

REMOVAL OF CU AND ZN FROM ACID WATER BY ALGAE

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ABSTRACT

The alga Cyanidium caldarium is capable of precipitating metals from acid water. This study demonstrates that changes in culture and oxidation-reduction conditions may result in a different bioaccumulation of metals. The advantages of metal precipitation are a high degree of metal removal even at low pH and the feasibility of selective metal recovery.

INTRODUCTION

Algae are known to accumulate metals up to 20% of their dry weight (ref 1). Such binding reactions hold promise as low-cost methods for selective metal recovery from industrial process streams. It is possible to characterize metal binding of nonliving algal cells by measuring metal binding with varying pH (ref 2). Algal cell walls behave as polyfunctional cation exchangers with negatively charged ligands depending on the pH and metal species. Adsorption on the cell surface decreases with pH until it is close to zero at pH 4.

An alternative type of bioaccumulation is the transformation of metal ions, during which living cells precipitate metals at their surface. The precipitation of insoluble metal complexes occurs through the biosynthesis of oxidizing agents such as oxygen or through the activities of sulfate reductases. These processes depend on the metabolic activity of the cell and are closely tied to oxidation and reduction processes. This paper investigates the potential of sulfide precipitation by the microalga Cyanidium caldarium.

MATERIALS AND METHODS

Cyanidium caldarium was obtained from the Algensammlung Göttingen, FRG (107.79, No. C-14.1.1). The medium described by Allen (ref 3) was used for mass culture. The pH was adjusted to 2.5. The cultures were illuminated (4000 lux) at 30 °C with a 16 h/ 8 h light/ dark cycle. The inoculum contained 3×10^5 cells/ml. Experiments were conducted in triplicate in culture tubes in an air/CO₂ (5%), in a N₂/CO₂ (5%) atmosphere (both with light), or in a oxygen-free N₂ atmosphere (in the dark) resulting in different redox potentials. Eh measurements were made with a platinum electrode. A separate double-junction Ag/AgCl reference electrode (Orion Research) was used and reference potential

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added to measured value. Heavy metals were analyzed using flame and carbon furnace atomic absorption spectrometry (ZAAS, Hitachi model 180-70).

RESULTS AND DISCUSSION

The effect of reaction time is investigated for the ZnS system with a heterotrophic culture, see fig. 1. Excellent bioaccumulation of zinc is achieved within 2-3 days, whereas chemical metal sulfide reaction is very rapid with a reaction time of 5 minutes (ref 4). However, the oxidation of sulfide and mobilisation of zinc is also reduced by the algae. In order to look closer to the selectivity of precipitation at the cell surface of Cyanidium, three series of experiments were conducted with an acid waste water (ref 5).

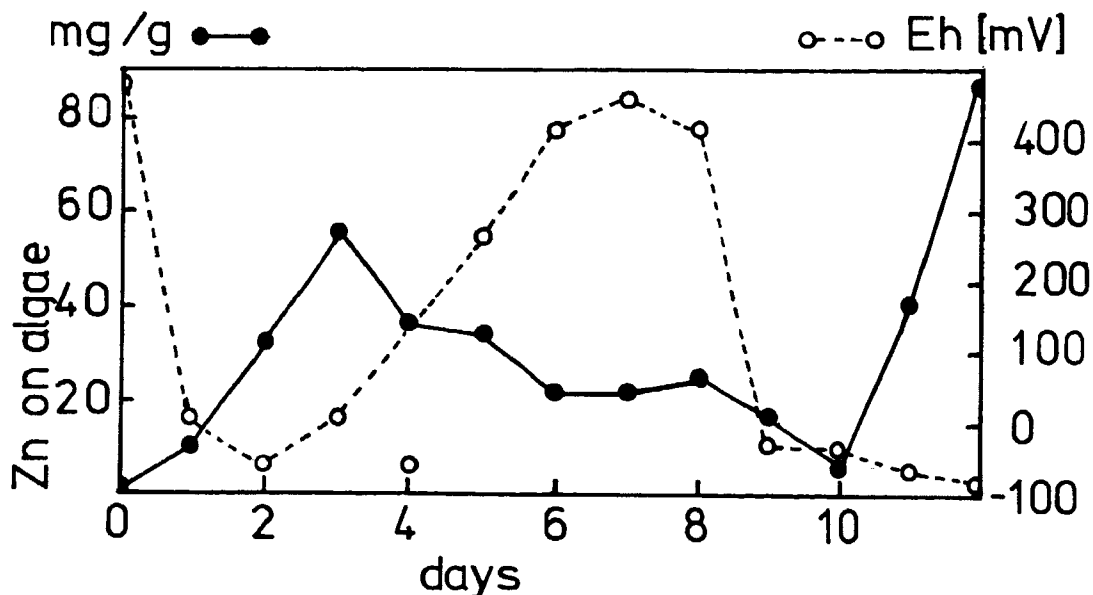


Fig.1 Effect of reaction time on ZnS precipitation with changing oxidation-reduction conditions

Table 1 presents data on the metal composition of acid extraction water. A strain of C. caldarium has been adopted to grow at 30 °C over the range of pH 2 - 4 in this medium.

Table 1. Heavy metal concentrations in acid waste water (mg/l)

| Cd | Cr | Cu | Fe | Pb | Zn |
|------|------|------|------|------|------|
| 0.34 | 0.62 | 6.06 | 83.5 | 0.53 | 41.5 |

Cyanidium grew under aerobic conditions in 5% CO₂ and with light as the major energy source with a doubling time of 1.25 days. Without light the doubling time was 3.3 days,

while under anaerobic conditions no measurable growth occurred (ref 6).

The effect of the changes in energy metabolism and oxidation-reduction potential results in marked differences in metal accumulation by Cyanidium (Table 2).

Table 2. Mean heavy metal concentrations in Cyanidium caldarium ($\mu\text{g/g}$ dry weight) grown for 96-h

| Element | Cd | Cu | Cr | Fe | Pb | Zn |
|---------|------|--------|------|--------|------|------|
| Eh | | | | | | |
| 400 mV | 3.2 | 50.5 | 8.3 | 68 000 | 110 | 974 |
| 280 mV | 21.0 | 532 | 63.3 | 20 410 | 95.1 | 3556 |
| 40 mV | 78.1 | 72 010 | 1950 | 370 | 427 | 461 |

The removal of metals by hydroxide precipitation may not be effective because little metal hydroxide precipitation occurs for $\text{pH} < 6$. However, solubilities of metals depend on their concentration in water and conditions at the cell surface, where oxygen was produced. The inverse relationship of Fe- and Cu- precipitation is in agreement with the stability constants of the metals for hydroxo- and sulfide-complexes (ref 4). The sulfide ion selectively removes the copper ion from solution. The use of algae, followed by sedimentation, greatly reduced the levels of heavy metals in solution; copper removal was near 99%.

The advantage of sulfide precipitation is a high degree of metal removal even at low pH (2-3) for most of the studied elements. Changing oxidation-reduction conditions is a useful way for selective removal of heavy metals from acid water.

REFERENCES

1. W Ahlf, U Irmer, A Weber, Z Pflanzenphysiol 100, 197 (1980)
2. U Förstner, W Ahlf, W Calmano, C Sellhorn, Vom Wasser 63, 141 (1984)
3. M B Allen, Arch Microbiol 32, 270 (1959)
4. R W Peters, Y Ku, Int Symp on Metal Speciation, Separation and Recovery. July 27-Aug. 1, Chicago, 53 (1986)
5. M A Lafraie, A Betz, Planta 163, 38 (1985)
6. W Calmano, W Ahlf, U Förstner, Proc Int Conf Heavy Metals in the Environment, 952 (1983)