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

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OUTLINE

INTRODUCTION

METHODS

RESULTS

DISCUSSION

CONCLUSIONS
INTRODUCTION

A PLANT-WIDE AQUEOUS PHASE CHEMISTRY MODULE DESCRIBING pH VARIATIONS AND ION SPECIATION/PAIRING INTERFACED WITH INDUSTRY STANDARD MODELS

ALKALINITY

anaerobic digestion
high-strength wastewater nitrification/denitrification
bioP removal
nutrient recovery/precipitation

pH

BIO-KINETICS

WWTP modelling community

PHYSICO-CHEMISTRY
WEAK ACID-BASE CHEMISTRY MODEL

COMPONENTS

<table>
<thead>
<tr>
<th>i/j</th>
<th>formula</th>
<th>$S_{CO_3^{2-}}$</th>
<th>$S_{Al^{3+}}$</th>
<th>$S_{Ca^{2+}}$</th>
<th>$S_{Fe^{2+}}$</th>
<th>$S_{Mg^{2+}}$</th>
<th>$S_{Na^+}$</th>
<th>log $K_i$</th>
<th>$\Delta H^0$</th>
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<td>$S_{NaCO_3^-}$</td>
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<td>-20.35</td>
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<td>$S_{NaHCO_3(aq)}$</td>
<td>NaHCO$_3$ (aq)</td>
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<td>1</td>
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<td>10.029</td>
<td>-28.33</td>
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</tbody>
</table>

→ 20 components
→ 120 species

All species can be expressed as combinations of components

LAW OF MASS ACTION (species)

$$a_i = K_i \prod_{j=1}^{N_c} a_{i,j}^v$$

MOLAR CONTRIBUTION BALANCE (component)

$$S_{j,tot} = S_j + \sum_{i=1}^{N_{sp}} v_{i,j} S_i = \frac{a_j}{\gamma} + \sum_{i=1}^{N_{sp}} v_{i,j} \frac{a_i}{\gamma}$$
METHODS

IMPLEMENTATION DETAILS

BIOCHEMICAL MODEL

Ordinary Differential Equations (ODEs)

explicit ODE solver

PHYSICOCHEMICAL MODEL

Nonlinear Algebraic Equations (AEs)

iterative solver with a multi-dimensional Newton-Raphson method
METHODS

WASTEWATER TREATMENT PLANTS UNDER STUDY

WWTP1

WWTP2

WWTP3
METHODS

INTERFACING WITH ASM

ALKALINITY

\[ S_{\text{ALK}} \to S_{\text{IC}} \cdot S_{\text{IC}} \] modelled as source-sink compound.

PHOSPHORUS

P is included using source-sink approach (non-reactive) in ASM1 & 3. Compositional analysis (C, H, N, O, P) of all state variables.

CO₂ STRIPPING INCLUDED

K⁺ AND Mg⁺² (ASM2d)

\[ S_{\text{K}^+} \text{ and } S_{\text{Mg}^2+} \] are subjected to process dynamics during modelling of formation/release of polyphosphates (\( X_{\text{pp}} \)).

INTERFACING WITH ADM

PHOSPHORUS

P is included using source-sink approach (non-reactive)

CATIONS & ANIONS

\[ S_{\text{cat}}: \ S_{\text{Al}^3+} \ S_{\text{Fe}^{2+}} \ S_{\text{Fe}^{3+}} \ S_{\text{Na}^+} \ S_{\text{K}^+} \ S_{\text{Ca}^{2+}} \ S_{\text{Mg}^{2+}} \]

\[ S_{\text{an}}: \ S_{\text{Cl}^-} \ S_{\text{NO}_2^-} \ S_{\text{pro}} \ S_{\text{SO}_4^{2-}} \ S_{\text{HS}^-} \]
RESULTS

INFLUENT WASTEWATER

<table>
<thead>
<tr>
<th>Species distribution</th>
<th>INFLUENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{IC}$:</td>
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<tr>
<td>$S_{HCO3}$ - $S_{H2CO3}$*</td>
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<tr>
<td>$S_{IN}$:</td>
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<tr>
<td>$S_{NH4}$</td>
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<td>$S_{IP}$:</td>
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<tr>
<td>$S_{HPO4}$ - $S_{H2PO4}$-</td>
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<tr>
<td>$S_{SO4}$:</td>
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<td>$S_{SO4}$-3</td>
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<tr>
<td>$S_{HSO4}$</td>
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<tr>
<td>$S_{CaSO4}$ (aq)</td>
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<tr>
<td>$S_{MgSO4}$ (aq)</td>
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<tr>
<td>$S_{NaSO4}$-</td>
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<tr>
<td>$S_{NH4SO4}$-</td>
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<td>$S_{ac}$:</td>
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<tr>
<td>$S_{ac}$-</td>
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</tr>
<tr>
<td>$S_{Ca-ac}$</td>
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<td>$S_{Mg-ac}$</td>
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<tr>
<td>$S_{Na-ac}$</td>
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<tr>
<td>$S_{K-ac}$</td>
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</tbody>
</table>
RESULTS

pH PREDICTIONS IN WWTP1 AND WWTP2

**WWTP1**

**WWTP2**

**ANOX 1 | ANOX 2**

**AER 1 | AER 2 | AER 3**

**CLARIFIER OVER UNDER**

**ANAER 1**

**ANAER 2**

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**PLANT LOCATION**

**pH**

- ASM1
- ASM2d
- ASM3
RESULTS

BIOGAS PRODUCTION FOR DIFFERENT SCENARIOS IN WWTP3

\[ \text{stronger affinity of Ca}^{+2} \text{ and Mg}^{+2} \text{ for carbonate} \]

\[ \text{G}_{CH4} \text{ not affected} \]

\[ \text{reduction of } G_{CO2} \text{ at higher ionic loads} \]

\[ \text{for the same scenario, even lower } G_{CO2} \text{ for divalent cationic loads compared to monovalent cationic loads} \]

\textit{attributed to:}
ion pairing
species distribution
DISCUSSION

GENERAL APPLICABILITY

- guidelines for interfacing
- can be implemented in other models:
  Barker and Dold model
  TUD extension of ASM2d
  sewer models

USEFULNESS in ASM/ADM

- pH affects biokinetic processes
- speciation model can be useful for estimating NH$_3$ and HNO$_2$

MINTEQ

- experimental validation

VERIFICATION AND EXPERIMENTAL VALIDATION

- need to characterize ionic behaviour
- continuously track ionic strength and activity corrections
The presented pH module is general and versatile, thus, it can be easily added to different ASM/ADM models.

pH and ion speciation are reliably predicted under different conditions (i.e. anaerobic, anoxic, aerobic) in ASM/ADM models.

The solving routine allows simultaneous solution of ODEs and DAEs with multiple algebraic interdependencies.

This approach can be used as a starting point to develop additional models such as multiple mineral precipitation.
Thank you!

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