



Simultaneous biodegradation of Ni–citrate complexes and removal of nickel from solutions by *Pseudomonas alcaliphila*

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ABSTRACT

The objective of this study was to study the simultaneous biodegradation of Ni–citrate complexes and removal of Ni from solutions by *Pseudomonas alcaliphila*. Adding excess citrate to 1:1 Ni–citrate complexes promoted the degradation of the complexes and removal of Ni. The alkaline pH generated by the metabolism of excess citrate caused partial dissociation of citrate from the Ni–citrate complexes, allowing degradation, and the released Ni was removed through bioaccumulation and precipitation. Addition of Fe^{3+} enhanced the degradation of Ni–citrate complexes and removal of Ni from solutions. The displacement of Ni from recalcitrant Ni–citrate complexes by Fe^{3+} and subsequent biodegradation of the degradable Fe(III) –citrate complex resulted in complete metabolism of citrate. The almost complete removal of Ni (>98%) can be attributed to the combination of coprecipitation with Fe^{3+} , bioaccumulation and precipitation. *P. alcaliphila* potentially could be applied in the treatment of effluent containing Ni–citrate complexes.

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1. Introduction

Complexing agents are widely used for metal finishing, painting, dying, photography and electroplating to enhance solubility of metals (Gyliene et al., 2009). They are also used in the extraction of toxic metals and radionuclides from wastes, sludges, sediments, and contaminated soils (Francis and Dodge, 1998). However, when treating metal-bearing wastewater, the presence of complexes makes chemical precipitation less effective (Malik, 2004), especially when the complexes are in excess of the metals (Gyliene et al., 2004). Adsorption, ion exchange and reverse osmosis processes have been utilized for the removal of chelated metals from solutions (Gyliene et al., 2009; Juang et al., 2006; Lu et al., 2010; Ozaki et al., 2002), but no satisfactory chemical or physical methods have been developed to cheaply remove or recover chelated metals from dilute solutions. One way by which metals can be released from complexes is biodegradation (Francis et al., 1992; Thomas et al., 1998).

Among the complexing agents, citrate is widely used in electroplating baths to avoid formation of insoluble metal compounds, and the wastes generated contain soluble metal–citrate complexes

(Tarozaite et al., 2005). Citrate can be utilized as a carbon and energy source by a variety of microorganisms (Suzuki et al., 2005); however, the formation of metal–citrate complexes limits the utilization of citrate by bacteria (Bergsma and Konings, 1983). The inability of bacteria to metabolize certain metal–citrate complex is not due to the toxicity of the metals, but a lack of transport systems for metal–citrate complexes or the inability of the citrate-degrading enzymes to utilize the complexes as substrate or both (Joshi-Tope and Francis, 1995). The transport of metal–citrate complexes inside the cell is determined by the type of complex between metal and citrate (Francis et al., 1992). For example, Zn and Ca form mononuclear bidentate complexes and can be transported inside the cell, whereas Cd, Cu and Pb form mononuclear tridentate, and U forms binuclear complexes that cannot be transported inside the cell (Joshi-Tope and Francis, 1995). Metal–citrate complexes are metabolized intracellularly by aconitase and citrate lyase (Joshi-Tope and Francis, 1995). During the metabolism process, the toxicity of metals released from the complexes may be alleviated by a cation efflux system (Nies, 1999).

Nickel, a commonly used metal for electroplating, forms different types of stable complex with citrate. In the pH range 5–8, Ni and citrate are present predominantly as a mononuclear bidentate $[\text{NiCit}]^-$ complex (Hedwig et al., 1980). Above pH 8, the complex exists in a tridentate form involving the hydroxyl group of citrate, and above pH 9, it exists in a polymeric form $[\text{Ni}_4(\text{OH})\text{Cit}_3]^{5-}$ (Still and Wikberg, 1980; Strouse et al., 1977). The bidentate Ni–citrate

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