

A plant-wide aqueous phase module describing pH variations and ion speciation/pairing in wastewater treatment process models

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Summary of key findings

The key outcomes can be summarized as follows:

- The presented approach is a versatile/general module that can be easily added to different ASM/ADM models.
- pH and ionic speciation/pairing are reliably predicted under anaerobic, anoxic and aerobic conditions in both ASM and ADM models.
- The computing routine developed in this study allows the simultaneous numerical solution of ODEs and DAEs with multiple algebraic inter-dependencies using different types of solvers (stiff/non stiff).
- Wastewater modelling studies can be complemented with a rigorous description (speciation) of the inorganic species. Thus, it is possible to visualize the changes in the inorganic species under anaerobic, anoxic or aerobic conditions.
- The presented approach is a starting point upon which additional models, such as multiple mineral precipitation can be developed.

Background and relevance

There is a growing interest within the Wastewater Treatment Plant (WWTP) modelling community to correctly describe physico-chemical processes after many years of mainly focusing on biokinetics (Batstone et al., 2012). Indeed, future modelling needs, such as a plant-wide phosphorus (P) description, require a major, but unavoidable, additional degree of complexity when representing cationic/anionic behaviour in Activated Sludge (AS)/Anaerobic Digestion (AD) systems (Ikumi et al., 2014). In this paper, a plant-wide aqueous phase chemistry module describing pH variations plus ion speciation/pairing is presented and interfaced with industry standard models. The module involves extensive consideration of non-ideality by including ion activities instead of molar concentrations and complex ion pairing. The general equilibria are formulated as a set of Differential Algebraic Equations (DAEs) instead of Ordinary Differential Equations (ODEs) in order to reduce the overall stiffness of the system, thereby enhancing simulation speed. Additionally, a multi-dimensional version of the Newton-Raphson algorithm is applied to handle the existing multiple algebraic inter-dependencies (Solon et al., 2015). Simulation results show pH predictions when describing Biological Nutrient Removal (BNR) by the activated sludge models (ASM) 1, 2d and 3 (Henze et al., 2000) comparing the performance of a nitrogen removal (*WWTP1*) and a combined nitrogen and phosphorus removal (*WWTP2*) treatment plant configuration under different anaerobic/anoxic/aerobic conditions (Flores-Alsina et al., 2012). The same framework is implemented in the Benchmark Simulation Model No. 2 (BSM2) version of the Anaerobic Digestion Model No. 1 (ADM1) (*WWTP3*) (Batstone et al., 2002; Rosen et al., 2006) as well, predicting pH values at different cationic/anionic loads. In this way, the general applicability/flexibility of the proposed approach is demonstrated by implementing the aqueous phase chemistry module in some of the most frequently used WWTP process simulation models. Finally, it is shown how traditional wastewater modelling studies can be complemented with a rigorous description of aqueous phase and ion chemistry (pH, speciation, complexation).

Results

The results of implementing the aqueous phase chemistry model in ASM1 and ASM3 using *WWTP1* are depicted in **Figure 1a**. In the anoxic zone (ANOX1 and 2) biological oxidation of organic substrates (S_{ac}) using nitrate (S_{NO_3}) as electron acceptor takes place. As a result S_{NO_3} is converted to nitrogen gas (S_{N_2}), removing an anion (i.e. strong acid), and thereby increasing pH. In the aerobic zone (AER1, 2 and 3) the organic acids (S_{ac}) and ammonium (S_{IN}) are oxidized to inorganic carbon (S_{IC}) and NO_3 , respectively, both of which cause a net pH decrease (production of a weaker acid S_{IC} from the acid S_{ac} and acid S_{NO_3} from the base S_{IN}). Nevertheless, the aeration in AER1, AER2 and AER3 promotes stripping of carbon dioxide (Gas_{CO_2}) which consequently causes a rise of pH. Note that aeration in AER3 is less intense compared to AER1 and 2, therefore the pH rise in that reactor is also lower. The effect of including an additional anaerobic section is also depicted in **Figure 1a**. Under these conditions, the uptake of organic acids (S_{ac}) produces poly-hydroxy-alkanoates (X_{PHA}). Concurrent with S_{ac} reduction, there is a release of inorganic phosphorus (S_{IP}) as well as free potassium (S_K) and magnesium (S_{Mg}) ions, which results from the decay of poly-phosphates (X_{PP}). As a consequence, there is a decrease of pH in ANAER2. A similar pattern as described for *WWTP1* also holds for the anoxic and aerobic zones in *WWTP2* (further information can be found in section 3 of the Supplemental information). In the two cases (*WWTP1* & 2) and for the three models (ASM1, 2d and 3) the oxidation of S_{ac} and S_{IN} (with no stripping), slightly decreases pH at the top of the clarifier (OVER). At the bottom of the clarifier (UNDER), in the systems without biological P removal, the extra denitrification in the reactive settler model increases pH as described above for anoxic conditions. On the other hand, when there is bio-P removal, and consequently P release, pH is predicted to decrease.

The study further evaluates the behaviour of *WWTP3* when increasing the cationic load. The objective of this additional exercise is to show the impact that monovalent/divalent ion pairing can have on the predicted overall process performance. Thus, an additional waste stream with a constant flow rate of $5 \text{ m}^3 \cdot \text{day}^{-1}$ is included. The cationic influent concentrations range from 0 to $2.5 \text{ mol} \cdot \text{L}^{-1}$, which leads to five additional scenarios to be evaluated (SC1, SC2, SC3, SC4 and SC5). The cationic loads are (equally) distributed either into sodium (Na) and potassium (K) (monovalent) or calcium (Ca) and magnesium (Mg) (divalent). A series of simulations are re-run to see the overall effect on 1) species distribution and 2) biogas production. **Figure 1b** depicts the total biogas generation for the different scenarios that are investigated. Results show a substantial reduction of Gas_{CO_2} stripping at high divalent cationic loads (S5_D) compared to a similar scenario but with monovalent cationic loads (S5_M). This is attributed to the effect of ion pairing and the resulting modifications of the $S_{HCO_3^-} / S_{H_2CO_3^*}$ ratio. Methane production (Gas_{CH_4}) is not affected.

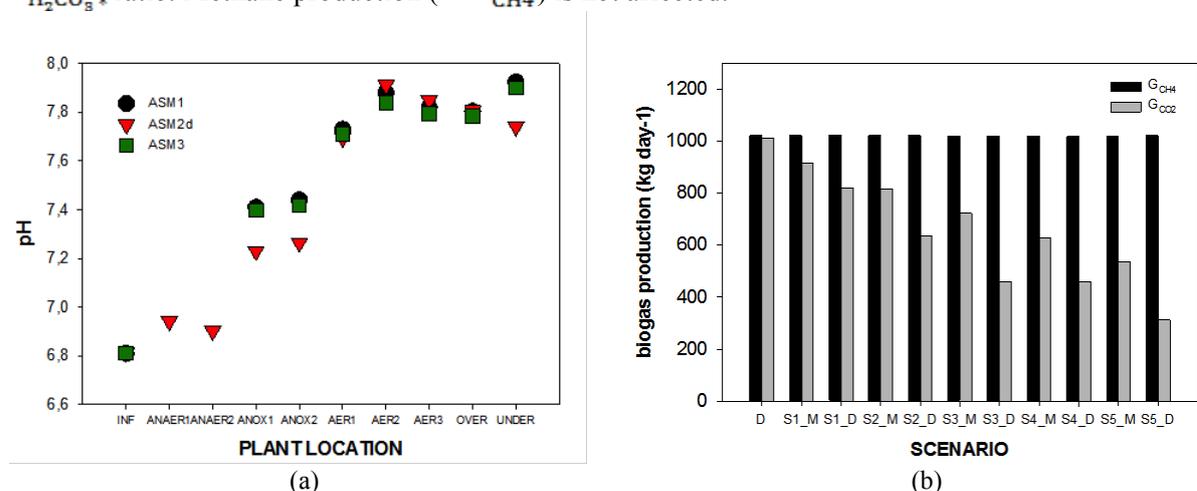


Figure 1. pH predictions in the different units for *WWTP1*(ASM1, 3) and *WWTP2* (ASM2d) (a) effect of (monovalent/divalent) ion pairing on the anaerobic digestion products for different cationic loads (b).

Discussion

The study presented in this manuscript demonstrates the general applicability of the aqueous phase chemistry module by providing guidelines on how to implement the presented approach into some of the most widespread ASM/ADM process models following a set of simple rules. Nevertheless, it is important to highlight that the pH/speciation model described in this paper could also be implemented in combination with other models, such as the Bio-P module of the ASM3 (Rieger et al., 2001), the Technical University of Delft (TUD) extension of ASM2d (Meijer, 2004), the Barker and Dold model (Barker and Dold, 1997) and the UCTPHO model (Hu et al., 2007). In addition, predictions of nitrification-denitrification models (Hellings et al., 1999) could be improved through consideration of activity corrections (Batstone et al., 2012). For anaerobic digestion, the model is not just limited to ADM1. The weak acid-base model could also be linked to models presented by Siegrist et al. (2002) and Sötemann et al. (2005). Last but not the least, the model could also be included in sewer models (Sharma et al., 2013; Gernaey et al., 2011) which already address the relevant sulphur and iron transformations. Since the pH/speciation model is broadly independent of the biological processes, it is applicable to any process where active compounds are explicitly calculated.

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