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Solubilization profiles of metal ions from bioleaching of sewage sludge as a function of pH

Lucienne D. Villar & Oswaldo Garcia Jr.*
Departamento de Bioquímica e Tecnologia Química, Instituto de Química, UNESP, 14.801-970 Araraquara SP, Brazil
**Author for correspondence (Fax: 55-16-222-7932; E-mail: oswaldo@iq.unesp.br)*

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Abstract

Two patterns of solubilization of metal ions resulting from bioleaching of sewage sludge by sulphur-oxidizing *Thiobacillus* spp. were established as a function of pH. Chromium and copper ions required a pH of 2–3 to initiate their solubilization, whereas nickel and zinc ions had their solubilization initiated at pH 6–6.5. The patterns obtained were independent of the sludge solids concentrations investigated (10, 17, 25, 32.5 and 40 g l^{-1}).

Introduction

Despite the continuous development in wastewater engineering, the generation of sludge at sewage treatment plants cannot be completely avoided. The final disposal of this residue has become a matter of great concern since heavy metals accumulate in the sludge during the process of wastewater treatment. Studies on bioleaching for metal solubilization from sludge have showed to be from 10 to 35% more effective than the acid treatment with sulphuric acid (Blais *et al.* 1992). Bioleaching studies have been performed, mostly in Canada, by employing sulphur- and iron-oxidizing *Thiobacillus* spp. (Couillard & Zhu 1992), some of which have recently been reclassified (Kelly & Wood 2000).

Solubilization efficiencies near to 80% have been reported for cadmium, copper, manganese, nickel, and zinc ions, when indigenous sulphur-oxidizing bacteria were enriched from sludge and used as inocula for bioleaching assays. However, for chromium and lead removal efficiencies of only 30 to 50% have been obtained. Although several research efforts have been carried out to study the influence of process parameters, such as total solids content, temperature, and initial pH, on the kinetics of metal leaching (Sreekrishnan *et al.* 1993, Tyagi *et al.* 1993, 1994), there is a lack of information about the solubilization patterns of metal ions during bioleaching, especially concerning the pH necessary to solubilize metals. Such information in conjunction with the knowledge of metal speciation in sewage sludge would be useful to understand the low removal efficiencies reported for some metal ions.

The aim of this work was to investigate the correlation between sludge acidification and the solubilization profiles of some metal ions during the bioleaching of anaerobically-treated sludge at different total solids concentrations, using indigenous sulphur-oxidizing bacteria. Distribution of the metals in the sludge was also analysed to evaluate its influence on metal solubilization.

Materials and methods

Sampling and characterization of sludge

Samples of anaerobically digested sludge (25 g total solids l^{-1}) were obtained from the municipal wastewater treatment plant in the city of Franca, state of São Paulo, Brazil. Metal contents in the sludge were determined after acid digestion (HNO_3/H_2O_2). Fractionation of metals in dried sludge samples was carried out by a sequential extraction procedure (Oake *et al.*

Table 1. Total metal concentration and metal fractions in the anaerobically-treated sludge.

Metal ions	Total metal concentration ($mg\ kg^{-1}$ dry sludge)	Extractant[a] (% w/w total metal)					Total extraction (% w/w)
		KNO_3	KF	$Na_4P_2O_7$	Na_2EDTA	HNO_3	
Chromium	255	1	3	44	6	19	73
Copper	222	3	34	15	25	23	100
Nickel	51	16	24	18	29	7	94
Zinc	702	nd	1	73	16	5	95

nd: not detected.
[a]KNO_3, exchangeable; KF, adsorbed; $Na_4P_2O_7$, organically bound; Na_2EDTA, carbonate; HNO_3, sulfide.

1984). The following metals were selected for analysis: cadmium, chromium, copper, lead, nickel, and zinc.

Metal bioleaching assays

Indigenous sulphur-oxidizing bacteria were enriched from the sludge with 1% (w/v) S^0. After 5 consecutive transfers, the enriched sludge was retained as the inoculum. To obtain different total solids concentrations, the sludge was either diluted with deionized water or concentrated by centrifugation. The solids concentrations obtained were 10, 17, 25, 32.5 and 40 g l^{-1}. For the experiments, 250 ml of sludge (initial pH of 7) was inoculated with 5% (v/v) of the enriched sludge, and supplemented with 0.5% (w/v) S^0. For each solids concentration investigated, duplicate flasks were used and two controls were included: (i) inoculated without S^0, and (ii) autoclaved sludge (at 121 °C for 20 min) amended with S^0, but not inoculated. All flasks were incubated in a gyratory shaker at 30 °C and 200 rpm.

Chemical analysis

Samples, 20 ml, were periodically withdrawn for pH measurement and subsequent centrifugation at 3300 *g* for 30 min, with the supernatant being analysed for solubilized metals by plasma emission spectroscopy. Metal solubilization efficiency was calculated as the ratio between the solubilized metal in the supernatant (in mg) and total metal present in the system (in mg) as defined by Couillard & Zhu (1992).

Results and discussion

Total-metal concentration and metal fractions in the sludge are presented in Table 1. Cadmium and lead were not detected in any sludge sample. The sequential extraction procedure applied to dried sludge samples resulted in high recovery of total-metal concentration, except for chromium, where only 72% of the total metal was extracted.

Figure 1 presents the solubilization obtained for chromium, copper, nickel, and zinc ions as a function of sludge acidification for all the total solids concentrations investigated. Both controls did not show significant changes in pH or metal solubilized during incubation (data not shown). Fitting of the data obtained was conducted following the sigmoidal model described in Boltzmann equation.

$$y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} + A_2, \tag{1}$$

where x_0 is the centre of the linear range of the function, dx is the width of the linear range, A_1 is the initial y value, i.e., y $(-\infty)$ and A_2 is the final y value, i.e., y $(+\infty)$.

In spite of the total solids concentration of the sludge being leached, two patterns of metal solubilization can be observed from Figure 1. The first pattern shows a threshold pH of 2–3, below which solubilization of chromium and copper ions sharply increased to a maximum solubilization yield, i.e., A_1 in Equation (1), of around 60 and 80%, respectively. For the second pattern, solubilization was initiated at pH 6–6.5 with higher solubilization efficiencies being obtained for nickel and zinc ions (near to 100% for both metals). Similar ranges of threshold pH can be verified from the results of metal solubilization reported by Sreekrishnan *et al.* (1993) and Tyagi *et al.* (1994) at various pH values when studying the bioleaching of metals from aerobically-treated sludge.

The low mobility observed for chromium and copper ions (threshold pH of 2–3) suggests that the adsorption strength of these metals to the various fractions present in the sludge is not easily overcome by the acid and oxidative environment of the bioleaching process. On the other hand, in previous works (Green

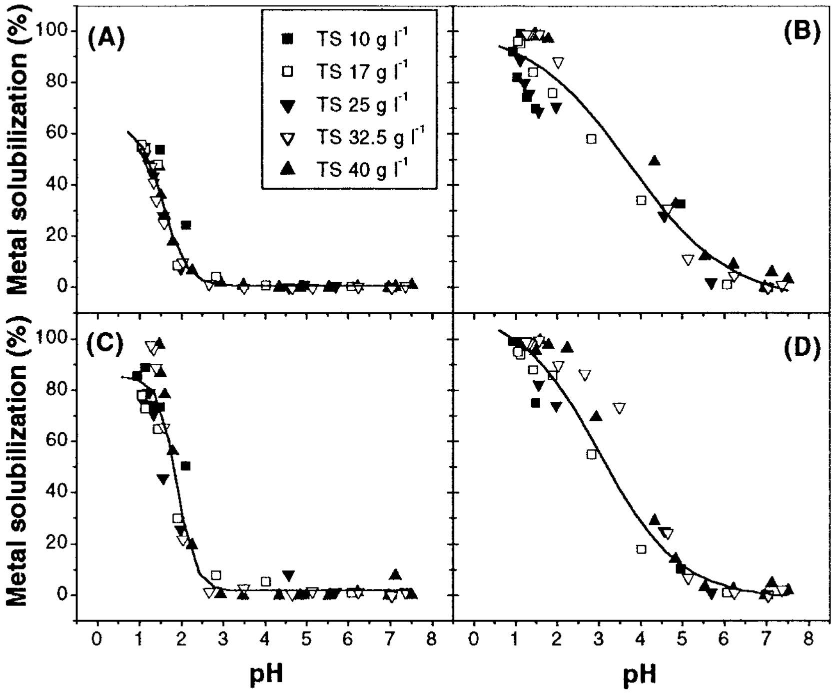

Fig. 1. Metal solubilization as a function of sludge acidification for various Total Solids (TS) concentrations. Metal solubilization is given in percentage, corresponding 100% to the solubilization of the total metal concentration present initially. (A) Chromium, initial concentration: 255 mg kg^{-1} dry sludge, (B) nickel, initial concentration: 51 mg kg^{-1} dry sludge, (C) copper, initial concentration: 222 mg kg^{-1} dry sludge, (D) zinc, initial concentration: 702 mg kg^{-1} dry sludge. ■, TS, 10 g l^{-1}; □, TS, 17 g l^{-1}; ▼, TS, 25 g l^{-1}; ▽, TS 32.5 g l^{-1}; ▲, TS, 40 g l^{-1}.

et al. 1998), nickel ions showed a low affinity to organic matter in sludge, whereas low stability constants were reported for zinc humic acid complexes (Takahashi *et al.* 1997). Such previous observations could explain the readily solubilization (threshold pH of 6–6.5) observed for nickel and zinc ions in the present study.

As a conclusion, from the present study, it was possible to obtain a consistent correlation between the sludge pH and the solubilization of chromium, copper, nickel and zinc ions during bioleaching of anaerobically-treated sludge. Some possible explanations were also raised for the solubilization profiles obtained based on fractionation analysis. Finally, the establishment of solubilization patterns independent of the sludge solids concentration can be of great usefulness when predicting the efficiency of bioleaching systems based on pH measurements.

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