Industrial Wastewater COD Degradation Technology–Taiwan Solar Cell Plant

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Industrial Wastewater COD Degradation Technology–Taiwan Solar Cell Plant

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The energy crisis has led to continuous cost increases for petroleum, and global climate change has exacerbated the environmental crisis. To cope with the energy crisis, many industrially developed countries have promoted photovoltaic cells as the most promising green energy alternative. However, their manufacture produces enormous amounts of pollutants that significantly impact the environment. To balance green energy and the environment, the manufacturing processes of photovoltaic cells should be environmentally benign. Therefore, a proper pollution prevention management strategy and control technologies should be developed accordingly. To adapt the growth of photovoltaic cell industries in Asia to the global green trend and contribute to environmental protection, we focused on the treatment of wastewater from plants producing photovoltaic cells. A bio-technology process was used to culture microorganisms based on wastewater characteristics from photovoltaic industries. This bio-treatment system was integrated with anaerobic and aerobic bio-treatments, which not only are capable of treating high chemical oxygen demand (COD) concentrations in influents but also can remove NO$_3$-N. This process is able to remove more than 85% of the COD from influent streams. The advantages are that less sludge produced, less space required, and operating costs are lower. This study successfully established an in-situ pilot plant capable of treating influent COD concentrations of 3000 mg L$^{-1}$ and producing effluent COD concentrations of 100−400 mg L$^{-1}$. The COD removal ratio was about 70−85% and can serve as a model reference for practical industrial treatment.

**Keywords:** Aerobic; Anaerobic; Bio-treatment system; Chemical oxygen demand (COD); Wastewater from photovoltaic cells

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1 Introduction

In the development of alternative green energy, photovoltaic cells are the most important alternative energy because they have the most mature technology, the highest potential for industrialization, and the extra benefit of economic development. At the current stage of their development, silicon processing has surpassed all other processing and materials in terms of production and benefits. In applying silicon substrates to photovoltaic cells, the main currently available products are polycrystalline and monocrystalline silicon materials, which constitute nearly 90% of the solar chip market share. However, the production of photovoltaic cells through silicon processing produces the greatest impacts on the environment due to pollution emissions. These emissions include the following contaminants:

- acid wastewater with high salinity, high nitrate nitrogen, high granularity, and a huge amount of silicon sludge from the upstream purification processing of silicon materials;
- wastewater containing fluorine/nitric acid discharged from crystal growing, abrasion, and slicing processes of silicon ingots;
- abrasive slurries containing polymers, e.g., pentylene glycol (PG) and polyethylene glycol (PEG), which can barely be dissolved in a natural environment during processing; and
- wastewater containing ammonia nitrogen and nitrate nitrogen discharged during the cleaning processing of board circuits for photovoltaic cells.

Current water treatment methods are not effective, and the chemical oxygen demand (COD) reduction rate is low in the industry [1]. In the absence of remediation measures, the eutrophication burden on rivers will become worse and cause hidden damage to the environment. In a traditional anaerobic reaction, if the hydrogen partial pressure is above 4–10 atm, the concentrations of propionic acid and butyric acid will increase [2, 3]. Additionally, when methanogens are restrained, the system can go only as far as generating hydrogen [4–6]. Among hydrogen-producing bacteria, clostridia are the most aggressive. They can grow from 25–60 °C at neutral pH [7] and are good at dissolving hydrocarbons and fermenting amino acid.

However, these bacteria may generate internal protection spores and become dormant in an inappropriate environment that lacks adequate sources of carbon and nitrogen [8]. In anaerobic reaction procedures, if a continuous-flow stirred tank
reactor (CSTR) is used with a shorter hydraulic retention time (HRT), the growth rate
of hydrogen-producing bacteria will be higher with a higher and more stable level of
hydrogen production [9–12]. Furthermore, methanogens and sulfate-reducing bacteria
in the methanation system are limited. A large amount of hydrogen can be produced
when the system reactions are maintained in only the hydrolysis and acidification
stages. The system cannot produce methane. This is why the experimental tank was
designed with a gas-liquid separation function. When the system is running, hydrogen
can be released at any time to avoid hydrogen accumulation that may restrain the
methanogens and sulfate-reducing bacteria.

The experimental location should be generally clean and dry, as the effect of
electric currents on microbes is negative and may restrain their growth. Moreover, the
microbes may even die. In practice, electric leakage from the equipment may also
indirectly influence the results of bio-treatment [13, 14]. At 29 °C, if the current
intensity or exposure time increases, the number of surviving bacteria is reduced [15].
If the temperature is maintained at 40 °C, as in a culture medium, the minimum
current that can kill bacteria is 25 mA [16]. Previously, there have been very few
studies on or reports of bio-treatment for photovoltaic cell wastewater [17]. Moreover,
aerobic microbiological remediation is the most economical approach to
wastewater treatment [18, 19].

The costs of land and facilities are relatively low, and it is possible to re-use
energy. We therefore used cultivated microbes for treating wastewater related to solar
chip processing, slicing, and abrasion. On the basis of photovoltaic cell wastewater
characteristics and using COD as the indicator, we developed a set of actual pilot data
for treatment that can be provided to photovoltaic wastewater treatment plants as a
planning reference for COD reduction [20].

2 Materials and methods

2.1 Sample sources

The wastewater from a solar wafer fab in Taiwan included effluents from the cleaning,
slicing, and abrasion processing of silicon materials consisting of organic substances,
such as abrasive grains and slurry, cleaning solvents (lactic acid and citric acid), and
high concentrations of nitrate nitrogen. The composition of the wastewater is given in
Tab. 1, including pH, SS, COD, and NO$_3$-N.

2.2 Equipment and operating parameters

Because the wastewater contained high concentrations of PEG/PG type organics, which were difficult to dissolve, we attempted to use a 10 L upflow anaerobic sludge blanket (UASB) as the main body [20–23] to build the AnBio-Cube® bio-processing experiment module to perform lab tests with the PEG organic wastewater discharged from the solar wafer fab. A flow chart of the AnBio-Cube® system is shown in Fig. 1. The operating processes are described below:

(1) Tubing pump (Masterflex® L/S®): used with two peristaltic pumps for feeding and circulation.

(2) Trifurcation connector, rubber hose, 100 kL plastic barrel: used to contain original wastewater.

(3) Bacterial source: approximately 8 L of granular substrate sludge from a piggery sewage farm located in Yunlin County, Taiwan, ROC.

(4) HRT: the tests were performed with different HRTs, from 2–10 mL min$^{-1}$.

(5) Recycle rate: the recycle rate was maintained at 60 mL min$^{-1}$ [19].

(6) pH: pH was controlled within the range of 6.8–7.2.

(7) Temperature: room temperature, ca. 25–33 °C [24–26].

2.3 Experimental method of AnBio-Cube® system

We applied the AnBio-Cube® system treatment method to photovoltaic wastewater treatment. The experimental conditions of the anaerobic system, aerobic system, and complete module are described as follows, and the results of experiments are depicted in Figs. 2–4.

A COD of 3000 mg L$^{-1}$ retrieved from the wastewater was directly derived using the tubing pump on the front-end anaerobic system. The cultivation was carried out under 2–7 mL min$^{-1}$, and the internal circulation of the recycling system was activated with the recycle rate maintained at 60 mL min$^{-1}$. At the beginning of activation with the inflow rate at 2 mL/min, the COD outflow concentration continued to increase, indicating that the microbes in the system had not yet adapted and were not able to treat the PEG high-COD wastewater. After replacing the granular sludge and re-activating the system with the COD of the original wastewater diluted to 500 mg L$^{-1}$,
inflow was again started. The COD at the outflow outlet dropped below 200 mg L\(^{-1}\), indicating that the microbes had adapted and their treatment abilities were activated. At that time, inflow was initiated. After a series of cultivations and tests, the microbes in the system that could tolerate COD value was close to 3000 mg L\(^{-1}\), and the inflow rate was increased from 2–7 mL min\(^{-1}\). This was the cultivation stage of the anaerobic system. The outflow of this anaerobic system was linked to the aerobic system, which is the AnBio-Cube\(^\text{®}\) system treatment method proposed by this study.

2.4 Analytical methods of wastewater indexes

Methods for analyzing water quality: during the operation period, COD, and pH values were monitored. The methods applied are all recognized by the Environmental Analysis Laboratory in Taipei, Taiwan, ROC, as listed in Tab. 2 [27, 28].

The method for determination of pH value is followed by NIEA W424.52A, where the activity of hydrogen ion can be evaluated via the differences of a sample’s potential between glass electrode and reference electrode.

The concentration index of hydrogen ion is determined as a pH value. From the aspect of suspended solid (SS), followed by NIEA W210.57A, a mixed and well-distributed sample was put in an evaporating dish which has weighted before further experimental process, and then the evaporating dish with sample underwent the process of drying by heat with an oven, maintained at 103–105 °C until the sample dried. The weight of the residual sample on the evaporating dish is called total solids (TS). Besides, the mixed and well-distributed sample was percolated with glass fiber filter, and for the glass fiber filter it was the process of drying by heat with an oven, maintained at 103–105 °C. The weight of sample covered on the filter is defined as SS.

The weight of total dissolved solids (TDS) is calculated as the difference between TS and SS.

For volatile suspended solids (VSS), followed by APHA 2540E, TS, SS, and TDS it was the process of dry by heat with an oven, maintained at 600 °C for 10–15 mins. The value of VSS can be calculated by the weight loss of those above three solids after the process of drying by heat.

Determination of COD was described as the method of NIEA W510.54A, where potassium dichromate solution was added into and mixed with sample before undergoing heating reflux with 50% strong sulfuric acid. The residual potassium
dichromate solution underwent ammonium ferrous sulfate titration method to calculate the consumed amount of potassium dichromate. The content of organic chemicals in a sample can be oxidized by potassium dichromate solution, and the amount regarding the above test can be determined as COD.

For nitrogen-nitrate (NO$_3$-N), followed by NIEA W419.51A, water-soluble organic compounds and nitrates could be absorbed by ultraviolet spectrophotometer (UV) at wavelength of 220 nm, but nitrates could be absorbed by UV at wavelength of 275 nm. Therefore, the difference of a sample’s absorption between wavelengths of 220 and 275 nm could be used to calculate the content of NO$_3$-N.

3 Results and discussion

3.1 Influence of inflow rate on COD removal efficiency

After the completion of cultivation, the inflow COD value and inflow rate were 3200 mg L$^{-1}$ and 7 mL min$^{-1}$, respectively. Although the inflow rate was adjusted to 5 mL min$^{-1}$ on the 6th and 12th days to alleviate the loading, the removal efficiency of the anaerobic system still could not reach 50%, as shown in Fig. 2, indicating that the polymerized binding of this poisonous PEG wastewater was indeed difficult to handle. Fig. 2 indicates that from the 26th day to the 30th day, the removal efficiency of the anaerobic system was under 50%. However, it reached 86% when the aerobic system was added (Fig. 3), reflecting the contribution of the aerobic system to the COD removal efficiency in the later stage. When the aerobic system was included in the operation through seeding, 14 days later, the aerobic microorganisms began to work normally and the COD removal efficiency began to increase.

3.2 Influence of pH on COD removal

In the experiments, the pH in the anaerobic system was maintained within the range of 6.8–7.2 throughout the entire process; these values are close to the growth range of anaerobic bacteria (6.5–7.5) proposed by Hu et al. and Saritpongteerakaa et al. [29, 30]. However, the time required for activation was quite long, possibly because of the low pH range required for acidophilic bacteria to grow [17, 31–33]. The pH in the anaerobic system was maintained in the range of 7.0–8.0 during the whole process,
avoiding a rise above 9.0 or a sudden drop so that sticky substances in bacterial clumps could be disintegrated and the sludge structure destroyed, leading to the fluid sludge phenomenon [34].

### 3.3 Influence of temperature on COD removal efficiency

No temperature controller was installed in the system. Previous studies have reported temperature ranges for the growth of *Nitrosomonas* and *Nitrobacter* of 30–36 °C and 8–28 °C, respectively, and the optimal temperature range for operation was 20–35 °C. Therefore, the overall proper temperature range for growth was 20–35 °C. Usually, the higher the temperature, the more complete is the oxidation of nitrate nitrogen. During the experiment, the temperature was lower at night. If a temperature controller had been available to ensure that the temperature was maintained at 35 °C, the treatment efficiency of the system would have been higher.

### 3.4 Influence of aeration on COD removal efficiency

The water was turbid in the aerobic system. This could be attributed to a poorly controlled aeration rate that led to stirring and facilitated the propagation of filamentous bacteria. One solution involves reducing the aeration rate or improving the distribution of aeration in the system, thus providing microbes with sufficient dissolved oxygen and stirring power resulting from a proper flow rate for their dissolution. Another possibility is to provide a proper nitrogen source or kill filamentous bacteria with H$_2$O$_2$. These approaches could increase the treatment efficiency of COD removal [35].

### 3.5 Bio-bacterial flora of the reactor

The formation of the sludge blanket was observed at the one-third level under the reactor. This is consistent with the bacterial flora of mature granular sludge of UASB described by Seghezzo et al. [36] and Lettinga et al. [21], and indicated that the system operation was normal. After the 32nd day, the overall treatment capacity of the AnBio-Cube® system tended to stabilize, with the COD value after treatment reaching 500 mg L$^{-1}$, as shown in Fig. 4 (AnBio-Cube® system).
No nutrients such as nitrogen and carbon sources were added during this biotreatment process. The organisms could adapt naturally to the PEG characteristics. We believe that this behavior is qualitative. Microbes first adapted to the substance characteristics and then to the substance concentrations. The quantitative approaches were considered after the qualitative ones. This two-stage method can be used as a reference for microbe cultivation. In addition, the environmental endurance of methane microbes is noteworthy because they belong to the Archaea.

3.6 Comparison of different treatment procedures for COD wastewater

The anaerobic system is usually employed on hard-degradable materials, especially nitrogenous and phosphorous materials, and the aerobic system is used on COD treatment. Therefore, the useful treatment of complex composition wastewater has usually adopted the anaerobic system first in removal of hard-degradable materials and aerobic system in the subsequent step for COD removal treatment.

In a traditional anaerobic system, bacteria are attached on loading materials, but loading materials are not necessary in UASB, where well-settleable anaerobic replicating microorganism can be bred by coagulation of bacteria for maintaining high concentration of bacteria in UASB.

The advantages of UASB are as follows.

1. High concentration of bacteria can be maintained by adopting this method, and then accompanied with high concentration of bacteria, high volume loading can be produced.

2. The available usage volume can be increased due to unnecessary loading materials in UASB.

3. This method acquires high efficiency of biodegradability, hence it is useful to conduct on hard-degradable COD by employing this method.

4. The structure of the whole-processed apparatus is simple and the function of this apparatus is easy to maintain, because gas, especially methane, will be produced during anaerobic system, and then sludge can be stirred with the gas-produced process.

As Tab. 3 shows, we can confirm that the AnBio-Cube® microbe treatment system proposed in this study is better than other treatment systems as being recorded in previous studies after comparison of different treatment procedures, such as Fenton
+ bio-treatment, ozone (O$_3$) + bio-treatment, and activated carbon + bio-treatment, for COD wastewater. Advantages of the AnBio-Cube$^\text{®}$ system include good resistance to concentration impacts, low operating cost, reduced amounts of sludge, and high removal efficiency of COD. It is suitable for treating highly concentrated PEG/PG organic and detergent wastewater, and water quality after treatment can meet the discharge requirements. With this system, the difficulty of treating wastewater in the solar wafer fab industry is effectively solved.

4 Conclusions

This study demonstrated through experiments that high-COD PEG wastewater could be degenerated with cultivated microbes. We also successfully developed a system for a real pilot treatment case. With 3000 mg L$^{-1}$ inflow, the normal COD concentration was between 100 mg L$^{-1}$ and 400 mg L$^{-1}$, and the COD removal efficiency was 70–85%. In the future, we plan additional field experiments to obtain a series of pilot data for the industry as a reference to treat this type of wastewater effectively.

Acknowledgments

We offer our sincerest appreciation to Dr. Guang-Zu Jin for his help and to Ms. Xiang-Lan Lin for her careful and attentive assistance with the lab tests.
References


[27] Environmental Analysis Laboratory (EAL), Environmental Protection Administration, Executive Yuan, ROC, Data quality system under national environmental structure. Analysis method: NIEA W424.52A, NIEA W210.58A, APHA2540E, NIEA W510.54A, and NIEA W419.51A.


[37] S. Shao, Post globe: Novel technology and presentation on wastewater treatment, Environmental Protection Administration, Executive Yuan, Taipei, Taiwan 2002.
Table captions

Table 1. Composition of wastewater from slicing and abrasion processing in a solar wafer fab

Table 2. Items to be analyzed and analytical methods applied (EPA, Executive Yuan, ROC; APHA, USA) [27, 28]

Table 3. Comparisons of different treatment procedures for COD wastewater from solar water abrasion and slicing [37]
Table 1. Composition of wastewater from slicing and abrasion processing in a solar wafer fab

<table>
<thead>
<tr>
<th>Composition</th>
<th>Polyethylene glycol (PEG)</th>
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<tr>
<td>pH</td>
<td>6–8</td>
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<tr>
<td>SS (mg L⁻¹)</td>
<td>&lt;100</td>
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<td>COD (mg L⁻¹)</td>
<td>2000–3100</td>
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<tr>
<td>NO₃-N (mg L⁻¹)</td>
<td>&lt;350</td>
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Table 2. Items to be analyzed and analytical methods applied (EPA, Executive Yuan, ROC; APHA, USA) [27, 28]

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<tr>
<th>Item</th>
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<tr>
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<td>NIEA W424.52A</td>
</tr>
<tr>
<td>SS</td>
<td>mg L⁻¹</td>
<td>NIEA W210.58A</td>
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<td>VSS</td>
<td>mg L⁻¹</td>
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<td>COD</td>
<td>mg L⁻¹</td>
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<tr>
<td>NO₃-N</td>
<td>mg L⁻¹</td>
<td>NIEA W419.51A</td>
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Table 3. Comparisons of different treatment procedures for COD wastewater from solar water abrasion and slicing [37]

<table>
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<tr>
<th>Procedure</th>
<th>AnBio-Cube® proposed by this study</th>
<th>Fenton + bio</th>
<th>O₃ + bio</th>
<th>Activated carbon + bio</th>
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<td><strong>Range of concentration</strong></td>
<td>500–10,000 mg L⁻¹</td>
<td>50–1000 mg L⁻¹</td>
<td>50–500 mg L⁻¹</td>
<td>50–500 mg L⁻¹</td>
</tr>
</tbody>
</table>
| **Target** | 1. Suitable for treatment of wastewater of high concentration  
2. Efficient for treatment of PEG/PG organic wastewater which is hard to be dissolved  
3. Workable for detergent wastewater | Suitable for treatment of wastewater of medium/low concentration (<300 mg L⁻¹)  
Unstable in efficiency for wastewater of high concentration | 1. Workable for degeneration of organic substances which are difficult to be biodegraded using O₃  
2. Bio-pretreatment using O₃ | Organic substances which are difficult to be dissolved |
| **Pretreatment removal efficiency** | >60% | <20% | <20% | <20% |
| **Cost** | 0.33–0.5 USD/kg-COD | 1–2 USD/kg-COD | 1.5–2 USD/kg-COD | 1.17–1.67 USD/kg-COD |
| **Advantages and disadvantages** | 1. Good impact resistance of the system  
2. Low operating cost  
3. Small amount of sludge  
4. Good quality of treated water, and treated water can match the discharge requirements | 1. Low initial set-up cost  
2. High operating cost  
3. Large amount of sludge  
4. Difficult to treat waste water, and treated water can match the discharge requirements | 1. Low initial set-up cost  
2. High operating cost  
3. Large amount of sludge  
4. Difficult to treat waste water, and treated water can match the discharge requirements |

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**Figure captions**

**Figure 1.** AnBio-Cube® system flow chart.

**Figure 2.** COD removal conditions in the anaerobic system.

**Figure 3.** COD removal conditions in the aerobic system.

**Figure 4.** COD removal conditions in the complete module.
Figure 1. AnBio-Cube® system flow chart.
Figure 2. COD removal conditions in the anaerobic system.
Figure 3. COD removal conditions in the aerobic system.
**Figure 4.** COD removal conditions in the complete module.