# 行政院國家科學委員會專題研究計畫　期中進度報告

## 總計劃及子計劃一:污泥前處理與資源化產氣之研究(1/3)

計畫類別： 整合型計畫
計畫編號： NSC91-2211-E-002-064-
執行期間： 91 年 08 月 01 日至 92 年 07 月 31 日
執行單位： 國立臺灣大學化學工程學系暨研究所

計畫主持人： 李篤中

計畫參與人員： 張繼文、蔡德耕

報告類型： 精簡報告
報告附件： 國際合作計畫研究心得報告
處理方式： 本計畫可公開查詢

中　華　民　國 92 年 5 月 21 日

# 行政院國家科學委員會專題研究計畫期中報告

污泥處理技術之研究

總計劃及子計劃一　污泥前處理與資源化產氫之研究 (1/3)

計畫編號：NSC 91-2211-E-002-064
執行期限：91 年 8 月 1 日至 92 年 7 月 31 日

主持人：李篤中 教授
計畫參與人員：張繼文、蔡德耕
執行機構及單位名稱：國立台灣大學化學工程學系

## I. 中文摘要

下水活性污泥成份中含有大量的有機質，如多醣與蛋白質，為具有潛力生物產氫物質。在第一年度的計畫中，我們分別使用污泥的固體部份與濾液部份進行產氫；與一般認知有所不同的是，含較多有機物的固體部份產氫效率較濾液部份為低；污泥濾液之單位有機物氫產率較過去文獻報告值高出一個數量級。

**關鍵詞**：氫氣、污泥、厭氧發酵、濾液、產率

## Abstract

Waste biosolids collected from sewage works is a biomass containing a vast amount of polysaccharides and proteins, and thus is considered a potential substrate for producing hydrogen using anaerobic fermentation. This work demonstrated that, on the contrary to the common assumption that the solids phase in waste activated biosolids presents extra nutrients for anaerobes, it in fact prohibits effective bio-hydrogen production. Using filtrate after removal of solids from biosolids produces more hydrogen than using the whole biosolids, with the former reaching a level an order magnitude higher than the literature results.

**Keywords**: hydrogen, biosolids, fermentation, filtrate, yield

## II. Introduction (計劃緣由與目的)

Bio-conversion of biomass to hydrogen production is technically feasible using anaerobic fermentation (Miyake *et al.*, 1999). Waste biomass collected from the activated sludge process of wastewater treatment plant contains high level of organic matter, and thus is a potential substrate for hydrogen production. Only limited data are available considering waste biosolids as the substrate to fermentation. Huang *et al.* (2000) revealed a very low yield, ca. 0.16 mg-$H_2$/g-dried solids, from waste biosolids produced in a municipal sewage works. Cheng *et al.* (2000) boiled the waste biosolids to release the insoluble organic matter from the solids phase, and noted in the subsequent anaerobic fermentation test a yield of 1.4 mg-$H_2$/g-COD. This value is comparable to that for protein fermentation, but is still far lower than that for polysaccharides. The very low hydrogen yield discourages the use of waste biosolids as the fermentation substrate.

With a *clostridium* strain purified from collected waste biosolids as seed bacteria, we demonstrated in this work that not only the solids phase in the waste biosolids could not be utilized by the anaerobes as nutrient, but also it effectively reduced the hydrogen production. Fermentation of filtrate rather than of the whole biosolids could produce a high bio-hydrogen yield comparable to that for glucose.

## III. Experimental (實驗方法)

The Substrate

Waste biosolids was taken from the Min-Sheng Municipal Wastewater Treatment Plant in Taipei, which handles 15,500 tons sewage per day using primary, secondary, and tertiary treatment stages. Two samples were collected at the recycle stream of activated sludge process on March 14 and on April 23, 2002, respectively, namely the sample #1 and #2 in this work. Typical floc morphology was demonstrated in **Fig. 1a**. The sample #1 was collected at normal operational condition, while the sample #2 was collected at a condition that the Plant had been shut down for a week at nutrient-insufficient stage that consisted of less digestible matters compared with the sample #1. The collected samples were gravitationally settled for 24 hrs and the sediments were stored at 4$^{o}$C. Then the filtrate was obtained from vacuum filtering the biosolids sample through a Whatman #2 paper. Both the whole biosolids and their filtrates were the substrates in the fermentation tests. **Table 1** lists their characteristics. The chemical oxygen demands (COD) for the biosolids were much higher than those for the filtrate, indicating that most organic compounds in the biosolids sample were in an insoluble form.


**(a)** **(b)**

**Fig. 1** The microphotographs of (a) biosolids sample #1, and (b) anaerobic inoculum (*Clostridium bifermentus)*.

**Table 1** Sample characteristics.

| Properties | Sample #1 | | Sample #2 | |
|---|---|---|---|---|
| | sediment | filtrate | sediment | filtrate |
| Solids content (mg/L) | 16500 | NA* | 15,000 | NA |

| | | | | |
|---|---|---|---|---|
| **pH** | 6.4 | 6.9 | 6.2 | 6.7 |
| **COD (mg/L)** | 24,800 | 436 | 244,00 | 510 |
| **Zeta potential (mV)** | -19.1 | -21.9 | -20.1 | -26.9 |
| **Floc size («m)** | 71.6 | NA | 47.6 | NA |

* not available.

The Inoculum

The inoculum was prepared from the original biosolids using the following procedures. Firstly the collected biosolids were pasteurized at 121°C and 1.2 kgf/cm$^2$ (HUXLEY AUTOCLAVE, HL-360) in an anaerobic chamber for 30 minutes (Lay *et al.*, 2000). This action would not effectively remove the heat-resistant bacteria, such as *clostridium sp.* 100 mM of methanogenic bacterial inhibitor, BESA ($C_2H_4BrO_3SNa$, sodium 2-bromoethanesulfonate, Sigma, USA), was added to the pasteurized biosolids. After incubation the dosed biosolids was spread on a gel-type reinforced clostridial medium (OXOID) and colonized for three days. Individual colonies were removed from the medium and incubated on the agar for strain purification. After three-time purification ten colonies of anaerobes were picked up and incubated in liqueur reinforced clostridial medium. These strains were seeded into pasteurized biosolids at anaerobic fermentor. Four strains with the highest hydrogen productivity were mixed and stored as the inoculum in the fermentation tests. The scanning electron microscopic photograph was shown in **Fig. 1b**.

Fermentation and Tests

45-ml of substrate (biosolids or their filtrates) was mixed with 5-ml seed bacteria suspension and was anaerobically incubated at 35°C in 125-ml serum bottles without stirring or further nutrient addition. The bottles were capped with butyl rubber stoppers and wrapped by aluminum foils to prevent possible photolysis reaction of the substrate (Chang *et al.*, 1996). Gas and liquor samples were collected at 8, 16, 24, 32, 40, 48, 72, and 96 hr of fermentation, at each time interval and for each substrate three serum bottles were randomly chosen. Restated, under identical condition three incubated samples were measured and their average was reported. After measurements these samples were abandoned to prevent any possible errors introduced by sampling procedures, such as gas leakage during sampling. The substrate had not been sterilized before tests. Control tests with substrate but without dosing of inoculum revealed negligible hydrogen production (less than 20% of the one with clostridium dosing). Hence, the hydrogen-producing species in the original biosolids played no significant role in the current tests.

GC-TCD (Shimadzu, GC-8A), equipped with a stainless column packed with Porapack Q (50/80 mesh) at 70°C and thermal-conductivity detector (TCD), measured the methane and hydrogen concentrations in gas phase. The temperatures of injector and of detector of GC were at 100°C. Nitrogen at a flow rate of 20 ml/min was the carrying gas. Integrator (HP3396 Series II) was used to integrate the peak area of the effluent curve, and hence quantifying the gaseous concentrations. The hydrogen content in the anaerobic glove box was measured as well, and was subtracted from the hydrogen concentrations in the serum bottles.

## IV. Results and Discussion (結果與討論)

Hydrolysis of Organic Matters

**Figure 2** depicts the COD data of filtrate of fermented biosolids samples and those for filtrate samples. These data are normalized by the chemical oxygen demand for the original biosolids, $COD_0$ (=24,800 mg/l for sample #1, for instance). Although some data scattering existed, two points are worthy noticing. Firstly, the soluble COD for the original biosolids comprises of only 4% of $COD_0$. During fermentation the soluble COD for the whole biosolids samples increase to 8-16%. Hydrolysis of solids phase occurred in the fermented biosolids samples. For the filtrate test, on the other hand, the total COD of the suspension initially comprises of 11% of $COD_0$, indicating the large contribution of the seed bacteria. The COD fluctuates with time but did not reveal an increasing trend. Most substances in biosolids sample ready to hydrolyze had been removed by the filter during vacuum filtration. Seed

bacteria contributed to the initial COD in filtrate test but did not further affect its value in subsequent tests.

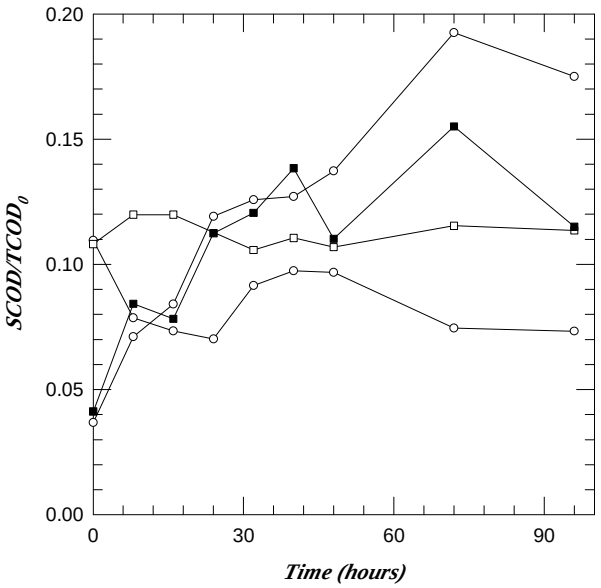


**Fig. 2** The $COD/TCOD_0$ of whole biosolids and filtrate tests. Solid circle: the soluble COD of biosolids sample #1; Solid square: the soluble COD of biosolids sample #2; Open circle: total COD of the filtrate test #1; Open square: total COD of the filtrate test #2.