Chinese Chemical Letters Vol. 13, No. 11, pp 1111 – 1114, 2002 1111
http://www.imm.ac.cn/journal/ccl.html

Generation of Hydrogen from Photolysis of Organic Acids by Photosynthetic Bacteria

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Abstract: Photodecomposition of ten kinds of organic acids by *Rhodopseudomonas palustris* for producing hydrogen has been investigated. By using acetate as hydrogen donor, dynamics of hydrogen production and cell growth has been determined; the influences of acetate concentration, temperature, light intensity and the effects of the interaction among metal ions (Fe^{3+}, Ni^{2+}), acetate and glutamate in aqueous solution on hydrogen production have been examined for optimizing the conditions of H_2 generation. The results show that H_2 production is partially correlated with cell growth; Ni^{2+} inhibits hydrogen production, but enhances cell growth; Fe^{3+} promotes hydrogen production evidently. The highest rate of H_2 production is 22.1 mL L^{-1} h^{-1} under the conditions of 35～37℃, 6000～8000 lx, 30 mmolL^{-1} of acetate, 9 mmolL^{-1} of glutamate, and 50 μmolL^{-1} of Fe^{3+}.

Keywords: Photodecomposition of organic acids, hydrogen, photosynthetic bacteria.

Hydrogen is considered to be a future fuel because it is almost pollutionless, yielding only water after combustion[1,2]. Nowadays a hot topic on environment chemistry is the combination of treatment of organic waste water with hydrogen energy generation. Photosynthetic bacteria have the capacity of degrading organic acids and converting solar energy to chemical energy by using organic acids[3]. *R. palustris* is an efficient kind of bacteria for the photodecomposition of organic acids when it absorbs visible or infrared lights. Nevertheless, little attention has been given on the photodecomposi- tion of organic acids with it[4]. The present work is, by using organic acids as hydrogen donor and *R. palustris* as producer, to investigate the influences of organic acid concentration, temperature, light intensity and metal ions on H_2 production and find the optimal conditions for the photoproduction of hydrogen from organic acids.

Methods

The equipment for hydrogen production is shown in **Figure 1**. H_2 content was assayed by Shimadzu Gas Chromatograph equipped with a molecular sieve 5A column and a

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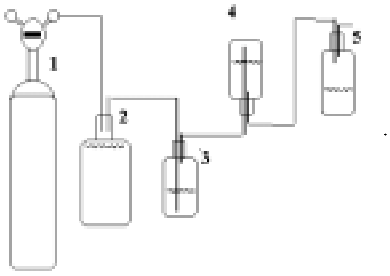
thermal conductivity detector. Argon was used as carrier. Cell growth was measured by determining optical density of the cultures at 660 nm ($OD_{660\ nm}$) with a Spectra Max 190 Model of Microplate Spectrophotometer. Light intensity was measured with a Model ST-85 Auto- Range- Illuminance-Meter.

Results and Discussion

According to the characteristics of photosynthetic bacteria metabolism and the dominant product types of organic wastewater degradation, ten organic acids were selected for this investigation. The efficiency of hydrogen production and cell growth was measured by the rate of H_2 production (RHP) and OD_{660nm} in this investigation, respectively. The experimental results are listed in **Table 1**, which showed that, for the linear fatty acids, both the RHP and OD_{660nm} values with even number of carbon atoms (acetate and butyrate) are much higher than those with odd number carbon atoms (formate and propionate) and both values decreased with the increment of carbon chain. It also showed that the highest RHP was given by using acetate as the sole electron donor.

Figure 1 The equipment for hydrogen production.



1. argon; 2. photoreactor; 3. CO_2 absorbed vessel; 4. H_2 collector; 5. gauge of H_2 volume

Table 1 The RHP and cell growth from different organic acids by *R. palustris*

Hydrogen donor /20 mmolL^{-1}	RHP /mL L^{-1}h^{-1}	Cell growth OD_{660nm}
formate	5.5	0.963
acetate	15.3	1.213
propionate	5.0	0.686
butyrate	12.0	0.872
pyruvate	3.0	1.182
lactate	4.5	1.280
malate	4.0	1.238
citrate	2.0	0.859
succinate	5.0	1.293
gluconate	10.0	0.580

Based on the results of **Table 1**, the dynamics of both H_2 liberation and cell growth from acetate were investigated, which is shown in **Figure 2.** It illustrates that both the amount of H_2 production (AHP) and cell growth have the same tendency. Conversion of acetate into H_2 by *R. palustris* was obviously observed over 36 hours with a 72-hour inoculum and ceased by 160-hour. The optimal AHP lies in the range of 36~96 hours.

The effect of different acetate concentrations on hydrogen production is shown in **Figure 3**. Among the five AHP~h curves with acetate concentration range from 10 to 100 mmol L^{-1}, the highest AHP was achieved from the concentration of 30 to 50 mmol L^{-1}. AHP only increases slightly in medium containing acetate of 10 mmol L^{-1} or 70 mmol L^{-1}. Acetate supplement of 100 mmol L^{-1} is the limiting factor for H_2 production under the experimental conditions.

The influence of temperature on AHP is shown in **Figure 4**, which indicates that raising temperature is favorable to both H_2 evolution and cell growth. The optimal temperature for H_2 production and cell growth lies in the range of 303 ~ 310 *K* and 308 ~310 *K*, respectively. This identity of temperature for both H_2 evolution and cell growth has significant potential application in the technology of splitting organic acid into H_2 by photosynthetic bacteria.

Figure 2 Dynamics of amount of hydrogen production (AHP) and cell growth from acetate by *R. palustris.*

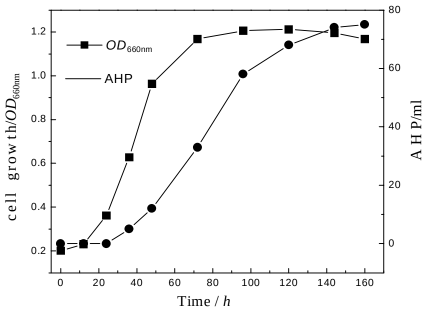


Figure 3 Influence of different acetate concentrations on AHP

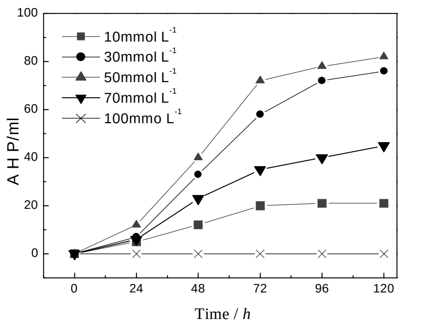


Figure 4 Influence of temperature on cell growth and AHP

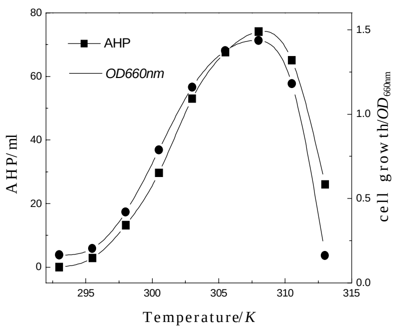
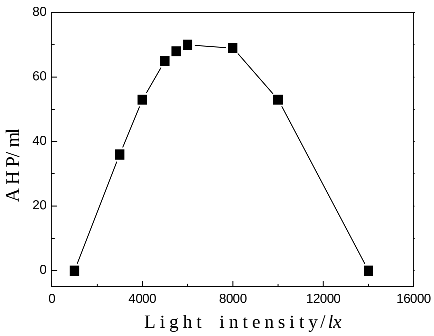


Figure 5 Influence of light intensity on AHP



Photolysis of organic acids generating H_2 is a light-dependent electron transfer process and the energy needed for the process in nature comes from sunlight. Therefore, light intensity plays a crucial role in turning solar energy into chemical form. The effect of different light intensities on AHP with acetate as hydrogen donor is shown in **Figure 5**, which demonstrates that the favorable light intensity for AHP occurs 4000 ~ 9000 lx. The optimal light intensity was between 6000 ~ 8000 lx. This result indicates that photo-split of organic acid into molecular hydrogen is regulated by light intensity. Saturation effect of light is found during this transform process.

By using orthogonal design, the influences of the interaction among metal ions, (Ni^{2+} and Fe^{3+}), acetate and glutamate in aqueous solution on H_2 production are tested, which are shown in **Table 2** and **Table 3**, respectively. **Table 2** illustrates that Ni^{2+} inhibits H_2 evolution, but accelerates cell growth. The influence of glutamate concentration on cell growth is higher than that of both acetate and Ni^{2+} concentrations. In contrast to Ni^{2+}, Fe^{3+} is a key to H_2 production **(Table 3)** and the effect of acetate concentration on H_2 production is higher than that of glutamate concentration.

Table 2 Effects of the interaction among Ni^{2+}, acetate and glutamate on AHP and cell growth

Test number	1	2	3	4	5	6	7	8	9
Acetate ($mmolL^{-1}$)	20	20	20	30	30	30	40	40	40
Glutamate ($mmol\ L^{-1}$)	5	7	9	5	7	9	5	7	9
$NiCl_2.6H_2O$($\mu molL^{-1}$)	3	5	7	5	7	3	7	3	5
OD_{660nm}	*	*	1.026	*	*	1.573	1.086	1.116	1.213
AHP(ml)	0	0	20	0	0	0	24	24	0

*: cell aggregation under these conditions.

Table 3 Effects of the interaction among Fe^{3+}, acetate and glutamate on AHP and cell growth

Test number	1	2	3	4	5	6	7	8	9
Acetate ($mmolL^{-1}$)	20	20	20	30	30	30	40	40	40
Glutamate ($mmol\ L^{-1}$)	5	7	9	5	7	9	5	7	9
$FeCl_3.6H_2O$ ($\mu mol\ L^{-1}$)	50	90	120	90	120	50	120	50	90
OD_{660nm}	0.753	0.723	1.212	0.856	0.798	1.231	0.864	0.912	1.165
AHP (ml)	12	36	16	80	65	106	40	55	90

Conclusion

It is obviously available to photo-split organic materials in wastewater into hydrogen and to convert solar energy into chemical form by *R. palustris* under the conditions of natural ecology. Undoubtedly, this technique is an environmental friendly hydrogen production technology and will have some influence on our future life.

Acknowledgment

The authors wish to express the deepest gratitude to the National Natural Science Foundation of China (grant No. 29973023) for financial support.

References

1. R. Nandi, S. Sengupt, *Crit. Rev. Microbiol*, **1998**, *24* (1), 61.
2. J. Benemann, *Nature Biotechnology*, **1996**, *14*, 1101.
3. K. Sasaki, *Biohydrogen*, Plenum Press, London, **1998**, 133.
4. P. Hillmer, H. Gest, *J. Bacteriol*, **1977**, *129* (2), 724.

Received 22 February, 2002