Hydrogen production affected by Pt concentration on TiO_2 produced from the incineration of dye wastewater flocculated sludge using titanium tetrachloride

H.K. Shon[a]*, S. Vigneswaran[a], I. El Saliby[a], Y. Okour[a], In S. Kim[b], J. Cho[b], H.J. Park[c], J.B. Kim[c,d], J.-H. Kim[c,d]

[a]*Faculty of Engineering, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia
Tel. +61 295142641, Fax +61 295142633; email: hkshon@eng.uts.edu.au*
[b]*Environmental Science and Technology, Gwangju Institute of Science and Technology, Gwangju, Korea*
[c]*Photo & Environmental Technology Co., Gwangju 500-460, Korea*
[d]*School of Applied Chemical Engineering & The Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, Korea*

ABSTRACT

TiO_2 from the incineration of dye wastewater flocculated sludge using $TiCl_4$ coagulant was produced. Optimal catalyst amount and Pt-loading on TiO_2 were studied for the production of H_2 by photocatalytic reforming of methanol (6% vol.). On the other hand, BTSE (biologically treated sewage effluent) was flocculated using $TiCl_4$ and produced sludge was incinerated to generate TiO_2. TiO_2 was loaded with optimum Pt and added to the supernatant in a photocatalytic reactor to test the efficiency of using remaining organics as a "sacrificial reagent" for photocatalytic hydrogen production. Dissolved organic carbon (DOC) and molecular weight distribution (MWD) were measured for nanofiltration (NF) and $TiCl_4$ flocculation followed by photocatalysis. TiO_2 (from the incineration of BTSE flocculated sludge using $TiCl_4$) was produced and loaded with 0.5% Pt. Results showed that the optimum concentration of TiO_2 (from dye wastewater) for H_2 production was 0.3 g/L, while the optimum amount of Pt was 0.5%. DOC and MWD removal was similar for the flocculation of BTSE followed by photocatalytic reaction and the NF process. Remaining organic compounds after flocculation could not be used as sacrificial reagent to induce H_2 production. Further investigations on studying the UV intensity and/or identifying organic/inorganic scavengers to inhibit H_2 production are underway.

Keywords: Dye wastewater; Hydrogen production; Platinum; Titanium dioxide

1. Introduction

The sustainability of conventional energy sources on earth, mainly fossil fuel, is becoming more and more a doubtful issue and the search for an economically feasible alternative has not yet been achieved. Most of predictions on the depletion of fossil fuel in the past 25 years were either imprecise or missed possible future technology improvement in this field. For instance, presently, 85% of energy consumed on earth is still originated from fossil fuel, while only 5% comes from renewable energy and the rest 10% being from nuclear and hydroelectrical power [1,2]. The combustion of fossil fuel has contributed significantly to the increase of CO_2 concentrations in the atmosphere and consequently created environmental problems. The need for an environmental friendly fuel

* Corresponding author.

that reduces the impact of energy production on the natural ecosystem and that does not halt the equilibrium of life on earth is essential. Hydrogen fuel that is extracted from water via biological production, or using electricity (by electrolysis), chemicals (by chemical reduction) or heat (by thermolysis) is considered as the future fuel that meets those criteria. This is mainly because it is produced from clean and renewable energy sources.

Among the possible ways of producing environmental friendly H_2, the photosplitting of water for producing H_2 has gained much attention due to its potential applications as a clean energy source [3]. The photosplitting of water can be divided into: i) the photoelectrochemical system [4–7] and ii) the the photocatalytic suspension system [8,9]. Extensive studies focused in the past decade on improving the production of hydrogen by using the photocatalytic suspension system with TiO_2 as catalyst [9–11]. TiO_2 is produced by different procedures but a novel synthesis reaction was developed by Shon et al. [12] to produce titania from the incineration of wastewater flocculated sludge using titanium tetrachloride. This methodology had a twofold environmental positive impact which summarized in eliminating the need to dispose of sludge in the natural ecosystem as well as which enabled the production of an essential catalyst for the production of H_2 through the photocatalytic suspension system. Presently, the energy conversion efficiency from solar to hydrogen by TiO_2 photocatalytic water-splitting is still low, mainly due to the: i) recombination of photogenerated electron/hole pairs; ii) fast backward reaction (recombination of hydrogen and oxygen into water); and iii) inability to utilize visible light [13].

Many efforts have been made to improve the photocatalytic suspension system through noble metal loading on TiO_2 surface [14–18] or the use of organic solvents as "sacrificial reagents" [17,19–22]. However, Ni et al. [13] reported that hydrogen production from pure water-splitting is difficult to achieve even if noble metal loading can reduce recombination to some extent. This is mainly due to: i) recombination cannot be completely eliminated; ii) backward reaction of H_2 and O_2 to form H_2O is thermodynamically favourable. Therefore, the addition of sacrificial electron donor (organic compounds) which becomes progressively oxidized toward CO_2 by consuming photogenerated holes and/or oxygen will increase hydrogen production rates [23]. Pastoura et al. [23] found that enhanced hydrogen production process is directly related to the amount of sacrificial reagent present in the suspension of Pt/TiO_2 and water. After the complete oxidation of the sacrificial reagent they recorded a drop of the rate of hydrogen production to values comparable to those obtained from pure water. The effects of various sacrificial reagents such as CH_3OH, CH_2O, Na_2S, I^- and IO_3^-, was investigated by Galinska and Walendziewski [24], who found that methanol is the best capture reagent for the photogenerated holes.

In the present study, we have synthesized TiO_2 from the incineration of dye wastewater flocculated sludge using $TiCl_4$. The synthesized catalyst was tested for hydrogen production from 6% (v/v) methanol/water solution to determine its optimum concentration. Later on, the identified optimum TiO_2 concentration was used to load the catalyst with different Pt concentrations and the resulted catalysts were tested again to estimate hydrogen production using the 6% (v/v) methanol/water solution. The characterization of the generated catalysts was also done. Additionally, photocatalytic organic removal for wastewater reuse with simultaneous photocatalytic hydrogen production was performed and the process efficiency was compared to nanofiltration (NF) membrane process in terms of dissolved organic carbon (DOC) removal and molecular weight distribution (MWD).

2. Materials and methods

2.1. TiO₂ and Pt/TiO₂ preparation

Dye wastewater (chemical oxygen demand, suspended solid, total nitrogen, total phosphorus and pH were 448.8 mg/L, 43.3 mg/L, 72.4 mg/L, 3.2 mg/L and 11.7, respectively) collected from Daegu Dyeing Industrial Center, South Korea was used to collect sludge after Ti-salt ($TiCl_4$) flocculation. Flocculated sludge was incinerated at 600°C to produce TiO_2 powder [12]. Different concentrations (0.1, 0.3, 0.5, 1 and 2 g/L) of TiO_2 were used later on in this study to test their effect on the production of H_2 gas and ultimately to determine the optimal concentration for platinum deposition on TiO_2.

TiO_2 powder produced from the incineration of dye wastewater flocculated sludge was used to test the effect of Pt concentration on the hydrogen production rate of Pt/TiO_2. The deposition of Pt on TiO_2 surface using the H_2 reduction method was performed following the methodology described by Ikuma and Bessho [16]. TiO_2 powder was mixed with H_2PtCl_6 solution and methanol. Solution mixture was continuously stirred while subjected to heating until the liquid was evaporated. After drying, TiO_2 powder was heated in H_2 atmosphere at a temperature of 425°C to reduce the H_2PtCl_6 to Pt. Different Pt concentrations (0.01, 0.05, 0.1 and 0.5%) were deposited on TiO_2 surface to identify the optimum Pt concentration for hydrogen production.

2.2. Characterization of TiO₂

TiO_2 produced from the flocculation of dye wastewater using $TiCl_4$ and Pt/TiO_2 were analysed using transmission electron microscope (TEM, Rigaku, Japan). MDI Jade 5.0 (Materials Data Inc., USA) was used to generate X-ray diffraction (XRD) patterns. BET surface area analysis was assessed using an automated surface area analyser (Micromeritics Gemini 2360, USA).

2.3. Catalytic reaction for hydrogen production

Different TiO_2 (0.1, 0.3, 0.5, 1 and 2 g/L) amounts were tested to determine the optimum concentration of catalyst that generates the highest H_2 production rate. Each concentration was adjusted to be added to 500 ml of 6% (v/v) methanol/pure water solution placed in a glass reactor with a head space of 40 ml. The temperature of the reaction was controlled at 30°C ± 1°C using a water condenser submerged in the solution suspension (Fig. 1). The solution was stirred using a magnetic stirrer and illuminated using a 15 W UVA lamp (365–380 nm). In order to remove dissolved oxygen from the solution and the head space, a flow of dry N_2 was purged into the reactor for 30 min prior to illumination. The reaction time was 5 h. Gas samples were removed from the reactor at specific time intervals and analysed using a gas chromatograph (GC/TCD) equipped with a capillary column (CP-PoraPLOT Q, 27.5 m × 0.53 mm × 20 μm, #CP7554, Varian Inc., CA, USA). Scotty gas standard was measured by mol % in N_2 balance (1% H_2, 1% O_2, 1% CO_2, 1% CH_4 and 1% CO).

After identifying the optimum concentration (0.3 g/L) of the catalyst, different Pt concentrations of 0.01, 0.05, 0.1 and 0.5% were loaded on the surface of TiO_2. In order to determine the optimum Pt deposition amount on TiO_2, hydrogen production reaction using different Pt/TiO_2 catalysts was performed by following the same procedure described earlier for determining the optimum TiO_2 concentration.
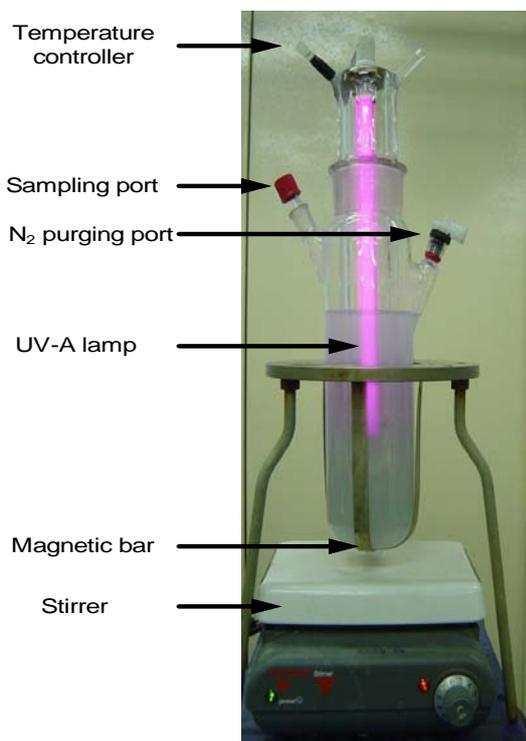
Fig. 1. Photocatalytic reactor for hydrogen generation.

2.4. Photocatalytic organic removal for wastewater reuse with simultaneous photocatalytic hydrogen production

The experiment was carried out using BTSE (biologically treated secondary effluent) drawn from a Gwanju sewage treatment plant (25,000 m³/d). Chemical oxygen demand, total nitrogen, total phosphorus and pH were 23.3 mg/L, 30.5 mg/L, 2.3 mg/L and 7.2, respectively. Ti-salt flocculation was conducted to remove large particle organic matter present in BTSE. After flocculation, sludge was incinerated at 600°C to produce TiO_2 nanoparticles, while the supernatant (500 ml) was placed in the reactor used and described earlier in this study for H_2 production. Produced TiO_2 were loaded with 0.5% of Pt using the H_2 reduction method (described before). Optimum Pt/TiO_2 amount (0.3 g/L) was added to the supernatant in the H_2 production reactor to study the effect of using building block, low MW acid and amphiphilic compounds as sacrificial reagent on the production of H_2. The reaction was carried out for 12 h.

Gas samples were removed from the reactor at specific time intervals and analysed using a gas chromatograph (GC/TCD) equipped with a capillary column (CP-Pora PLOT Q, 27.5 m × 0.53 mm × 20 μm, #CP7554, Varian Inc., CA, USA).

2.5. Dissolved organic carbon (DOC) and molecular weight distribution (MWD)

Dohrmann Phoenix 8000 UV-persulfate TOC analyzer equipped with an autosampler was used to measure the DOC. All samples were filtered through 0.45 μm membrane prior to the DOC measurement. High performance size exclusion chromatograph (HPSEC, Shimadzu Corp., Japan) with an SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the MW distribution of organic matter. Standard solutions of different polystyrene sulfonates (PSSs) with known MW (210, 1800, 4600, 8000, and 18000 Da) were used to calibrate the equipment.

2.6. Crossflow filtration set-up

Fig. 2 shows the schematic diagram of the cross-flow NF experimental setup. A cross-flow membrane filtration unit (Nitto Denko Corp., Japan) was used to determine the DOC and MWD of particles in BTSE after NF (NE90), the characteristics of which are presented in Table 1. Contact angle measurements using the sessile drop method with a contact angle meter (Tantec, Co., USA) were used to determine membrane polarity; 20 μL of Milli-Q water was dropped onto the dried membrane surface and the contact angle was measured within approximately 10 s. The Zeta potential of membrane was measured by the electrophoresis method (ELS 8000 Otzca, Japan) using polylatex in 10 mM NaCl solution as a standard particle. The pH of the solution was adjusted with 0.1 N HCl and
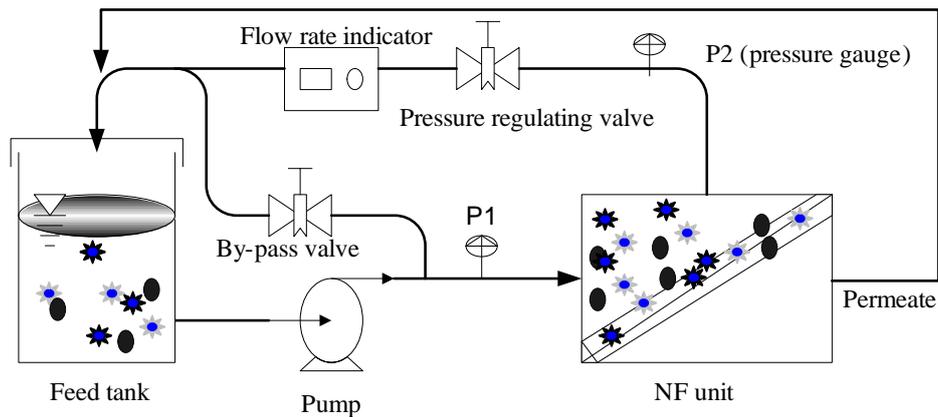
Fig. 2. Schematic drawing of cross-flow NF unit.

Table 1
Characteristics of NF90 membrane used

Code	NE90
Material	Meta-phertylene diamine based polyamides
MWCO* (Da)	200
Contact angle (°)	50.6
Zeta potential at pH 7 (mV)	–50.5
Roughness (nm)	43

*MWCO: molecular weight cut off

Fig. 3. XRD patterns of TiO$_2$ and 0.01, 0.05, 0.1 and 0.5% Pt/TiO$_2$.

NaOH. The operating transmembrane pressure and cross-flow velocity were controlled at 300 kPa and 0.5 m/s by means of bypass and regulating valves. The Reynold's number and shear stress at the wall were 735.5 (laminar flow) and 5.33 Pa, respectively. Both permeate and concentrate were recycled back to the feed tank except for the sample withdrawn for DOC and MWD measurement. The characteristics of the feed may be considered as constant during the experiment. The experiment was conducted over a period of 12 h.

3. Results and discussion

3.1. Characteristics of TiO$_2$ and Pt/TiO$_2$ produced from the incineration of dye wastewater TiCl$_4$ flocculated sludge

Crystal structures of the catalysts studied (identified by XRD patterns) are shown (comparatively) in Fig. 3. XRD patterns were used to identify the particle structure of the TiO$_2$ produced from the incineration at 600°C of dye wastewater TiCl4 flocculated sludge as well as the Pt/TiO$_2$ deposited with different Pt concentrations. Catalysts (TiO$_2$ and 0.01, 0.05, 0.1 and 0.5% Pt/TiO$_2$) showed the dominant anatase peaks at 2 θ = 25°, 38°, 48°, 54°, and 55° (Fig. 4). It is noteworthy mentioning that no peak of platinum at 2 θ = 40° was observed in the case of Pt/TiO$_2$.

The surface area of TiO$_2$ nano-particles produced from the incinerated sludge was 71 m^2/g.

The TEM micrograph of the Pt particles is illustrated in Fig. 4. The particle size of the Pt particles was measured to be around 3–5 nm. The picture shows a relatively uniform dispersion of tiny platinum particles onto the surface of TiO$_2$ particles. As shown in Fig. 4, the larger boundary represents TiO$_2$ with the size distribution of around 100–150 nm in diameter, and the relatively uniform distributed dark patches on the surface of the TiO$_2$ particles are platinum. These two types of particles, i.e., TiO$_2$ and Pt particles can be clearly distinguished because of their different electron density when exposed to electron beam.

3.2. Hydrogen production using TiO$_2$ and Pt/TiO$_2$

3.2.1. Effect of TiO$_2$ amount

Fig. 5a shows the effect of TiO$_2$ concentration on its photocatalytic activity for H$_2$ production by photocata-

(a) 0%

(b) 0.01%

(c) 0.05%

(d) 0.1%

e) 0.5%
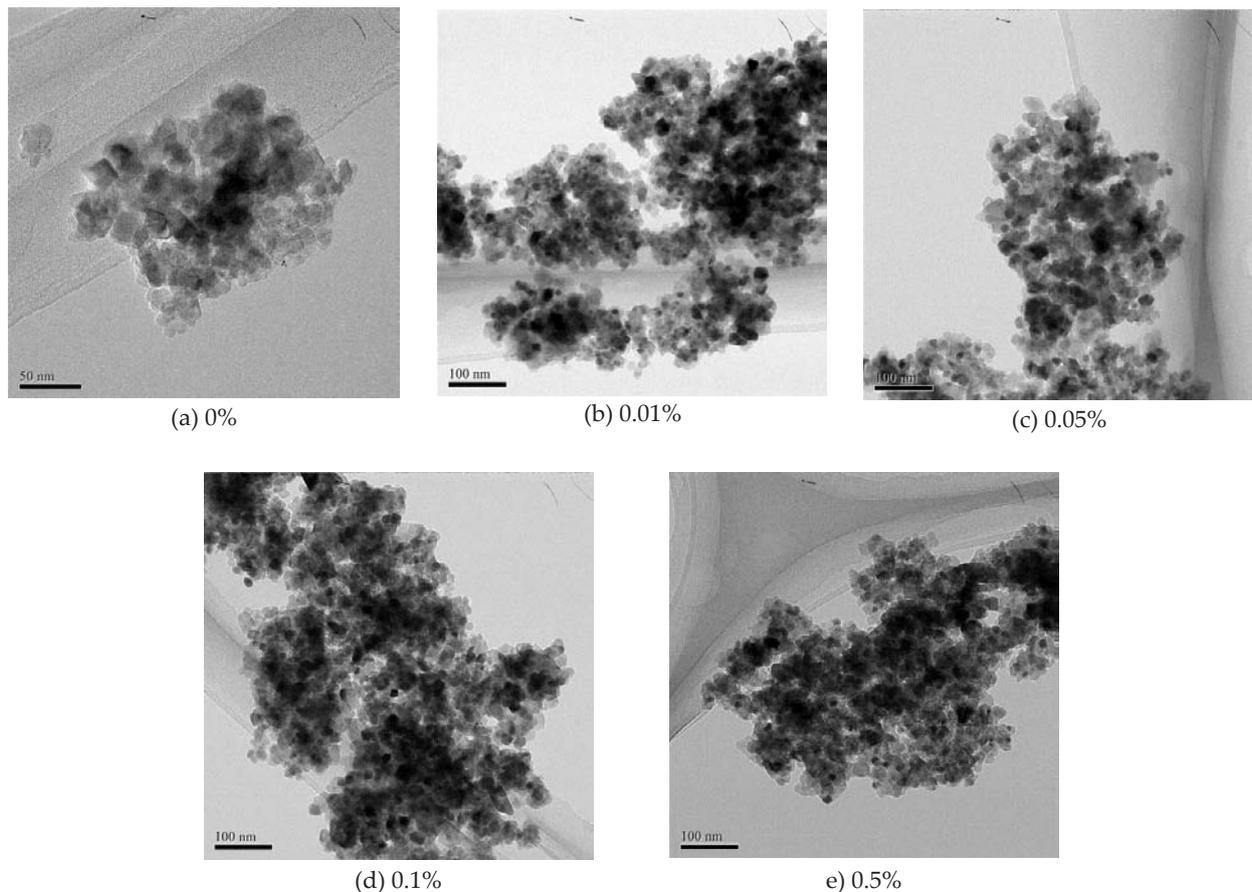
Fig. 4. TEM images of TiO_2 deposited with (a) 0%, (b) 0.01%, (c) 0.05%, (d) 0.1%, (e) 0.5% of Pt.

lytic reforming of methanol. The amount of H_2 generated by TiO_2 produced from the incineration of dye wastewater flocculated sludge was the highest for the concentration of 0.3 g/L of catalyst. 191 μmol of H_2 by photocatalytic reforming of methanol with 0.3 g/L TiO_2 was produced after 5 h of photocatalytic reaction. A significant increase in hydrogen production was observed when the concentration of catalyst was increased from 0.1 g/L to 0.3 g/L. But when the amount of TiO_2 was further increased the production of H_2 decreased. This can be caused by: i) the decrease in the availability of active sites on the TiO_2 surfaces, ii) or the decrease in light absorption due to high catalyst concentration in the suspension. In the first case, a small portion of TiO_2 will be present near the reactor wall and absorb the incident light from lamps, while the rest of particles will be shaded in the middle of the suspension. In the second case, particles agglomeration caused by high TiO_2 concentrations will cause light scattering and minimize the light penetration depth in the suspension [21].

Low catalyst concentration (0.1 g/L) was insufficient to allow the efficient absorption of the incident light and produce high H_2 amounts, while high concentrations (0.5, 1 and 2 g/L) decreased the photonic flux entering the irradiated solution that resulted in low H_2 generation. Therefore, 0.3 g/L was found to be the optimum concentration of catalyst for H_2 production by photocatalytic reforming of methanol.

3.2.2. Effect of Pt-loading amount

Fig. 5b shows the variation of H_2 production by photocatalytic reforming of methanol in relation to Pt deposition concentration on the TiO_2 produced from the incineration of dye wastewater flocculated sludge. To prevent the recombination, TiO_2 produced from sludge was doped with Pt metal to hold electrons. These Pt-deposited TiO_2 nanoparticles were placed in the photoreactor containing pure water and methanol. As the doping concentration of Pt (deposited) on TiO_2 produced from dye wastewater sludge was gradually increased from 0.01% to 0.5%, the amount of H_2 increased. The H_2 amount with 0.5% Pt/TiO_2 was 10201 μmol. The increase in H_2 production rate in relation to the increased Pt deposition on TiO_2 may be due
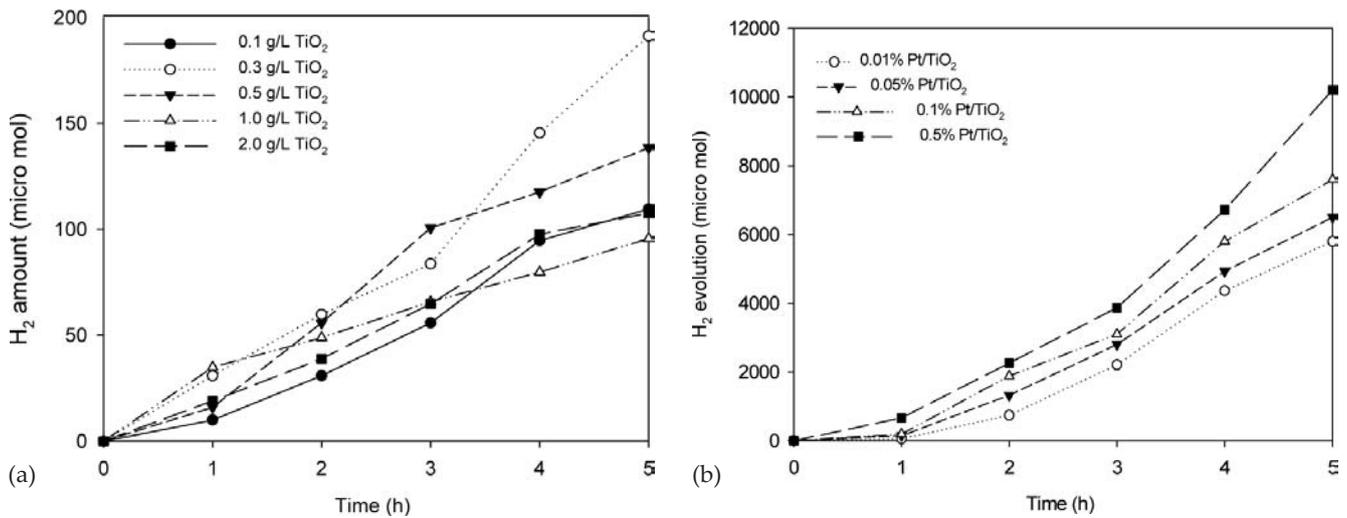
Fig. 5. Effect of TiO_2 concentration (a) and Pt deposition concentration on TiO_2 for H_2 production by photocatalytic reforming of methanol (6 vol.%).

to effective loading of the co-catalyst (Pt) on the catalyst (TiO_2) and the formation of increased Schottky barriers (potential barrier formed at a metal–TiO_2 junction which has rectifying characteristics) between Pt and TiO_2 [21].

3.3. Photocatalytic organic removal for wastewater reuse with simultaneous photocatalytic hydrogen production

MWD of BTSE included 34000 Da (biopolymers), 1100 Da (humic substance), 840 Da (building block), 210 Da (low MW acids) and less than 210 Da (amphiphilic). After Ti-salt flocculation, 34000 Da were completely removed and 1100 Da were partially removed, while the small MW could not be removed by flocculation (Fig. 6). Similar findings were also found elsewhere [25]. The photoreactor was used to remove the remaining building block, low MW acids and amphiphilic compounds. After flocculation followed by photocatalytic organic removal, 92% of organic removal was accomplished. The photoreactor preferentially removed the majority of humic substance, building block and amphiphilic, while low MW acids partially remained. The removal trend of MWD of organic matter was compared with (NF) with 200 Da molecular weight cut off, which is the widely used technology for wastewater reuse. NF removed 93% of organic matter, whereas low MW acids slightly remained after NF filtration. This suggests that flocculation followed by photocatalytic organic removal can be an alternative technology to remove organic matter for wastewater reuse.

The effect of $TiCl_4$ flocculation followed by photocatalytic degradation of organic compounds was investigated in terms of DOC removal (Fig. 7). $TiCl_4$ flocculation followed by photocatalysis indicated high DOC removal by up to 92.1% after 6 h of the reaction. This removal
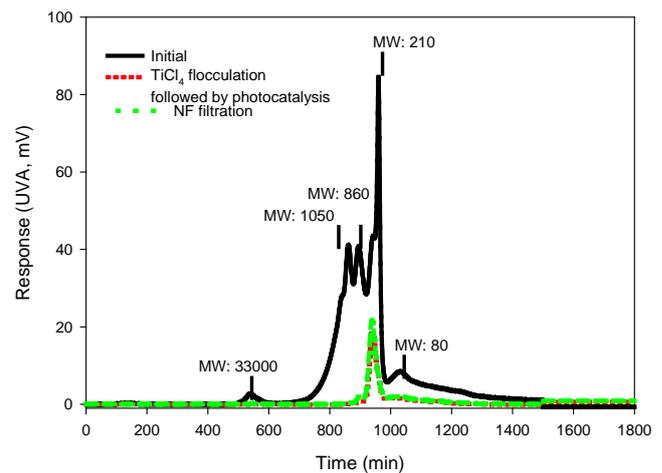
Fig. 6. Initial molecular weight distribution of organic compounds in BTSE (black solid line), MWD after the flocculation of BTSE using $TiCl_4$ followed by photocatalysis (red dotted line), and MWD after NF (green dotted line).

efficiency was similar to that of NF. The flocculation-photocatalysis hybrid system could therefore be an alternative effective way to remove DOC from BTSE.

Fig. 8 shows the GC/TCD profiles of standard gas and the gas produced from the reaction of photocatalytic organic removal for wastewater reuse with simultaneous photocatalytic hydrogen production using 0.3 g/L of 0.5% Pt/TiO_2. A large variety of organic compounds have been used as electron donors for photocatatlytic H_2 production to improve H_2 production, including alcohols, polyalcohols, sugars and organic acids (Patsoura et al., 2007). A number of previous studies have been conducted
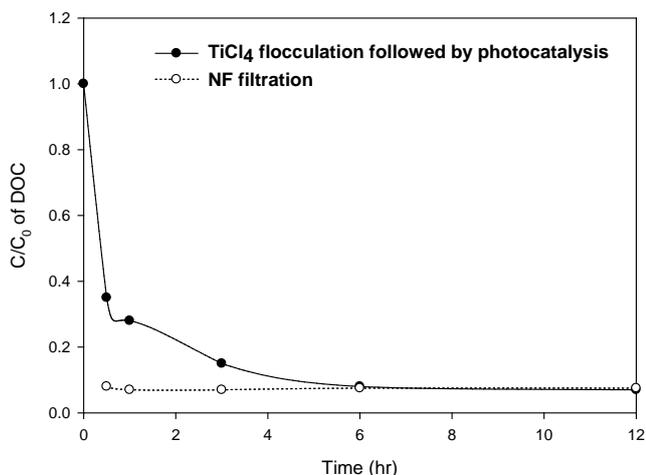
Fig. 7. C/C_0 of DOC variation of $TiCl_4$ flocculation followed by photocatalysis (initial concentration = 6.5 mg/L; Pt/TiO_2 concentration = 0.3 g/L; air = 25 L/min).

Fig. 8. Gas chromatogram produced measured by GC/TCD from standard gas (compounds are shown in solid vertical lines) and from the reaction of photocatalytic organic removal for wastewater reuse with simultaneous photocatalytic hydrogen production using 0.3 g/L of 0.5% Pt/TiO_2 produced from the incineration of BTSE flocculated sludge.

with only single organic sacrificial reagent. In this study, H_2 production was monitored with simultaneous photocatalytic organic removal by using complex organic contaminants from BTSE. As previously mentioned, the remaining organic compounds after Ti-salt flocculation in BTSE were building block, low MW acid and amphiphilic. These compounds as a sacrificial agent were used to produce H_2 in photoreactor. 0.3 g/L of 0.5%-Pt/TiO_2 was added in the photoreactor with the supernatant after Ti-salt flocculation of BTSE. H_2 production was marginal and CO_2 production evolved from the photocatalytic reaction. This suggests that there are organic/inorganic inhibitors that scavenged H_2 production.

4. Conclusions

In conclusion, the optimum concentration of TiO_2 produced from the incineration of dye wastewater flocculated sludge for H_2 production by photocatalytic reforming of methanol (6% vol.) was identified to be 0.3 g/L. Additionally, the optimum amount of Pt deposited on TiO_2 surface was determined which was found to be equal to 0.5%Pt/TiO_2.

The characterization of catalysts (TiO_2 and 0.01, 0.05, 0.1 and 0.5% Pt/TiO_2) produced from the incineration of the dye wastewater flocculated sludge and loaded with platinum by using the H_2 reduction method showed the dominant anatase structure. The surface area of TiO_2 produced from dye wastewater was 71 m^2/g. TEM images indicated that the particle size of the Pt particles was around 3–5 nm and they were uniformly dispersed onto the surface of TiO_2 particles (100–150 nm in diameter).

Flocculation of BTSE followed by photocatalytic reaction can be used as an alternative technology for waste-

water reuse in terms of organic removal. However, the remaining organic compounds after flocculation cannot be functioned as electron donors to improve H_2 production. Further study could settle this issue between the simultaneous photocatalytic H_2 production and photocatalytic organic removal while increasing UV intensity and/or identifying organic/inorganic scavengers to inhibit H_2 production.

References

[1] C. Okkerse and H.Van Bekkum, Green Chemistry, 1999, pp. 107–114.
[2] S. Shafiee and E. Topal, Energy Policy, 36 (2008)775–786.
[3] S. Sato and J.M. White, Chem. Phys. Lett., 72 (1980) 83–86.
[4] A. Fujishima and K. Honda, Nature, 238 (1972) 37–38
[5] J. Akikusa and S.U.M. Khan, Int. J. Hydrogen Energy, 22 (1997) 875–882.
[6] P.R. Mishra, P.K. Shukla, A.K. Singh and O.N. Srivastava, Int. J. Hydrogen Energy, 28 (2003) 1089–1094.
[7] Y.A. Shaban and S.U.M. Khan, Int. J. Hydrogen Energy, 33 (2008) 1118–1126.

[8] S.M. Ji, H. Jun, J.S. Jang, H.C. Son, P.H. Borse and J.S. Lee, J. Photochem. Photobiol. A: Chem., 189 (2007) 141–144.

[9] A.J. Bard, J. Phys. Chem., 86 (1982) 172–177.

[10] A.A. Nada, M.H. Barakat, H.A. Hamed, N.R. Mohamed and T.N. Veziroglu, Int. J. Hydrogen Energy, 30 (2005) 687–691.

[11] S.S. Rayalu, N. Dubey, N.K. Labhsetwar, S. Kagne and S. Devotta, Int. J. Hydrogen Energy, 32 (2007) 2776–2783.

[12] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, G.J. Kim, J.B. Kim and J.H. Kim, Environ. Sci. Technol., 41 (2007) 1372–1377.

[13] M. Ni, M.K.H. Leung, D.Y.C. Leung and K. Sumathy, Renewable Sustain. Energy Rev., 11 (2007) 401–425.

[14] Y.Z. Yang, C.-H. Chang and H. Idriss, Appl. Catalysis B: Environ., 67 (2006) 217–222.

[15] J.W. Park and M. Kang, Int. J. Hydrogen Energy, 32 (2007) 4840–4846.

[16] Y. Ikuma and H. Bessho, Int. J. Hydrogen Energy, 32 (2007) 2689–2692.

[17] F. Alonso, P. Riente, F. Rodriguez-Reinoso, J. Ruiz-Martinez, A. Sepulveda-Escribano and M. Yus, J. Catalysis, 260 (2008) 113–118.

[18] W. Sun, S. Zhang, Z. Liu, C. Wang and Z. Mao, Int. J. Hydrogen Energy, 33 (2008) 1112–1117.

[19] H.J. Choi and M. Kang, Int. J. Hydrogen Energy, 32 (2007) 3841–3848.

[20] C. Tao, W. Guopeng, F. Zhaochi, H. Gengshen, S. Weiguang, Y. Pinliang and L. Can, Chinese J. Catalysis, 29 (2008) 105–107.

[21] H. Yi, T. Peng, D. Ke, D. Ke, L. Zana and C. Yan, Int. J. Hydrogen Energy, 33 (2008) 672–678.

[22] M.S. Park and M. Kang, Mater. Lett., 62 (2008) 183–187.

[23] A. Patsoura, D.I. Kondarides and X.E. Verykios, Catalysis Today, 124 (2007) 94–102.

[24] A. Galinska and J. Walendziewski, Energy Fuels, 19 (2005) 1143–1147.

[25] H.K. Shon, S. Vigneswaran and S.A. Snyder, Crit. Rev. Environ. Sci. Technol., 36 (2006) 327–374.