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# Swine sewage as sacrificial biomass for photocatalytic hydrogen gas production: Explorative study

Andrea Speltini\*, Michela Sturini, Federica Maraschi, Daniele Dondi, Andrea Serra, Antonella Profumo, Armando Buttafava, Angelo Albini

Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia, Italy

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## ABSTRACT

This is the first-time reporting on the photocatalytic production of hydrogen gas ( $H_2$ ) via water splitting in the presence of swine sewage (SS) as sacrificial agent.  $H_2$  was evolved upon both UV-A and solar light irradiation in presence of platinised titania as the catalyst. The influences of irradiation time, catalyst amount, pH and SS concentration on the reaction yield were investigated. Under the best conditions, up to 50  $\mu\text{mol}$  of  $H_2$  were produced from aqueous SS (1.7% v/v, COD 82  $\text{mg L}^{-1}$ ), with good within-laboratory reproducibility (RSD <3%,  $n = 3$ ). The batch-to-batch reproducibility was verified, too. Despite the complexity of the matrix, the amount of evolved  $H_2$  was about a half of that obtained by use of model sacrificial agents as glucose, sucrose and glycerol, known to be excellent electron donors. The catalyst, recovered after irradiation, was regenerated by mere washing with acidic water and conserved part of the activity for reusing for at least 3 runs. The proposed procedure is at low environmental impact, does not release carbon dioxide and proceeds also under solar light with reaction yields up to 94% compared to those observed under UV-A radiation. This explorative study demonstrates that a waste such as SS is a rewarding and inexpensive feedstock to produce a high-value chemical as hydrogen gas. The results suggest that further work should be addresses in this direction. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

The demand for hydrogen gas ( $H_2$ ) is expected to increase significantly in the next years, in view of the growing need for a clean energy vector as an alternative to traditional hydrocarbon fuels. This gas is an appealing storable energy source. In fact, its conversion in fuel cells efficiently generates energy, producing only water as a by-product [1]. Currently, the largest part of the  $H_2$  produced is derived

from natural gas through steam-methane reforming, while only about 5% is produced from renewable resources, mainly via water electrolysis [2]. Unfortunately, producing  $H_2$  from natural gas carries out some problems in view of the limited availability of fossil fuels and the large amount of carbon dioxide ( $\text{CO}_2$ ) released through this process. For these reasons, the development of innovative methods to produce  $H_2$  from renewable materials, such as biomass and water, is required and will be a hot research topic in the near future [2].

\* Corresponding author. Tel.: +39 0382 987349; fax: +39 0382 528544.

E-mail address: [andrea.speltini@unipv.it](mailto:andrea.speltini@unipv.it) (A. Speltini).

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Photocatalysis is thought to have a key role for the generation of alternative energy carriers such as H<sub>2</sub> [2,3]. Indeed, H<sub>2</sub> can be obtained by photocatalytic water splitting, to date the most appealing and rewarding process because water is an abundant and renewable resource [2]. The process has often been carried out with titanium dioxide modified with platinum [4,5] because of the large overpotential required for the evolution of H<sub>2</sub> and O<sub>2</sub> [2]. Anoxic conditions are mandatory, as photogenerated electrons would be otherwise consumed by oxygen chemisorbed on the catalyst [4]. TiO<sub>2</sub> is the most widely used catalyst in view of its strong catalytic activity, high chemical stability and long lifetime of hole/electron pairs, while Pt is among the most efficient metals [6] because it is endowed with the lowest overpotential and largest work function [2].

However, the application of water splitting requires that some limitations are overcome, such as the full elimination of hole/electron recombination and of the thermodynamically favoured backward reaction of H<sub>2</sub> with O<sub>2</sub> to form H<sub>2</sub>O [2]. The reaction yield is strongly improved when an organic substrate is oxidized at the same time and behaves as sacrificial reagent. In this way, TiO<sub>2</sub> valence holes and OH radicals are scavenged and electrons are pumped into the catalyst conduction band or into Pt islands (current-doubling effect). This favours reduction of hydrogen ions to give gas-phase H<sub>2</sub>. The role of Pt is to favour charge carriers separation through the formation of a Schottky barrier [2] and, as above mentioned, to make electrons in the conduction band more readily available.

A variety of organic substances have been tested as sacrificial donors with different photocatalysts in recent years, including methanol, ethanol, glycerol, glucose and many others [3–11]. A convenient choice from the environmental and economic standpoints is combining H<sub>2</sub> production with synthesis of useful chemicals [1] or recovery of contaminated wastewater, a path that has been recently explored [12]; in particular, experiments aimed at exploiting the organic content of olive mill wastewater to photocatalytically obtain H<sub>2</sub> and at the same time to remedy water from the organic contaminants have been carried out [12].

Great efforts are now devoted to hydrogen production starting from renewable resources [1]. In this context, a green enzymatic process that allows to obtain H<sub>2</sub> under controlled conditions from cellulose derivative, by using visible light and avoiding release of CO<sub>2</sub>, has been proposed [13]. Biohydrogen production by dark fermentation of starch using mixed bacterial cultures was revealed as a rewarding process [14]. Also pre-treated olive mill wastewater was tested as feedstock for photosynthetic bacteria-mediated hydrogen photo-production [15,16].

These studies appeared to us an appealing advancement in the frame of sustainable chemistry and prompted an exploratory study of recycling a low-value biomass, namely swine sewage (SS), to obtain H<sub>2</sub>. This material is attractive as an easily available energy source due to its high organic content, low cost and large availability. In a recent paper, swine wastewater has been used as microalgae biomass culture medium for the production of biohydrogen and bioethanol by bacteria-promoted fermentative processes [17]. Hydrogen evolution from anaerobic digestion of pig manure has also been evaluated [18]. However, to the best of our knowledge,

the photocatalytic production of H<sub>2</sub> using liquid SS has not been investigated as yet.

In this work we explored an alternative and environmentally improved route for the photocatalytic production of H<sub>2</sub> from liquid SS. Platinised TiO<sub>2</sub> was used as the catalyst under either UV-A or solar irradiation. The main variables involved in the process, viz., catalyst amount, pH, irradiation time and biomass concentration were investigated. The reaction yields were compared to those observed by using model sacrificial agents (i.e. polyols). Evolved H<sub>2</sub> was quantified by gas chromatography (GC) with thermal conductivity detection (TCD). The possibility of regenerating and recycling the catalyst was tested.

## Materials and methods

### Chemicals

Degussa P25 titanium dioxide, a known mixture of 80% anatase and 20% rutile with an average particle size of 30 nm and a reactive surface area of  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ , was purchased from Degussa AG (Frankfurt, Germany). H<sub>2</sub>PtCl<sub>6</sub>, glucose, sucrose and glycerol were supplied by Sigma Aldrich (Milan, Italy). H<sub>2</sub>SO<sub>4</sub> (96% w/w), and CH<sub>3</sub>COOH (99.9% w/w), NaOH anhydrous pellets (97% w/w) and rhodamine B dye were purchased from Carlo Erba Reagenti (Milan, Italy). Ultrapure water (resistivity  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  at 25 °C) was produced in laboratory by means of a Millipore (Milan, Italy) Milli-Q system.

### Synthesis of the photocatalyst

Pt-loaded TiO<sub>2</sub> (0.5 and 1.0 wt%) was prepared by conventional photochemical deposition, following a consolidated procedure [19]. Briefly, 1.0 g of P25 TiO<sub>2</sub> was added to a solution made of 10 mL 0.1 M glacial acetic acid and containing either 330 or 660  $\mu\text{L}$  0.077 M H<sub>2</sub>PtCl<sub>6</sub> (pH 4.1); the suspension was irradiated under magnetic stirring for 24 h (366 nm, 30 W) and then filtered. The grey powder obtained was washed with plenty of ultrapure water until neutrality of the eluate and dried at 100 °C for 4 h. Actual Pt amounts were determined by scanning electron microscopy (SEM). SEM was performed by a Leo 1530 Gemini instrument, field emission gun (FEG); acceleration voltage  $V_{\text{acc}} = 0.2\text{--}30 \text{ kV}$ , resolution 1.0 nm at 20 kV, 2.5 nm at 1 kV, 5 nm at 0.2 kV; detectors: Inlens, conventional SE, BSE; methods: SEM, HRSEM; manufacturer: Zeiss, Oberkochen.

The photocatalytic activity of the Pt-loaded catalysts was checked by degradation of rhodamine B dye. 5 mg of catalyst were added to 10 mL of aqueous dye ( $30 \text{ mg L}^{-1}$ ) and stirred for 30 min in the dark for adsorption equilibrium; the suspension was irradiated under UV-A light (366 nm, 30 min) and residual rhodamine B was spectrophotometrically determined at 554 nm.

### Sample preparation

The raw SS, average composition: pH 7.9, COD  $46.4 \text{ g L}^{-1}$ , total N  $3.6 \text{ g L}^{-1}$ , N(NH<sub>4</sub><sup>+</sup>)  $1.7 \text{ g L}^{-1}$ , total P  $1.1 \text{ g L}^{-1}$ , P(soluble PO<sub>4</sub><sup>3-</sup>)

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