DESORPTION RATE OF VOLATILE COMPOUNDS IN POLISHING PONDS

Eudes M. Alves, Paula F.C. Cavalcanti and Adrianus van Haandel

Federal University of Campina Grande, Aprigio Veloso 882, 58.109-920 Campina Grande – PB Brazil
prosab@uol.com.br
pH in natural waters

- Stability and value of pH in waste water treatment systems are set by weak acid-base systems
- Carbonic CO$_2$ - HCO$_3^-$ - CO$_3^{=}$
- Ammonium NH$_3$ – NH$_4^+$
- Phosphate H$_3$PO$_4$–H$_2$PO$_4$– HPO$_4^{2-}$ – PO$_4^{3-}$
- Sulphide H$_2$S – HS$^-$ - S$^=\$
- The carbonic system has overriding importance
Desorption of CO$_2$ and NH$_3$ affect the pH in polishing ponds

- (a) Alk = 2[CO$_3^{2-}$] + [HCO$_3^-$] + [OH$^-$] - [H$^+$]
- (b) Ac = 2[CO$_2$] + [HCO$_3^-$] +[H$^+$] - [OH$^-$]

CO$_2$ desorption reduces acidity, but does not affect alkalinity

NH$_3$ desorption increases acidity and reduces alkalinity

NH$_4^+$ → NH$_3$ + H$^+$
Deffeyes diagram relates alkalinity, acidity and pH for 25 °C
pK1 = 6.33; pK2 = 10.33
Desorption rate is expressed by Fick’s law

\[ r_d = (dC/dt)_d = K_d(C-C_s) \]

\( r_d \) = desorption rate
\( K_d \) = desorption constant
\( C_s \) = saturation value of desorbing compound

For NH\(_3\): \( C_s = 0 \) (no NH\(_3\) in air)
For CO\(_2\): \( C_s = 0.01 \) mmolCO\(_2\)/l at 25 \(^\circ\)C
Experimental set-up

Ponds had different depths: 0.2, 0.4 and 0.6 m
Experiment 1: CO$_2$ desorption

Pond 1: Tap water + NaHCO$_3$ + HCl:
   to produce supersaturated CO$_2$ solution
   (no interference of biological CO$_2$ removal)

Pond 2: Polishing pond effluent (stirred)
   DO$\approx$DO$_s$: avoids biological CO$_2$ removal

Pond 3: Polishing pond effluent (not stirred)
Determination of CO$_2$ desorption constant

- Measure pH and alkalinity = $f(t) \rightarrow$ acidity
- $C_{\text{tot}} = (A_c + A_l)/2 = f(t)$
- $C_{\text{tot}}$ variation yields desorption rate, $R_{d\text{CO}_2}$

- $K_{\text{CO}_2} = r_{d\text{CO}_2}/([\text{CO}_2]_s - [\text{CO}_2]_{\text{liq}})$
Experiment 2: NH$_3$ desorption

Pond 1: Tap water + NaOH (settle) + NH$_4$Cl: to produce supersaturated NH$_3$ solution

Pond 2: Polishing pond effluent (stirred)

Pond 3: Polishing pond effluent (not stirred)
Determination of NH₃ desorption constant

• Measure pH and ammonium = f(t) → NH₃
• Calculate rate $R_{dNH3}$ from ammonium concentration

• $K_{NH3} = R_{dNH3} / N_{tot} / \{K_a / [H^+] + 1\}$
Result 1: CO$_2$ desorption

<table>
<thead>
<tr>
<th>Depth</th>
<th>Tap water Stirred</th>
<th>PP effl stirred</th>
<th>PP effl Not stirred</th>
<th>Average</th>
<th>Extrapolated to H = 1 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.56</td>
<td>0.58</td>
<td>0.57</td>
<td>0.57</td>
<td>0.336</td>
</tr>
<tr>
<td>0.4</td>
<td>0.88</td>
<td>0.85</td>
<td>0.81</td>
<td>0.85</td>
<td>0.352</td>
</tr>
<tr>
<td>0.2</td>
<td>1.77</td>
<td>1.65</td>
<td>1.59</td>
<td>1.67</td>
<td>0.354</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Result 1: NH\textsubscript{3} desorption

<table>
<thead>
<tr>
<th>Depth</th>
<th>Tap water Stirred</th>
<th>PP effl stirred</th>
<th>PP efl Not stirred</th>
<th>Average</th>
<th>Extrapolated to H = 1 m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tap water Stirred</td>
</tr>
<tr>
<td>0,6</td>
<td>0,55</td>
<td>0,52</td>
<td>0,47</td>
<td>0,51</td>
<td>0,33</td>
</tr>
<tr>
<td>0,4</td>
<td>0,78</td>
<td>0,85</td>
<td>0,81</td>
<td>0,81</td>
<td>0,312</td>
</tr>
<tr>
<td>0,2</td>
<td>1,92</td>
<td>1,86</td>
<td>1,62</td>
<td>1,8</td>
<td>0,384</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,33</td>
</tr>
</tbody>
</table>
CO₂ desorption rate as a function of pH for different depths

required desorption: ≈ 10 meq/l
NH₃ desorption rate as a function of pH for different depths.

Required desorption: ≈ 3-4 meq/l
CONCLUSIONS

• pH in ponds is affected by desorption of CO\textsubscript{2} and NH\textsubscript{3}
• Desorption from ponds can be described as a first order process according to Fick’s law.
• The experimentally determined desorption constants are (25 °C)
  \[ K_{\text{CO}_2} = 0.34/\text{H d}^{-1} \text{ and } K_{\text{NH}_3} = 0.33/\text{H d}^{-1} \]
• For nitrogen removal a high pH (>9) is required and can only take place if significant biological CO\textsubscript{2} removal occurs.
• Nitrogen removal in ponds is accompanied by transfer of ammonium to the atmosphere, which may be undesirable (acid rain).
Acknowledgements

• This research was supported by the Brazilian government through its agencies FINEP (PROSAB) and CNPq.