Journal of Hazardous Materials 288 (2015) 51–59

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of trace metals and improvement of dredged sediment dewaterability by bioleaching combined with Fenton-like reaction

Xiangfeng Zeng[a,d,e], Irena Twardowska[b], Shuhe Wei[a,*], Lina Sun[c], Jun Wang[d], Jianyu Zhu[d], Jianchao Cai[f]

[a] Key Laboratory of Pollution Ecology and Environment Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, PR China
[b] Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze 41-819, Poland
[c] Key Lab of Regional Environment and Eco-Remediation (Ministry of Education), Shenyang University, 110073, PR China
[d] Center for Environmental Biotechnology, The University of Tennessee, Knoxville, TN 37996, USA
[e] University of Chinese Academy of Sciences, Beijing 100039, PR China
[f] Institute of Geophysics and Geomatics, China University of Geosciences, Wuhan 430074, PR China

HIGHLIGHTS

- The combined bioleaching/Fenton-like process was optimized for sediment treatment.
- *A. niger* is an efficient and environmentally advantageous bioleaching agent.
- Significant reduction of metal content and increase of dewaterability was achieved.
- After sediment treatment residual metals were enriched mostly in immobile fractions.

ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form 5 February 2015
Accepted 6 February 2015
Available online 7 February 2015

Keywords:
Bioleaching
Aspergillus niger
Fenton-like reaction
Trace metal removal
Dewaterability
Sediments

ABSTRACT

Bioleaching by *Aspergillus niger* strain SY1 combined with Fenton-like reaction was optimized to improve trace metal removal and dewaterability of dredged sediments. The major optimized parameters were the duration of bioleaching and H_2O_2 dose in Fenton-like process (5 days and 2 g H_2O_2/L, respectively). Bioleaching resulted in the removal of ≈90% of Cd, ≈60% of Zn and Cu, ≈20% of Pb, and in decrease of sediment pH from 6.6 to 2.5 due to organic acids produced by *A. niger*. After addition of H_2O_2, Fenton-like reaction was initiated and further metal removal occurred. Overall efficiency of the combined process comprised: (i) reduction of Cd content in sediment by 99.5%, Cu and Zn by >70% and Pb by 39% as a result of metal release bound in all mobilizable fractions; (ii) decrease of sediment capillary suction time (CST) from 98.2 s to 10.1 s (by 89.8%) and specific resistance to filtration (SRF) from 37.4×10^{12} m/kg to 6.2×10^{12} m/kg (by 83.8%), due to reducing amount of extracellular polymeric substances (EPS) by 68.7% and bound water content by 79.1%. The combined process was found to be an efficient method to remove trace metals and improve dewaterability of contaminated dredged sediments.

1. Introduction

Dredged sediments disposed at the surface are a serious source of secondary pollution of water bodies, and pose a threat to public health and natural ecosystems, in particular due to high concentrations of potentially toxic trace elements, discharged over decades to rivers with metal-enriched industrial wastewaters and municipal sewage [1–7]. Besides, dredged sediments, despite mechanical dewatering, always have high moisture content [8,9]. These adverse properties negatively affect their disposal options such as composting, incineration and landfilling [10,11]. Therefore, development of efficient technologies for removing potentially toxic elements and for improving dewatering efficiency is crucial for the environmentally safe management of dredged sediments.

Currently, bioleaching is becoming popular to treat metal-rich sediments, sludge and other similar wastes. Sulfur-oxidizing bacteria and filamentous fungi present in acidic environment can mobilize metals through oxidizing sulfur compounds and metallic sulfides and the production of weak organic acids that form water-soluble complexes with trace metals [11–18]. Among different microbial strains, *Aspergillus niger* fungi are particularly advantageous due to their high ability to produce organic acids. Thus,

* Corresponding author. Tel.: +86 24 83970382/52740776; fax: +86 24 83970436.
E-mail address: shuhewei@iae.ac.cn (S. Wei).

http://dx.doi.org/10.1016/j.jhazmat.2015.02.017
0304-3894/

A. niger is one of the most widely used fungal strains for bioleaching [19–21]. Besides, *A. niger* was found able to entrap solid particles and compress the solids within its filamentous (hyphae) mycelia. This causes alteration of the porous structure of biosolids and enhances dewatering efficiency and filtration properties [15,21].

However, bioleaching is a relatively slow process compared to chemical methods, making it less applicable for bulk waste treatment. This induces numerous researchers, besides optimization of bioleaching [22] or chemical methods such as AOPs (advanced oxidation processes) [23–28], to develop combined hybrid methods using both bioleaching and chemical treatment to facilitate this process [e.g.,29]. One of such methods is a combination of bioleaching with AOPs, such as Fenton (Fe^{2+}/H_2O_2) or Fenton-like (Fe^{3+}/H_2O_2) reactions [e.g.,28,30,31]. Fenton and Fenton-like reactions, i.e., the reactions of H_2O_2 with ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions that generate hydroxyl radicals (•OH), have been proven methods of enhancing dewatering efficiency of biosolids through degrading EPS, in which bound water is retained, and maintaining porous structure, through which water is being withdrawn [24,25,32–34].

Fenton and Fenton-like reactions were also reported to release trace metals from soils [35]. Bioleaching experiments using iron-oxidizing bacteria combined with Fenton-like reaction were found to be considerably more effective for trace metal removal from sludge and other biosolids than bioleaching alone or other leaching methods with the use of inorganic acids due to reciprocal effect of both processes: Fenton-like reaction shortens the total processing time, while bioleaching acts as a catalyst and generates acidic pH required for Fenton-like reaction [36]. However, the use of sulfur- or iron-oxidizing bacteria in bioleaching can produce excessive amounts of sulfur, leading to soil acidification when the treated sludge or sediment is applied to farmland, or produce sulfur dioxide when it is incinerated [22]. Besides, the method causes the formation of ferric sludge, which is a limiting factor of the process application due to disposal problems. Bioleaching with the use of heterotrophic microorganisms such as *A. niger* can overcome these problems. Organic acids produced by *A. niger* could be biodegradable and serve as nutrients for microbes participating in biodegradation of contaminants, as well as acidifying agents for the chemical oxidation. They act as a buffer at the level of pH 2–4, at which Fenton's reaction actively proceeds. In addition, they have strong abilities to chelate metal ions and keep them in solution at higher pH values, at which the metals would otherwise precipitate.

In this study, we investigated bioleaching using *A. niger* and Fenton-like reaction with the aim to enhance trace metal removal and improve sediments dewaterability. These objectives were achieved by the comparative study on the bioleaching with the use of *A. niger* only and the combined bioleaching and Fenton-like processes. In particular, a comparison of: (1) the leaching ability and chemical speciation of trace metals and (2) the dewaterability characteristics of the studied dredged sediment before and after bioleaching with the use of both processes were performed. The experimental design was basically similar to that applied by Zhu et al. [36] to enable a direct comparison of efficiency of both systems, which besides different target material (municipal sludge and dredged sediment), applied different microorganisms in the bioleaching stage (iron-oxidizing bacteria and *A. niger* fungi).

2. Materials and methods

2.1. Sediment sampling and characterization

The contaminated sediment used in this study was collected from the dredging operation at the Xihe River in Shenyang, Liaoning Province, China (41°39′10N, 123°6′24E). The air dried sediment sample was analyzed for trace metals by ICP–AES, and for total N, P, K, and organic matter content according to APHA, as described by Wijekoon et al., [37]. For assessment of contamination level, metal concentrations in sediments were compared with background concentrations, ISQG and PEL – interim sediment quality guideline values and probable effect levels for freshwater sediments and soil [38]. Additionally, for designation of sediment quality, geoaccumulation indices I_{geo} for studied metals were evaluated [39–41].

2.2. Spore collection and inoculum preparation

A fungus strain was originally isolated from the highly metal-contaminated sediment from the Xihe River, following the procedure described by Tahir et al. [42]. It was identified by sequencing 26S rDNA (D1/D2) and ITS as *Aspergillus niger*. Adaptation of the fungus strain was carried out through a series of sub-cultures exposed to the sediment used in the study. The adapted *A. niger* strain SY1 was incubated three times on potato dextrose agar (PDA) slants using a sterile platinum loop at 30 °C for 5 days. The obtained resultant spores were harvested in 0.1% Tween 80 solution and used to inoculate the raw liquid at the dose of 2×10^9 spores/L.

2.3. Bioleaching experiments

Bioleaching experiments were performed in 250 mL autoclaved conical flasks; 25 g of sediment pasteurized at 80 °C for 15 min and 1 mL of spore suspension were added to 99 mL of culture medium. A control experiment without inoculation was carried out in parallel. For compliance check, both raw and pasteurized sediments were used as a control in each experiment, showing no significant differences ($p < 0.05$). All flasks were agitated in a rotary shaking incubator (220 rpm) at 30 °C for the period from 1 to 15 days. All the experiments were run in triplicate. The samples were weighed and water lost due to evaporation was replenished with distilled water every day.

2.4. Bioleaching combined with Fenton-like reaction

After completing the bioleaching stage with *A. niger* for the selected optimum time, when pH of the sediment declined to a value below 2.5, the Fenton-like process was conducted for 1 h after addition of different final doses (from 0.5 to 10 g/L) of H_2O_2 to the bioleached sediment for the overall process optimization. For comparison, a control without H_2O_2 addition was also used. The basic working parameters applied in this procedure were identical with parameters used by Zhu et al. [36] for two-stage municipal sewage sludge bioleaching by indigenous iron-oxidizing bacteria and Fenton-like reaction.

2.5. Analysis

The total trace metal contents in the sediment were determined in accordance with the US EPA standard 3052 by digestion with the acid mixture (HCl, HNO_3, $HClO_4$ and HF) and subsequent analysis for metals with FAAS technique (Varian AA240). The chemical fractionation of trace elements in the sediment was determined using modified BCR sequential extraction procedure [43–46]. Organic acids in the leaching liquid were determined with a HPLC system (Agilent 1100 Series, USA) equipped with a Bio-Rad Aminer HPX-87-H column (300mm × 7.8 mm) and a diode array detector at 210 nm [47].

CST was measured by CST analyzer (Model 304M, Triton) [48,49]. SRF was assessed by the Buchner funnel test, and the bound water content in sediment samples was determined by the dilatometric method at −20 °C, with the use of xylene as an indicator [50].