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Microbial recovery of Lime from beamhouse effluent

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Beamhouse operations

- The steps in the production of leather between curing and tanning are collectively referred to as beamhouse operations.
- They include, in order, **soaking, liming, removal of extraneous tissues (unhairing, scudding and fleshing), deliming, bating or puering, drenching, and pickling**.

Liming

- Liming is one of the most important steps in beamhouse operations
- The hides are soaked in liming drums which contain a solution made of lime and sulphur compounds.
- The main purpose of this process is **to separate the hair from the hides**.

Lime Recovery & Recycling

- Can be done using bacteria
- Process is Microbial Carbonate precipitation
- Requires a facultative bacteria (exists in both aerobic and anaerobic environments)

Microbial Carbonate Precipitation (MCP)

- MCP occurs as a byproduct of common microbial metabolic processes such as
  - Photosynthesis
  - Sulfate reduction
  - Urea hydrolysis

MCP by bacterial surface charge

- Done by microbes with –ve net surface charge
- Remove divalent cations including Ca^{2+} & Mg^{2+} from the aquatic environment by binding them onto their cells surfaces (eqs 1-3)
- Become ideal crystal nucleation sites

$$Ca^{2+} + \text{Cell} \rightarrow \text{Cell-}Ca^{2+} \qquad (1)$$

$$Cl^{-} + HCO_3^{-} + NH_3 \leftrightarrow NH_4Cl + CO_3^{2-} \qquad (2)$$

$$\text{Cell-}Ca^{2+} + CO_3^{2-} \rightarrow \text{Cell-}CaCO_3 \downarrow \qquad (3)$$

MCP by photosynthetic organisms

- Occur in aquatic environment
- Metabolic processes of algae and cynobacteria utilize dissolved CO_2 (eq. 4) which is in equilibrium with HCO_3^- & CO_3^{2-} (eq. 5)
- Removal of CO_2 induces equilibrium shift (eq. 6)
- In a calcium rich environment, $CaCO_3$ is precipitated (eq. 7)

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2 \quad (4)$$

$$2HCO_3^- \leftrightarrow CO_2 + CO_3^{2-} + H_2O \quad (5)$$

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \quad (6)$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3\downarrow + 2H_2O \quad (7)$$

MCP by heterotrophic organisms

- Abiotic dissolution of gypsum ($CaSO_4^{2-}.2H_2O$) provides an environment rich in calcium and sulfate ions (eq. 8).
- In the presence of organic matter in an anaerobic environment, the sulfate reducing bacteria (SRB) reduce sulfate to H_2S and releasing the HCO_3^- ions (eq. 9).
- If H_2S degasses, pH increase occurs which favors $CaCO_3$ precipitation (eq. 7)

$$CaSO_4.2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (8)$$

$$2(CH_2O) + SO_4^{2-} \rightarrow HS^- + HCO_3^- + CO_2 + H_2O \qquad (9)$$

MCP by Urea hydrolysis

- Done by ureolytic bacteria -*Sporosarcina (Bacillus) pasteurii* (rest of the world) and *Bacillus Sphaericus* (mostly in Europe)
- These bacteria
  - Are Alkalophilic (growth between pH 6.5 and 9).
  - Are Facultative
  - Are non pathogenic
  - Uses urease enzyme to hydrolyse urea
  - Have high zeta potential

MCP by Urea hydrolysis Cont’

- During urea hydrolysis
  - Urease enzyme hydrolyzes urea intracellularly to produce NH_3 & CO_2.(eqs 10 & 11)
  - NH_3 released increases the pH (eq. 12-14)
  - In the presence of Ca^{2+} ions, $CaCO_3$ is precipitated (eqs. 15&16)
    - $CO(NH_2)_2 + H_2O \rightarrow NH_2COOH + NH_3$ (10)
    - $NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3$ (11)
    - $H_2CO_3 \leftrightarrow HCO_3^- + H^+$ (pKa = 6.37) (12)
    - $2NH_3 + 2H_2O \rightarrow 2NH_4^+ + 2OH^-$ (13)
    - $HCO_3^- + H^+ + 2NH_4^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2NH_4^+ + 2H_2O$ (14)
    - $CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3$ (Kso = 3.8×10^{-9}) (15)

Generally: $CO(NH_2)_2 + 2H_2O + Ca^{2+} \rightarrow 2NH_4^+ + CaCO_3 \downarrow$ (16)

Recovery of Lime

- From equation 16, lime can be recovered, cleaned, dried and reused
- Coast Calcium is recovered??
- Optimal pH is 9
- Liming effluent pH is 11.3
- The process
  - Economically saves money
  - Promotes environmental sustainability

Thank you

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