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Bioresource Technology 96 (2005) 459–464

BIORESOURCE TECHNOLOGY

Effect of natural zeolite on methane production for anaerobic digestion of ammonium rich organic sludge

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Received 23 April 2004; received in revised form 17 May 2004; accepted 17 May 2004
Available online 6 July 2004

Abstract

The effect of an inorganic additive on the methane production from NH_4^+-rich organic sludge during anaerobic digestion was investigated using different kinds of inorganic adsorbent zeolites (mordenite, clinoptilolite, zeolite 3A, zeolite 4A), clay mineral (vermiculite), and manganese oxides (hollandite, birnessite). The additions of inorganic materials resulted in significant NH_4^+ removals from the natural organic sludge ($[NH_4^+] = 1$, 150 mg N/l), except for the H-type zeolite 3A and birnessite. However, an enhanced methane production was only achieved using natural mordenite. Natural mordenite also enhanced the methane production from the sludge with a markedly high NH_4^+ concentration (4500 mg N/l) during anaerobic digestion.

Chemical analyses of the sludge after the digestion showed considerable increases in the Ca^{2+} and Mg^{2+} concentrations in the presence of natural mordenite, but not with synthetic zeolite 3A. The effect of Ca^{2+} or Mg^{2+} addition on the methane production was studied using Na^+-exchanges mordenite and Ca^{2+} or Mg^{2+}-enriched sludge. The simultaneous addition of Ca^{2+} ions and Na^+-exchanged mordenite enhanced the methane production; the amount of produced methane was about three times greater than that using only the Na^+-exchanged mordenite. In addition, comparing the methane production by the addition of natural mordenite or Ca^{2+} ions, the methane production with natural mordenite was about 1.7 times higher than that with only Ca^{2+} ions. The addition of 5% and 10% natural mordenite were suitable condition for obtaining a high methane production.

These results indicated that the Ca^{2+} ions, which are released from natural mordenite by a Ca^{2+}/NH_4^+ exchange, enhanced the methane production of the organic waste at a high NH_4^+ concentration. Natural mordenite has a synergistic effect on the Ca^{2+} supply as well on the NH_4^+ removal during anaerobic digestion, which is effective for the mitigation of NH_4^+ inhibition against methane production.

Keywords: Anaerobic digestion; Zeolite; Methane; Ammonia

1. Introduction

Inhibition of anaerobic digestion of high organic wastes, for example, livestock and dewatered sewage sludge, is often caused by a high ammonia concentration (Gallert et al., 1998; Kayhanian, 1999; Angelidaki and Ahring, 1994). A high NH_4^+ concentration is toxic for anaerobes (Truper and Pfenning, 1981; Sprott and Patel, 1986; Hendrinksen and Ahring, 1991). McCarty reported that NH_4^+-N concentrations in excess of 3000 mg/l were expected to be toxic at any pH value (1961). Hobson and Shaw (1976) reported that 235 mmol (3290 mg N/l) NH_4^+ completely prevented the growth of *Methanobacterium formicicum* in the pure culture.

To avoid NH_4^+ inhibition, organic wastes were usually diluted with water; however, dilution of organic

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doi:10.1016/j.biortech.2004.05.025

waste causes the reactor size and costs to increase. That is why NH_4^+ removal during anaerobic digestion is necessary for improving the digestion efficiency of organic waste.

Except for dilution studies, only a few studies have dealt with reducing ammonia inhibition, for example, MAP (the magnesium ammonium phosphate) process (Demeestere et al., 2001) and the lighted upflow anaerobic sludge blanket method (Sawayama et al., 1999). Some research has been focused on zeolite and clay as a means to reduce the inhibition by ammonia during anaerobic digestion (Milan et al., 2001; Angelidaki and Ahring, 1993; Hansen et al., 1999). Some zeolites and clays are able to absorb NH_4^+ by a cation exchange reaction. Angelidaki and Ahring (1993) used bentonite clay for anaerobic thermophilic digestion of cattle manure. Milan et al. (2001) used a natural zeolite, a mixture of clinoptilolite, mordenite, montmorillonite and others, for the anaerobic digestion of piggery waste. Hansen et al. (1999) used glauconite for the anaerobic digestion of swine manure. These studies revealed that the addition of clay and zeolite improved the methane production. However, zeolite and clay have many different structures and chemical characteristics; it is not obvious what kind of zeolite is most suitable for the methane production. In this study, we carried out methane production studies with different kinds of inorganic additives, zeolites, clay, minerals, or manganese oxides, in order to clarify the factors that improve the methane production during anaerobic digestion.

2. Methods

2.1. Seed sludge and zeolites

The anaerobic digestion seed sludge for sewage sludge studies was collected from a sewage treatment plant in Ibaraki prefecture, Japan. Dewatered anaerobic digestion sludge was fully fed into a plastic box and encapsulated, then stored at 4 °C. Before using as the seed for the anaerobic microorganisms, the sludge was mixed with distilled water and stirred anaerobically for 10 days at room temperature.

Zeolite, clay and manganese oxide porous crystals were used as additives to the sludge. Five kinds of zeolites (natural clinoptilolite, natural mordenite, synthetic Na-type zeolite 3A, synthetic zeolite 4A, and synthetic H-type zeolite 3A), a type of clay (natural vermiculite) and two forms of manganese oxides (hollandite and birnessite) were used in the tests.

2.2. Zeolites, clay and manganese oxides addition

Twenty ml of the sludge (10% dry matter) was placed in a 50 ml glass vial, and 1 g of zeolite, clay or manganese oxide was added to the anaerobically digested sludge. Nitrogen gas was added to remove the air from the glass vial. The vial was sealed with a rubber septum held in place with a thin aluminum cover-cap for the anaerobic conditions. A 50 ml volume of plastic syringe was injected into the top of vial for measurements of biogas volume. The vials were then placed in a thermostated incubator at 35 °C. Biogas production was periodically measured by the increase of gas volume. After a 12-day digestion, the NH_4-N (nitrogen in NH_4 form) concentration of sludge and methane concentrations of evolved gas were measured.

Standard deviations were evaluated by error propagation from triplicate applications of the sample (Leclerc et al., 1998). Significant differences in the methane volume and concentration of ammonium ion between control and other conditions were based on Student's *t*-test (Schlten et al., 2002).

2.3. Ammonium ion-rich conditions

Twenty ml of sludge was mixed with sodium acetate (final concentration; 2 g/l), glucose (final concentration; 2 g/l) and NH_4Cl (final concentration; 4500 mg N/l) in a 50 ml glass vial. The mixture contained 98% water. Natural mordenite or zeolite 3A was added to 5% of NH_4^+-rich sludge (w/w). The vials were sealed and placed in a thermostated incubator at 35 °C. After a 12-day digestion, NH_4^+-N, Ca^{2+}, Mg^{2+}, K^+, Na^+, PO_4^{3-}-P (phosphorus in PO_4^{3-} form concentration of the sludge), methane concentrations of evolved gas and pH of the sludge were analyzed. Statistical analysis was calculated by the same methods as described Section 2.2.

2.4. Addition of cations

To clarify the effect of the cations released from the zeolites, the digestion studies were carried out with Na^+-exchanged mordenite in $CaCl_2$- or $MgCl_2$-enriched sludge. The Na^+-exchanged mordenite was prepared by treating natural mordenite with a NaCl solution. The $CaCl_2$- or $MgCl_2$-enriched sludge was prepared by adding $CaCl_2$ or $MgCl_2 \cdot 6H_2O$ to the sludge up to a concentration of 0.5 g Ca^{2+}/l or 0.05 g Mg^{2+}/l, respectively. Conditions of the sludge were taken under the same ammonium ion and nutrients concentration as described in Section 2.3. Five percent natural mordenite, 5% Na^+-exchanged mordenite, 5% Na^+-exchanged mordenite +0.5 g/l Ca^{2+}, 5% Na^+-exchanged mordenite +0.05 g/l Mg^{2+} and no additive as the control were separately added to the vials, and incubated for 12 days at 35 °C. The methane production from the vials was then measured. Statistical analysis was calculated by the same methods as described Section 2.2.