006). The molecular weight and the nature of chemical bonds may also provide information about the transformation pathways (Sophonsiri & Morgenroth 2004).
Fractionation for nutrients

Plants facing very low effluent nutrient limits (one tenth to one hundredth milligram per litre, Neethling et al. (2010), may need to consider several things including refined fractionation methods as well as model extensions. Nutrient sources and fractionation becomes important (e.g. treating return liquors from digesters) and the modelling of municipal wastewaters containing some industrial discharges with unbiodegradable nitrogen may become significant.

Urea and ammonia are the main sources of nitrogen in raw municipal wastewater ($S_{\text{NH}4}$ ~ 60–75% of total Kjeldahl nitrogen) while the rest is typically organic nitrogen, split into slowly biodegradable ($X_{\text{BN}}$ ~ 22%), readily biodegradable ($S_{\text{BN}}$ ~ 2%) and inert soluble ($S_{\text{UN}}$ ~ 1%) (Henze 1992; Rieger et al. 2012). Future experimental methods should be developed to characterise the dissolved organic nitrogen in a discharged effluent. As nutrient limits decrease, this fraction becomes increasingly important and could account for 0.7–2.1 mgN/L (Pehlivanoglumantas-Mantas & Sedlak 2008). Often, this nitrogen is incorrectly believed to be inert whereas it may be composed of very slowly biodegradable substances. Baiyang et al. (2011) found degradation of up to 30% of this nitrogen in 5-day degradation tests. Arnaldos & Pagilla (2010) reported that amino acids account for less than 50%, with the rest being heterogeneous in nature, and composed of low-molecular weight nitrogenous substances.

Some of these concepts are research focused, while others are dedicated to engineering application.

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