Titrimetric monitoring of chemical equilibrium and pH dynamics in a pilot-scale treatment plant

Using buffer capacity

Maryam Tohidi,
Céline Vaneeckhaute, Peter A. Vanrolleghem

33rd Eastern Symposium on Water Quality, Montréal
25/10/2019

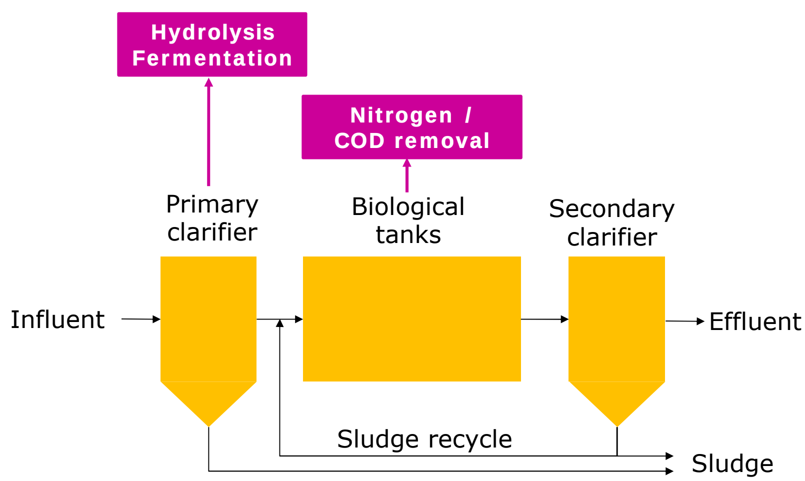
Presentation plan

- Why wastewater characterization?
  - Which processes?
- Methodology
  - Study site - pil*EAU*te plant
  - Titrimetry
- Experimental results
  - Limitations
  - Developments
- Conclusion

Wastewater characterization

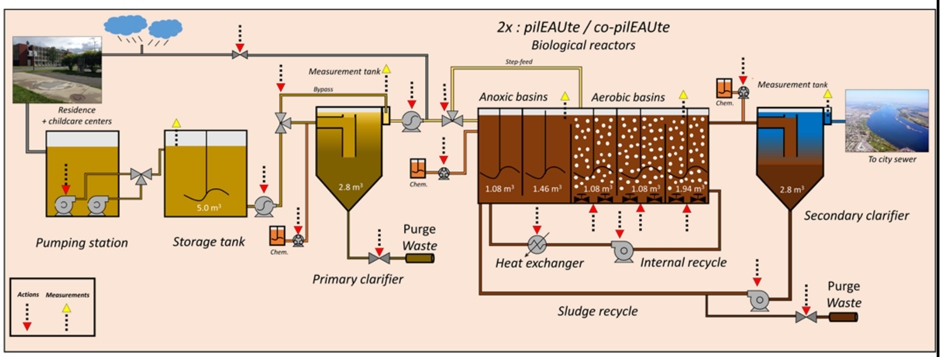
- Assesses quality and dynamics of plant loading
- Optimizes efficiency of the treatment process
- Serves as basis for:
  - Design purposes
  - Modelling plants
  - Control strategies

Wastewater treatment plant

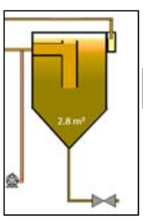


pil*EAU*te

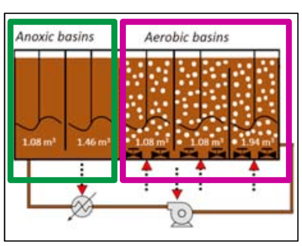
- Online since 2015
- 2 identical process lanes: *pilot and co-pilot*
  - Data collection system: sensors
  - Nitrification / Denitrification



Biological reactions



VFAs ▶ **Complex Organics** (Carbohydrate, Protein, Lipid) —Hydrolysis→ **Monomers** (Amino acids, Sugars, Fatty acids) —Acidogenesis→ **Volatile Fatty Acids (VFAs)** CH_3COO^-



NH_4-N ▶ NITRIFICATION

$$NH_4^+ + \boxed{2HCO_3^-} + 2O_2 \rightarrow NO_3^- + 2H_2CO_3 + H_2O$$

2moles alk/N↓

HCO_3^- ▶ DENITRIFICATION

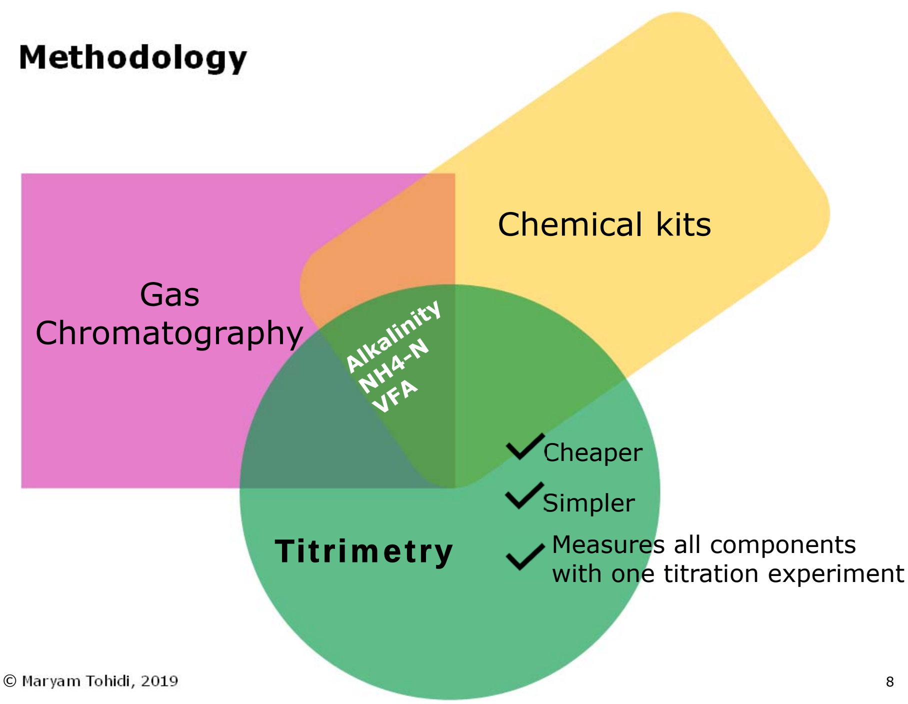
$$NO_3^- + \boxed{VFAs} + H_2CO_3 \rightarrow N_2 + \text{biomass} + \boxed{HCO_3^-}$$

Carbon source — 1mol alk/N↑

Objectives

- Characterize influent/effluent samples in terms of:
  - NH_4-N
  - VFA
  - Alkalinity
- Apply an efficient methodology

Methodology



Chemical equilibrium

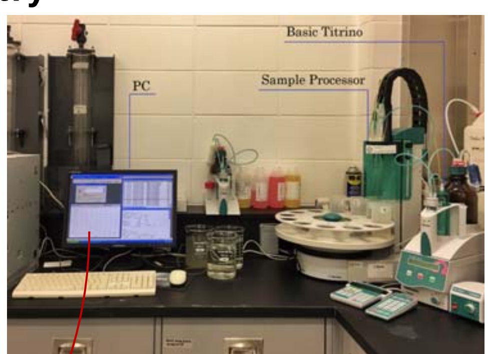
Dissociation reaction	Equilibrium constant
$HA + H_2O \leftrightarrow A^- + H_3O^+$	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$ $pK_a = -\log K_a$

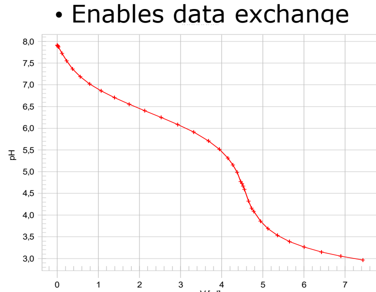
Participating buffers and their chemical equations with pK_a values at 20°C

Buffer	Chemical equations	pK_a
TAN	$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$	9.24
VFAs	$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$	4.76
TIC	$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+$	6.37
	$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$	10.5

Methodology: Titrimetry

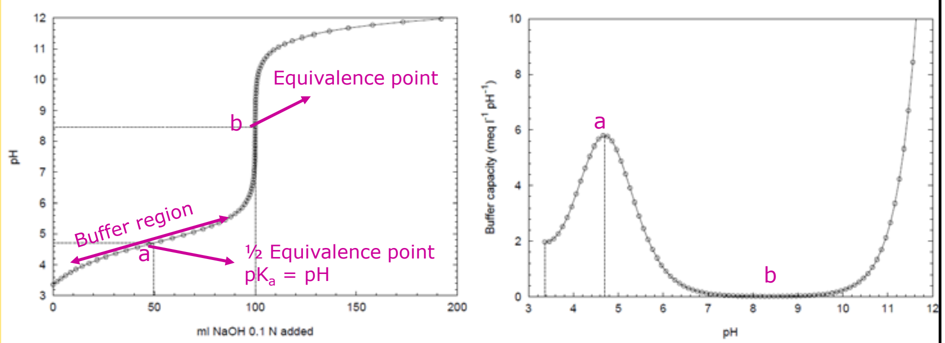
- Basic Titrino
    - pH meter
    - Acid/base container
    - Stirrer
    - Enables single titration
- Sample processor
    - Enables multiple titrations
- PC
    - Enables data exchange





Titration curve

Methodology: Buffer capacity model



Titration and buffer capacity curves for 0.1M acetic acid (PhD Van Vooren, 2000)

$$\beta = \frac{dC_B}{dpH}$$

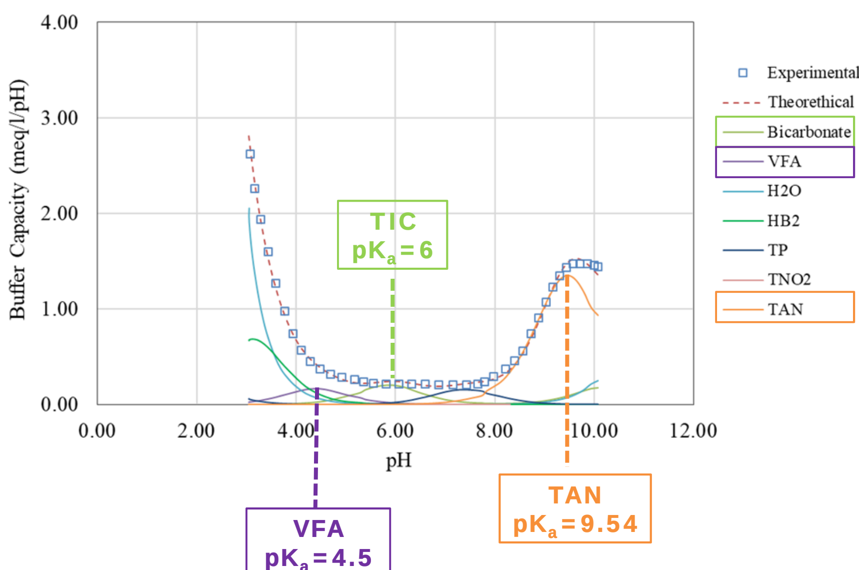
β: buffer capacity

dC_B: differential quantity of strong base added (meq L^{-1})

dpH: differential change in pH due to addition of dC

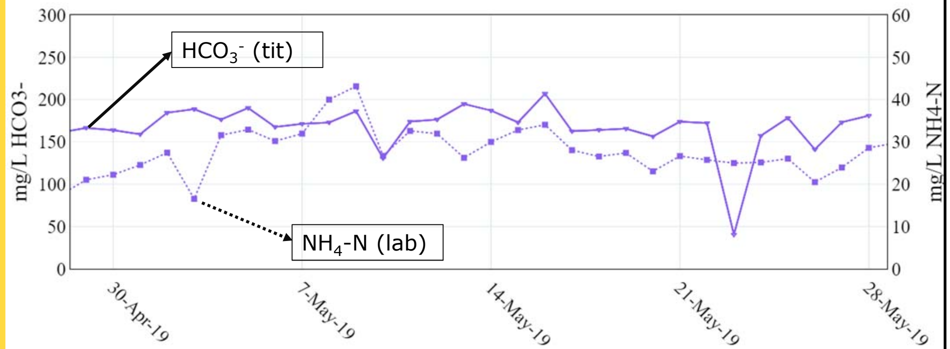
Buffer capacity model

For an influent sample…



Experimental results

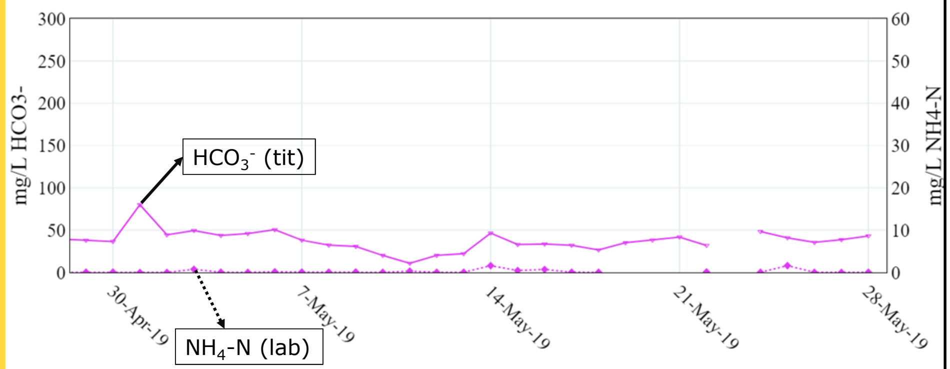
- High ammonia and alkalinity in the **influent**



 13

Experimental results

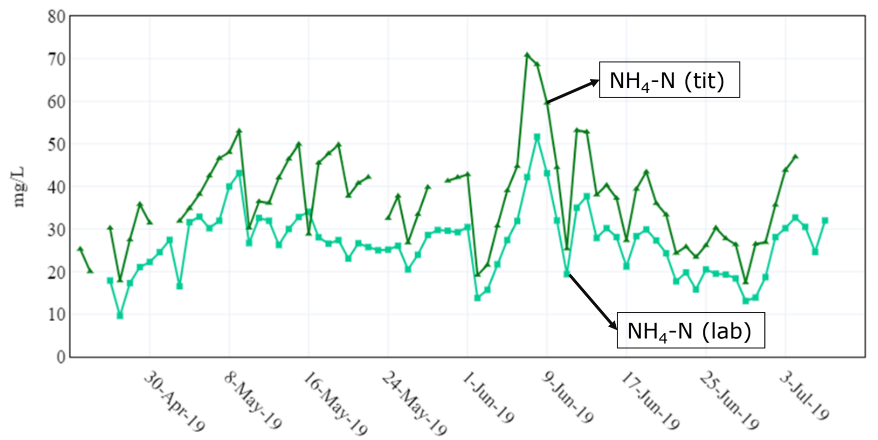
- All NH_4-N is removed in the **effluent**
- Loss of 1 mole/N alkalinity in the **effluent** after **N/DN**



 14

Experimental results

- Difference between laboratory and titration NH_4-N in **influent**
  - Titration data ≥ lab data
  - $Ratio_{(tit\backslash lab)} = 1.60$

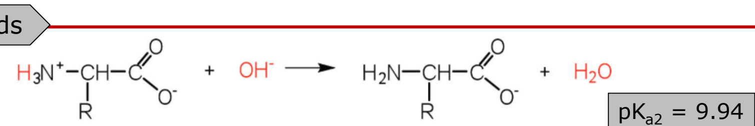


Experimental results

- Explanation:
  - Lab data: Inorganic-N ($NH_4^+ + NH_3$)
  - Titration data: Inorganic-N ($NH_4^+ + NH_3$) + Organic-N ?

Samples contain *amino acids* as organic-N

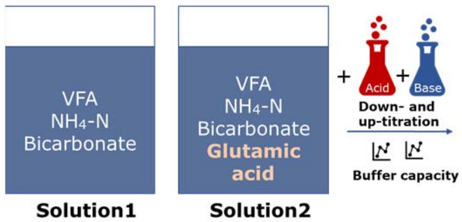
Amino acids



Very close to the pK_a value of TAN (9.24)!

The model considers amino acids as TAN and thus overestimates its concentration

Experimental results



Component	Solution 1	Solution 2
NH_4-N (mmol/L)	1.42	2.15
NH_4-N (mg/L)	19.81	30.03
ratio	1.52	

Hypothesis is valid! Adding glutamic acid compensates for the difference between lab data and titration data ☺

Conclusions

- Characterize influent/effluent samples in terms of:
  - NH4-N
  - VFA
  - Alkalinity

✓ **Titrimetry analysis estimates wastewater's components**

- Apply an efficient methodology

✓ **Titrimetry is an affordable and simple method**

✓ **With a single titration test, all buffers can be quantified**