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Removal of heavy metals from contaminated sewage sludge using *Aspergillus niger* fermented raw liquid from pineapple wastes

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Abstract

The environmental benefits derived from using citric acid in the removal of heavy metals from contaminated sewage sludge have made it promising as an extracting agent in the chemical extraction process. At present, citric acid is produced commercially by fermentation of sucrose using mutant strains of *Aspergillus niger* (*A. niger*), and chemical synthesis. In recent years, various carbohydrates and wastes (such as pineapple wastes) have been considered experimentally, to produce citric acid by *A. niger*. This study investigated the potential of using *A. niger* fermented raw liquid from pineapple wastes as a source of citric acid, in extracting chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) from anaerobically digested sewage sludge. Results of the study revealed that metal removal efficiencies varied with pH, forms of metals in sludge and contact time. At pH approaching 4, and contact time of 11 days, *A. niger* fermented liquid seemed to remove all Cr and Zn while removing 94% of Ni. Moreover, chemical speciation studies revealed that metals which are predominantly in the exchangeable and oxidizable phases seemed to exhibit ease of leachability (e.g., Zn). The by-products of the process such as pineapple pulp and mycelium which are rich in protein, can still be used as animal feed. It can be said therefore that this novel process provides a sustainable way of managing contaminated sewage sludge.

Keywords: *A. niger* fermented raw liquid; Citric acid; Heavy metals; Pineapple wastes; Sewage sludge

1. Introduction

One of the main concerns in the land disposal of sludge is the presence of toxic heavy metals which concentrate during various physico-chemical and biological interactions occurring in sludge treatment. Another factor that heightens the concern over the presence of these heavy metals in the environment is their non-biodegradability and consequent persistence (Dutta, 2002; McBride, 1995). One of the various technologies used in the removal of these heavy metals from contaminated sewage sludge is chemical extraction. This process uses extracting chemicals such as inorganic acids (sulfuric, hydrochloric and nitric), organic acids (citric and oxalic acid), chelating agents (ethylenediaminetetraacetic acid or EDTA and nitrilotriacetic acid or NTA) and inorganic chemicals such as ferric chloride, for treatment (Babel and Del Mundo Dacera, 2006). The chemical extraction process works on the principle that when acid is added to the sludge, metal solubilization occurs due to the exchange of protons supplied by the addition of acid solution. The pH of the solution therefore, is one of the most important factors affecting the solubilization of metals in sludge (Waidmann et al., 1984). After extraction, removal of heavy metals from the extracting agents is accomplished by chemical sulfide precipitation and selective ion-exchange (Veeken and Hamelers, 1999).

Among the extractants used in the chemical extraction process, organic acids, especially citric acid, are more promising because metal extraction can be performed at mildly acidic condition (pH 3–4) and the acids are readily

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degradable under aerobic and anaerobic conditions (Del Mundo Dacera and Babel, 2006; Marchioretto et al., 2002; Veeken and Hamelers, 1999). Citric acid [$C_3H_5O(COOH)_3$] is a 6-carbon containing tricarboxylic acid and exists as an intermediate in the citric acid cycle when carbohydrates are oxidized to carbon dioxide. The acidic nature of citric acid results from the three carboxyl groups (COOH) which can lose a proton in solution forming the citrate ion. Citrates can chelate metal ions, and thus, can be used as preservatives, water softeners, chelating and sequestering agent. Citric acid is produced by direct extraction from fruits; fermentation of sucrose by fungi; and by chemical synthesis (Alben and Erkmen, 2004; Sun, 1984; Yigitoglu, 1992). At present, citric acid is produced commercially by fermentation of sucrose using mutant strains of *Aspergillus niger* (*A. niger*), and chemical synthesis. Carbohydrates and wastes that have been considered experimentally to produce citric acid by *A. niger* include date fruit syrup, soya whey, cheese whey, pineapple wastes, corncobs and cane molasses (Ali et al., 2002; El-Holi and Al-Delaimy, 2003; Hang and Woodams, 1998; Sun, 1984). Among those wastes which can be potential sources of citric acid, pineapple solid waste is of interest especially in Thailand where pineapple is one of the major food products in the country. It was reported that in 2002, fresh pineapple production in Thailand reached up to 2.0 million tons (Food Market Exchange, 2006). Since 70–80% of the pineapple fruit is discarded as solid waste (Sun, 1984), an equivalent of 1.4–1.6 million tons of pineapple solid wastes is also produced. Although some research has been conducted on the utilization of these wastes (such as for animal feed, alcohol, vinegar and wine production), this enormous quantity of discarded material has not been utilized efficiently. At present, the pineapple solid wastes are still disposed into the environment at a considerable cost for transportation and environmental degradation. Therefore, research on the alternatives for utilization of these wastes is still of interest.

This study was conducted to investigate the potential of using *A. niger* fermented raw liquid from pineapple wastes as a source of citric acid in extracting Cr, Cu, Pb, Ni and Zn from anaerobically digested sewage sludge. Extraction efficiency of the liquid at various pH and leaching times was observed. Chemical speciation studies were also done to determine the forms of metals in sludge which affect extraction efficiency.

2. Methods

2.1. Sludge characterization

The sludge sample was collected from the sludge treatment facility at Nongkhaem, in Bangkok, Thailand, which receives dewatered sludges mainly from five central wastewater treatment facilities under the Bangkok Metropolitan Administration (BMA). The central wastewater treatment plants treat mostly domestic wastewater and a small amount of industrial wastewater. Sludge sent to the treatment facility in Nongkhaem undergoes anaerobic digestion and dewatering using filter press prior to disposal mostly by landfill. The sludge sample collected was analyzed in terms of its physical and chemical characteristics, including heavy metals content according to the Standard Methods for the Examination of Water and Wastewater (APHA et al., 1998). Heavy metals were analyzed using flame atomic absorption spectrophotometer (AAS Hitachi Z-8230) after microwave digestion with nitric acid (HNO_3), hydrofluoric acid (HF), hydrochloric acid (HCl) and boric acid (H_3BO_3).

2.2. Chemical speciation studies

Chemical speciation studies were done using the sequential chemical extraction (SCE) procedure modified from Marchioretto et al. (2002), Sims and Kline (1991) and Tessier et al. (1979), and is summarized in Table 1. The sequential extraction was carried out in 2 g of air-dried sludge samples in 250 ml erlenmeyer flasks. Between each of the successive extractions, separation was done by centrifuging at 4000 rpm for 30 min where the supernatant was removed and analyzed for trace metals by flame AAS and the residue washed with 40 ml deionized water.

Table 1
Sequential chemical extraction procedure

Chemical form of metals	Extraction conditions	
	Reagent	Time and temperature
Exchangeable (Tessier)	$MgCl_2$ 1 mol/l, pH 7, 8 (v/w)[a]	1 h at 20 °C
Bound to carbonates or acid extractable phase (Tessier)	NaAc[b] 1 mol/l, pH 5, 8 (v/w)	5 h at 20 °C
Bound to Fe–Mn Oxides or reducible phase (Tessier)	$NH_2OH \cdot HCl$ 0.04 mol/l, pH 2, 20 (v/w)	6 h at 96 °C (occasional shaking)
Bound to organic and inorganic matter or oxidisable phase (modified Sims and Kline, Marchioretto)	Na_2 EDTA 0.05 mol/l, pH 4.5, 20 (v/w)	6 h at 20 °C
Residual (modified Tessier and Sims and Kline)	5 ml H_2O, 4 ml HNO_3 70%, 1 ml HCl 35%, 2 ml HF 48%	24 h at room temperature
	HNO_3 4 mol/l, pH 0.6, 12.5 (v/w)	16 h at 80 °C (occasional shaking)

[a] Liquid-to-solid ratio (v/w); *v* is the volume of the extractant (ml); *w* is the mass of the sample (g).
[b] Ac: acetate.