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Use of organic substrates as electron donors for biological sulfate reduction in gypsiferous mine soils from Nakhon Si Thammarat (Thailand)

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HIGHLIGHTS

- Development of a new SRB based bioremediation technique for gypsiferous soils.
- The gypsum content of treated soil could be reduced from 25% to 7.5%.
- Mixtures of PWTS + RH + CHC can be utilized as low cost electron donor for SRB.
- Characterization of soils from a lignite coal mine and a gypsum mine.

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ABSTRACT

Soils in some mining areas contain a high gypsum content, which can give adverse effects to the environment and may cause many cultivation problems, such as a low water retention capacity and low fertility. The quality of such mine soils can be improved by reducing the soil's gypsum content. This study aims to develop an appropriate *in situ* bioremediation technology for abbreviating the gypsum content of mine soils by using sulfate reducing bacteria (SRB). The technology was applied to a mine soil from a gypsum mine in the southern part of Thailand which contains a high sulfate content (150 g kg^{-1}). Cheap organic substrates with low or no cost, such as rice husk, pig farm wastewater treatment sludge and coconut husk chips were mixed (60:20:20 by volume) and supplied to the soil as electron donors for the SRB. The highest sulfate removal efficiency of 59% was achieved in the soil mixed with 40% organic mixture, corresponding to a reduction of the soil gypsum content from 25% to 7.5%. For economic gains, this treated soil can be further used for agriculture and the produced sulfide can be recovered as the fertilizer elemental sulfur.

1. Introduction

Soils containing significant quantities of gypsum, which may interfere with plant growth, are defined as gypsiferous soils (FAO, 1990). In the natural environment, gypsum can be transported by water or wind, be re-deposited at new locations forming individual gypsum dunes or it can be incorporated in the soil layer (FAO, 1990). The main reason for gypsum accumulation in the soil is its precipitation from supersaturated underground or runoff waters, as a result of intensive evaporation. Gypsum is also formed in acidic sulfate soils (Dent, 1986). In these soils, the origin of the sulfate ions is due to the oxidation of sulfur rich minerals such as pyrite. Due to natural weathering and oxidation cycles, the sulfur in these minerals is transformed into sulfuric acid, causing calcareous soils to react with calcium carbonate forming gypsum (Dent, 1986; FAO, 1990).

Gypsiferous soils have received little curative attention as compared to most other affected soil types, and have been considered to have little or no agricultural potential (FAO, 1974; USDA, 1975). The presence of gypsum in gypsiferous soils creates several problems for their agricultural use and development, including low water retention capacity, shallow depth to the hardpan and vertical crusting (Khresat et al., 2004). The accumulation of gypsum in soils results in very low fertility, and consequently, their productivity remains low under irrigation even with application of fertilizers or organic manures (FAO, 1990). With this kind of soils, larger

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amounts of phosphorous application are needed because of the phosphorus immobilization by the gypsum (Verheye and Boyadgiev, 1997). Compared to a non-gypsiferous soil, the amount of the calcium and sulfate ions in the soil solution is increased due to the solubility of gypsum, resulting in calcite precipitation (Kordlaghari and Rowell, 2006). The impact of these adverse properties depends on the gypsum content and the depth at which the gypsiferous layer occurs in the root zone (Verheye and Boyadgiev, 1997). Under saturated conditions, gypsum may impregnate most of the soil matrix. When less calcium sulfate is present in the system, gypsum precipitates in localized spots (Verheye and Boyadgiev, 1997).

The physical structure of gypsiferous soils such as its porosity and permeability can be improved by reducing the soil's gypsum content (Alfaya et al., 2009). A gypsum content of 2–10% does not interfere significantly with the soil structure. The gypsum crystals, however, tend to break the continuity of the soil mass in soils which contain 10–25% of gypsum. Soils with more than 25% gypsum are considered unsuitable for most crops. Under such conditions, gypsum may precipitate and can cement soil material into hard layers, thus roots cannot penetrate except for those of very tolerant crops such as alfalfa, clover or oats (Smith and Robertson, 1962; Verheye and Boyadgiev, 1997).

The problems mentioned above also occur in several mining areas, especially gypsum mines, where the soils have a high gypsum content and cannot be used for agriculture. For instance, soils in the gypsum mine in the southern part of Thailand (Fig. 1a) have a high sulfate content that can induce adverse effects on the environment. Moreover, the soils of some mines can also generate acid mine drainage (AMD) and mass mortalities of plants and aquatic life (Kijjanapanich et al., 2012). This AMD has a low pH and high concentrations of sulfate and toxic metals. Such land cannot be used for agriculture, and these soils have a poor fauna and flora.

Little research has been done on the bioremediation of gypsiferous soils. Alfaya et al. (2009) ascertained that calcareous gypsiferous soils contain an endogenous sulfate reducing bacteria (SRB) population that uses the sulfate from gypsum in the soil as an electron acceptor. The sulfate reduction rate doubled when anaerobic granular sludge was added to bioaugment the soil with SRB. In the presence of anaerobic granular sludge, a maximum sulfate reduction rate of 567 mg L^{-1} d^{-1} was achieved with propionate as the electron donor. Most of the gypsiferous soils have a relatively low organic matter (OM) content (Ghabour et al., 2008). Therefore, appropriate electron donor needs to be added for the SRB when designing a bioremediation scheme for gypsiferous soils based on biological sulfate reduction.

This research aimed to study the characteristics of soils from a lignite coal mine and a gypsum mine. Gypsiferous soils from a gypsum mine (Fig. 1a), containing a high gypsum content, was treated by biological sulfate reduction (batch experiments) in order to reduce the gypsum content by using no or low cost organic substrates as electron donors for SRB.

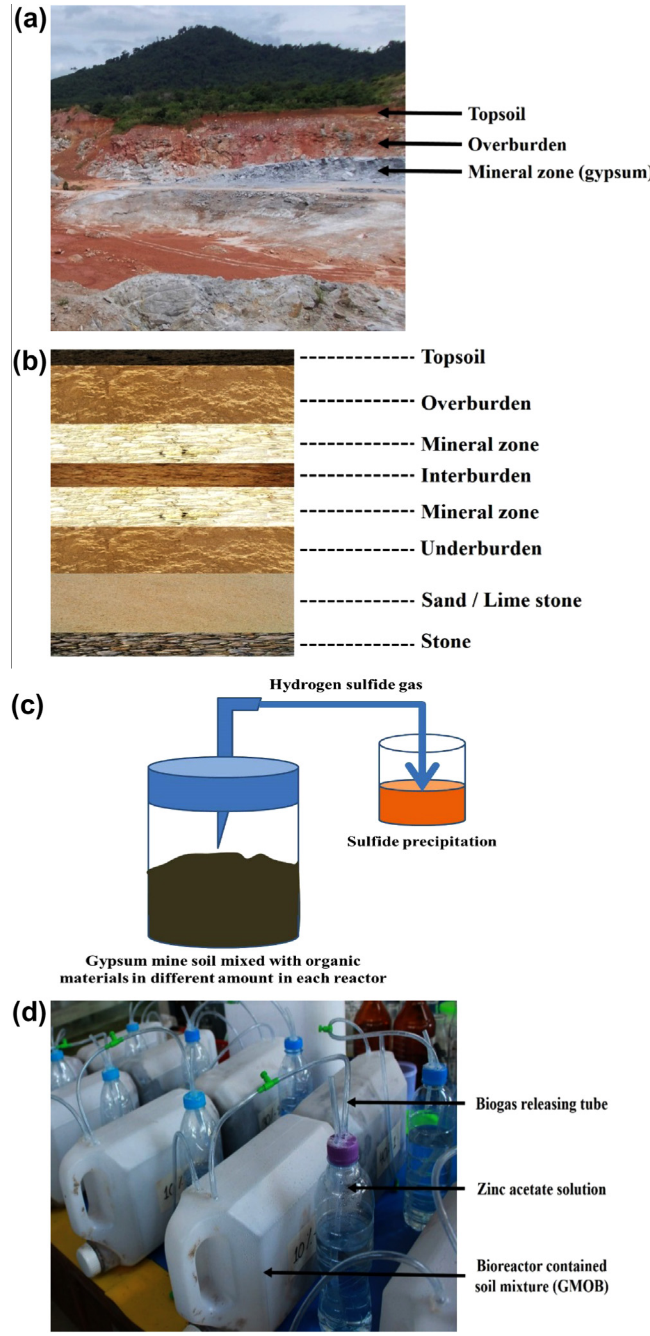

Fig. 1. Mining site and bioreactor studied in this experiment: (a) gypsum mine in Nakhon Si Thammarat, Thailand, (b) schematic representation of soil profile in a mining zone, (c) reactor schematic and (d) lab-scale bioreactor.

2. Materials and methods

2.1. Mine soils (overburdens)

Two different types of soil samples were used in this study: gypsum mine overburden (GMOB) and lignite coal mine overburden (LMOB). The overburdens of a mine are the rock and soil part that lies above the ore body and needs to be excavated by open pit mining (Fig. 1b). GMOB and LMOB were collected from a gypsum mine in Nakhon Si Thammarat (Thailand) and a lignite coal mine in Lam Phun (Thailand), respectively. All samples were air-dried and sieved at 2 mm. These overburden samples were then analyzed for pH, soil texture, OM, cation-exchange capacity (CEC), synthetic precipitation leaching procedure (SPLP) and waste extraction test (WET).

2.2. SRB inoculum

Sludge from a pilot scale mesophilic anaerobic channel digester and upflow anaerobic sludge blanket reactor treating pig farm wastewater operated at the Energy Research and Development Institute-Nakonping (Chiang Mai University, Thailand) was used as source of SRB. The seed sludge had a TSS and VSS content of 33.3 and 21.3 g L^{-1}, respectively, corresponding to a VSS/TSS ratio of 0.64.