Hydrogen from wastewater by photocatalytic and photoelectrochemical treatment

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Abstract
In recent years, the intensification of human activities has led to an increase in waste production and energy demand. The treatment of pollutants contained in wastewater coupled to energy recovery is an attractive solution to simultaneously reduce environmental pollution and provide alternative energy sources. Hydrogen represents a clean energy carrier for the transition to a decarbonized society. Hydrogen can be generated by photosynthetic water splitting where oxygen and hydrogen are produced, and the process is driven by the light energy absorbed by the photocatalyst. Alternatively, hydrogen may be generated from hydrogenated pollutants in water through photocatalysis, and the overall reaction is thermodynamically more favourable than water splitting for hydrogen. This review is focused on recent developments in research surrounding photocatalytic and photoelectrochemical hydrogen production from pollutants that may be found in wastewater. The fundamentals of photocatalysis and photoelectrochemical cells are discussed, along with materials, and efficiency determination. Then the review focuses on hydrogen production linked to the oxidation of compounds found in wastewater. Some research has investigated hydrogen production from wastewater mixtures such as olive mill wastewater, juice production wastewater and waste activated sludge. This is an exciting area for research in photocatalysis and semiconductor photoelectrochemistry with real potential for scale up in niche applications.

Keywords: Hydrogen production, wastewater, photocatalysis, photoelectrochemical cell

1. Introduction
The current society is based on a linear production route, where the extraction of raw matter follows its industrial conversion into products, and its disposal as waste. This linear practice creates long-term problems because resources are limited and inefficiently used. The impact of
this approach includes climate crisis, water pollution and reduction of biodiversity. Therefore, it is necessary to adopt different strategies conforming to the circular economy concept, where products and materials are in the economy as long as possible.

Wastewater has a great potential for resource recovery, being a source of nutrients such as phosphorus and nitrogen, materials including precious metals, and also a potential source for energy recovery. Conventional wastewater treatment plants are energy intensive. Energy can be extracted from wastewater in diverse forms, including electricity, heat or fuels, as methane or hydrogen. Biogas production by anaerobic digestion is one of the most utilized methods for energy recovery from wastewater [1]. In this process, bacteria degrade the organic waste in the absence of oxygen to produce biogas, a gas mixture mostly composed of methane and carbon dioxide. Anaerobic digestion has been and is widely used in wastewater treatment plants around the world.

Hydrogen production is another promising approach to energy recovery from wastewater. Hydrogen is considered as clean energy carrier for the transition to a decarbonized society fuelled by renewable energy. Its use in combustion or fuel cells generates only water resulting in zero carbon emissions and the high gravimetric heating value makes hydrogen a competitive energy carrier. In 2019, the International Renewable Energy Agency (IRENA) reported that more than 95% of hydrogen production comes from fossil fuel based processes, such as steam-methane reforming and oil and coal gasification [2]. This fact highlights the urgent need to develop alternative and sustainable H₂ production processes, which may include recovery from wastewater.

Hydrogen can be generated from wastewater using biological processes. Wastewater has a high organic content making it a good candidate for hydrogen production via fermentation. Possible biohydrogen production methods include photo-fermentation and dark fermentation [3]. In photo-fermentation, photosynthetic bacteria powered by sunlight transform organic compounds into hydrogen and CO₂. Dark fermentation is a complex process in which several groups of bacteria participates in a series of biochemical reactions to convert organic substrate into biohydrogen. Often, dark fermentation is coupled to photo-fermentation; the organic acids, by-products of dark fermentation, are then converted to hydrogen by the photosynthetic bacteria during photo-fermentation [4]. An alternative bio-based technology to recover energy from wastewater is the use of Microbial Fuel Cells (MFC). MFC use bacteria on the anode to oxidize the organic matter and inject electrons, where these electrons can be used to produce electricity or hydrogen at the
cathode. MCF are considered a promising technology for wastewater treatment and energy recovery; however the slow electron transfer, low power generation, membrane fouling and low rate of microbes growth impede the rapid scaling-up of MFC [5,6].

Among non-biological processes, an interesting approach is the use of photocatalysis to produce hydrogen from wastewater. Photoexcitation of the photocatalyst results in charge carrier formation with the necessary electrochemical reduction potentials to drive hydrogen evolution. In 1972, Fujishima and Honda reported for the first time photoelectrolytic water splitting to produce hydrogen and oxygen using a UV excited single crystalline TiO₂ electrode [7]. Since then, research in the photocatalysis field gained attention producing a substantial number of studies. While extensive research has been carried out in either photocatalytic hydrogen production or degradation of organic compounds, only a limited number of studies focus on hydrogen production from the degradation of components in wastewater. Therefore, this review is aimed to emphasise the relevance of this approach, as promising application for the simultaneous recovery of energy and the removal of pollutants from wastewater.

The present article starts with an overview of the fundamentals, materials and the parameters used to evaluate the performance of photocatalytic processes (section 2) and photoelectrochemical cells (section 3). The following section reviews hydrogen production from several wastewater compounds, which are categorized in groups, using both photocatalysis and photoelectrochemistry (section 0). This section focuses in discussing materials used, possible mechanisms and performance of these processes. Finally, this review concludes with a critical evaluation of the current limitations on this field and future opportunities.

2. Photocatalysis

2.1 Fundamentals

In photocatalysis, a semiconductor is irradiated with photons with energy equal to or greater than the band gap energy, resulting in the excitation of electrons from the valence band (VB) to the conduction band (CB). The photo-excited electron leaves a positively charged hole in the VB. These charge carriers are referred to as an electron-hole pair. The charge carriers can recombine in the semiconductor bulk dissipating energy as heat or light or they can migrate to the surface of the semiconductor. At the surface, they can undergo charge transfer processes driving redox reactions with chemical species which are adsorbed at the surface of the photocatalyst.
Photocatalysis has been widely studied for the degradation of organic pollutants, extensive information can be found in previous reviews [8–11]. The organic pollutants can either undergo direct oxidation by holes, indirect oxidation by reactive oxygen species including hydroxyl radicals, or they may be transformed by a reductive route involving CB electrons. The most employed electron acceptor in photocatalytic oxidation reactions is molecular oxygen since it is abundant in the air and is reasonably soluble in aqueous solutions. The oxygen is reduced by the CB electrons to form the superoxide radical anion (O$_2$$^{-}\bullet$). Subsequent reduction reactions lead to H$_2$O$_2$, •OH, and eventually H$_2$O. A representation of this process is shown in figure 1(a).

Photocatalysis has also been investigated for hydrogen production through water splitting, as detailed described in several reviews [12–15]. In this application, the photogenerated holes are used to oxidize the water molecules to evolve oxygen, while the photo-generated electrons in the CB reduce protons and evolve hydrogen, as shown in figure 1(b). However, photocatalytic hydrogen production from water splitting is a challenging reaction because it is thermodynamically unfavourable ($\Delta G^\circ$= +237 kJ mol$^{-1}$) requiring a high energy input and the transfer of four electrons. It should be recognised that technically, uphill thermodynamic processes are photosynthetic, however, to avoid confusion, in this review both uphill and downhill reactions will be referred as photocatalytic. Hydrogen production from the oxidation of other compounds with reactions requiring less energy or being thermodynamically favourable ($\Delta G^\circ$< 0) have also been investigated. This is schematically represented in figure 2. These compounds can donate electrons and scavenge the VB holes while also acting as a source of protons. There are many compounds present in wastewater that could act as a hydrogen source.
Figure 1. Schematic representation of photocatalytic process. (a) Photocatalytic degradation of organic pollutants with oxygen as the electron acceptor. (b) Photocatalytic water splitting. (c) Photocatalytic oxidation of pollutant with H₂ evolution as the reduction reaction.

Figure 2. Thermodynamic energy diagram with examples for hydrogen production from water, ammonia, and glucose.

Most studied compounds have been organics, but this is also possible with inorganic compounds as e.g. ammonia. In this application, the photo-generated holes are used to oxidize the unwanted compounds, which can take place through direct oxidation or indirect oxidation via hydroxyl radicals (•OH). The photo-generated electrons reduce the protons to form hydrogen. A schematic representation of this process is shown in figure 1(c), with the oxidation of a generic organic compound. The photocatalytic oxidation of organic substances to form hydrogen is also referred as photoreforming and it follows the general equation given in (1).

\[ C_xH_yO_z + (2x-z) H_2O \rightarrow x CO_2 + \left(2x + \frac{1}{2} y - z\right) H_2 \]  \hspace{1cm} (1) 

The ability of a semiconductor to perform the desired redox reactions depends on the band gap energy and the band edge potentials for the VB and the CB. For the reactions to be thermodynamically possible, the CB edge potential should be more negative than the desired reaction reduction potential and the VB edge potential should be more positive than the desired
reaction oxidation potential. In the water splitting reaction, the CB should be more negative than the hydrogen evolution reaction (HER) potential (0 V vs. NHE at pH 0), and the VB should be more positive than the oxygen evolution potential (+1.23 V vs NHE at pH 0). While in the reactions with oxidation of wastewater compounds, the conduction band needs to be more positive than the oxidation potential of the waste compounds and pollutants. These potentials are more negative than the potential for water oxidation, requiring less energy for the overall reaction. The CB and VB of several semiconductor materials, together with the oxidation and reduction potential of these reactions are given in figure 3.

![Diagram of semiconductor band gap positions](image)

**Figure 3.** Band gap position of semiconductors in relation to oxidation and reduction reactions from wastewater compounds. Energy levels were previously reported in [16–22].

The ideal semiconductor material for photocatalytic hydrogen production from wastewater compounds would have the following general requirements: suitable band edges position, good light absorption, efficient charge transport, chemical and photochemical stability, low overpotentials for the desired reduction and oxidation reactions, low cost and being abundant. It is important to consider that almost half of the incident solar energy on the earth's surface is in the visible region (400 nm < \( \lambda \) < 800 nm), and therefore, for solar applications the photocatalyst should be able to utilise both the UV and visible photons.

### 2.2 Materials

While a wide range of materials have been investigated for photocatalytic hydrogen production [12–15], the present review will focus on the materials reported for \( \text{H}_2 \) production coupled to the
oxidation of pollutants found in wastewater. Titanium dioxide is the most reported photocatalyst to investigate the coupling of \( \text{H}_2 \) production to the degradation of compounds found in wastewater [23–30]. Other materials as cadmium sulphide [31,32] and graphitic carbon nitride [33,34] have also been reported for \( \text{H}_2 \) production from wastewater compounds.

Titanium dioxide (\( \text{TiO}_2 \)) is employed in a wide variety of fields, ranging from energy applications such as hydrogen production and \( \text{CO}_2 \) reduction, to environmental applications as water treatment, air purification and water disinfection [35]. \( \text{TiO}_2 \) exists as three different polymorphs: anatase, rutile and brookite. Its properties include high photo-activity, low cost, low toxicity and good chemical and thermal stability. Nevertheless, it suffers from having a high electron-hole recombination and a large band gap. \( \text{TiO}_2 \) band gap is 3.2 eV for anatase, 3.0 eV for rutile, and \( \approx 3.2 \) eV for brookite [35]. This wide band gap limits the light absorption to the ultraviolet range, which just accounts for 4-5 % of the solar spectrum, consequently, limiting its practical application.

Developments to improve light absorption of \( \text{TiO}_2 \) include doping, metal deposition, dye sensitization and coupled semiconductors [16]. Non-metal doping has been extensively researched, being nitrogen one of the most promising non-metal dopants that has achieved visible light absorption [36]. Nitrogen is easily inserted in the \( \text{TiO}_2 \) structure since it has a high stability, small ionization and its atomic size is similar to oxygen [37]. Other promising non-metal dopants are carbon and sulphur [38,39]. Alternatively, the generation of oxygen rich \( \text{TiO}_2 \) has been reported to produce an increase in the Ti-O-Ti bond strength and a upward shift in the VB, achieving visible light absorption [40]. Doping with metals as chromium, cobalt, vanadium and iron has also been reported to improve the light absorption [16]. Dye sensitization has been considered as one of the most effective strategies to extend the spectral response into the visible region, benefiting from the knowledge of dye sensitized solar cells. Moreover, coupling \( \text{TiO}_2 \) with other semiconductors has also resulted in an improvement of the light absorption and a reduction of the recombination losses [41].

A commercially available \( \text{TiO}_2 \) product, Degussa (Evonik) P25, has been often used as a benchmark in research. It contains a combination of the polymorphs anatase and rutile with proportions of around 80 % anatase and 20 % rutile. This configuration enhances the photoactivity
since the rutile phase, which has a more positive conduction band potential, can act as electron sink for the photogenerated electrons of the anatase phase [16].

When TiO$_2$ is used for HER, usually metal co-catalysts are added. Since the work function of noble metals is typically larger than TiO$_2$, the photogenerated electrons transfer from the semiconductor CB to the metal [35]. Pt has been one of the most used co-catalysts for HER since it has the largest work function among the noble metals, creating a stronger electron trapping ability and has a low activation energy for proton reduction [16,35]. Pt co-catalyst ability strongly depends in its particle size and loading [35].

Cadmium sulphide (CdS) is a widely researched visible light photocatalyst. It has been investigated in diverse applications, such as hydrogen production, carbon dioxide reduction to hydrocarbons or pollutants degradation [20]. CdS is characterized by a narrow bandgap of 2.4 eV, which enables the absorption of light until 516 nm [20]. It exhibits good photochemical properties and quantum efficiency [42,43]. However, it suffers from photo-corrosion, since the photogenerated holes react with the sulphur ions oxidizing them to sulfur [44]. CdS low stability makes difficult its application in industry. Some of the strategies to improve CdS stability and inhibit photo-oxidation include the addition of surface protective layers, constructing heterojunctions and combining them with microporous and mesoporous materials [31,45].

Graphitic carbon nitride (g-C$_3$N$_4$) has received lot of attention as visible light photocatalyst, and it has been reported to be a promising photocatalyst for a diverse number of applications including H$_2$ production [46]. g-C$_3$N$_4$ is usually produced by thermal condensation of nitrogen-rich precursors. Its polymeric nature allows the modification of properties such as morphology, conductivity and electronic structure which modifies the bandgap energy and bandgap edges potential position [21]. g-C$_3$N$_4$ photocatalytic activity and efficiency have been improved using several strategies. Heteroatom doping and copolymerization have been employed to modify the electronic band structure to enhance light absorption [47]. Moreover, the heterojunction with other semiconductors as CdS [48] or TiO$_2$ [49] have been reported to achieve an improved separation of the photogenerated charges [21].

2.3 Efficiency

The photocatalytic performance can be evaluated using quantum efficiency. The quantum efficiency or yield is defined as the useful photo-conversion events per absorbed photons at a
determined wavelength. The useful events are usually calculated by the reaction rate. This is given in (2) where \( r \) is the reaction rate given in number of molecules converted per second, and \( \Phi_{pa} \) is the flux of absorbed photons expressed as number of photons per second. However, it is challenging to determine the absorbed photons in the semiconductor. Therefore, the external or apparent quantum efficiency, which is also referred as photonic yield, is usually used instead [50]. It can be defined as the useful events per incident photons in the system at a determined wavelength. This expression is given in (3), where \( r \) is the reaction rate given in number of molecules converted per second and \( \Phi_{pi} \) is the flux of incident photons expressed as number of photons per second. The incident photons can be measured using radiometric or actinometric procedures. Moreover, the external quantum efficiency takes into account the efficiency of the overall process including the efficiency of the material absorbing photons as well as catalysing the reaction and the efficiency of the reactor design [50].

\[
QE(\lambda) = \frac{r}{\Phi_{pa}} \tag{2}
\]

\[
EQE(\lambda) = \frac{r}{\Phi_{pi}} \tag{3}
\]

If one is using a polychromatic irradiation source then the Formal Quantum Efficiency (FQE) should be reported, normally integrating the number of photons which can be utilised by the semiconductor in question. Of course, for many semiconductors the true solar efficiency will be very low due to only a small proportion of the solar spectrum being utilised.

Additionally, the performance of a photocatalytic hydrogen production process can also be evaluated using the solar-to-hydrogen conversion efficiency (\( \eta_{\text{SHT}} \)), which relates chemical hydrogen energy produced to the solar energy. This expression is shown in (4), where \( \Phi_{H_2} \) is the hydrogen rate in mol s\(^{-1}\) m\(^{-2}\), \( \Delta G_{H_2}^0 \) the Gibbs free energy of hydrogen formation and \( P \) is the photon flux in mW cm\(^{-2}\) measured for a light source with a spectra equal to air mass global (AM) 1.5 [51].
3. Photoelectrochemical cells

3.1 Fundamentals

An approach to enhance the efficiency of photocatalysis is the use of electrochemically assisted photocatalysts in a photoelectrochemical cell (PEC). In this configuration, the oxidation and reduction reactions are performed by two different electrode materials that are connected through an external circuit. The oxidation is driven by the holes in the (photo)anode, while the electrons travel from the photoanode through the external circuit to the (photo)cathode, where the reduction reaction takes place. This process is schematically represented in figure 4. When a photoelectrochemical cell is utilized to produce a fuel (e.g., hydrogen) from solar energy it can be referred as photosynthetic cell. Similarly, when the photoelectrochemical cell is employed to produce electricity from the photodegradation of substances, it can be defined as photo fuel cell [52]. In systems where wastewater compounds are being oxidized in a PEC to generate H₂, depending on the thermodynamics of reaction, the system can also produce electricity and therefore being a combination of both cells; not clearly defined as one or the other. Moreover, a system without applied bias, where hydrogen is produced by a flow of current, could also be considered a photo fuel cell.

Photoelectrochemical cells can be used with different configurations, i.e. semiconductor photoanode with metallic cathode, semiconductor photocathode with metallic anode, or photoanode with photocathode. These cells are driven by the potential difference between the Fermi levels of the two electrodes. For a typical n-type semiconductor photoanode, the Fermi level is close to the CB while for a typical p-type semiconductor photocathode the Fermi level is close to the VB [53]. If the photoelectrochemical cell uses a dark anode or cathode, these potentials are ideally dependent on the reaction oxidation and reduction reaction potentials, respectively. If the reaction oxidation and reduction potentials have the right positions with respect to the CB and VB, the cell produces electric power in open circuit voltage. When this is not the case, an external voltage can be applied to drive the reactions.
Figure 4. Schematic representation of a photoelectrochemical cell, containing a photoanode and a dark cathode, for the oxidation of a generic organic and H₂ production.

With electrochemically assisted photocatalysis, an external electrical bias can be applied to assist the reactions. This may allow the use of semiconductors photoanodes with more positive CB potentials than the H⁺/H₂ reaction and which would not drive HER purely photocatalytically.

3.2 Materials

Titanium dioxide is the most used photoanode material for H₂ production from wastewater compounds [54–57]. Other photoanode materials that have also been used for H₂ production are tungsten trioxide, bismuth vanadate and hematite [58–60]. Concerning the cathode material, platinum is widely used [54,55,61,62], while cuprous oxide is a common choice for photocathode [57].

3.2.1 Photoanodes

Titanium dioxide (TiO₂), is as well the most used semiconductor material for photoanodes. Its properties and applications have been described in the previous section. When compared with other photoanodes semiconductor materials as tungsten trioxide, bismuth vanadate or hematite, titanium dioxide shows good charge transport properties and a very high hole diffusion length, which is in the order of 10⁴ nm [58]. However, TiO₂ has one of the lowest theoretical solar-to-hydrogen (STH) conversion efficiency just accounting for around 2.2 %, due to its excitation being limited to the UV region [59]. One of the strategies studied to improve activity and reduce...
recombination losses, is to synthesize one- or two-dimensional nanostructures which increases the specific surface area and decreases internal resistance. A very popular approach is the nano-engineering of TiO$_2$ to form either dispersed or aligned self-organised nanotubes (TNT) [63]. Other used strategies include non-metal doping, co-catalyst deposition, dye sensitization and coupled semiconductors as explained previously [16].

Tungsten trioxide (WO$_3$), is a very popular metal oxide semiconductor used for photoanodes. It has been extensively researched for water splitting applications. It has a bandgap of 2.5-2.8 eV, absorbing light in the visible range up to 500 nm which accounts for 12 % of the solar radiation on earth surface [60]. Its theoretical STH conversion efficiency is around 4.8% [58], and it has a modest hole diffusion length of around 150 nm [58]. Moreover, its conduction band is positioned at positive potentials of around +0.4 V vs. NHE [17], therefore a bias is necessary to drive the HER. Unfortunately, its stability is limited to acidic environment [58]. Some strategies to improve the activity of WO$_3$ include the enhancement of light absorption with anion doping as C [64] or N [65] or forming heterojunctions with other semiconductors as WO$_3$/BiVO$_4$ [66].

Bismuth vanadate (BiVO$_4$), is the most popular visible light absorption semiconductor used as photoanode, it attracted interest for water-splitting applications. BiVO$_4$ occurs in three polymorphs, from which monoclinic scheelite is the one being used as photoanode. It has a bandgap of 2.4 eV, a high theoretical STH conversion efficiency of 9.1% [59] and its conduction band potential is located slightly under than the HER potential [67]. However, it suffers from an extensive electron-hole recombination and a low charge mobility, consequently a bias is always necessary to obtain significant photocurrents [59]. In order to increase BiVO$_4$ carrier concentration doping with elements as Mo or W has been studied [68,69]. Other strategies to improve BiVO$_4$ activity include the loading of co-catalysts as Co-Pi [70] to decrease the bias potential and help the oxidation reaction or the heterojunction with other semiconductors as SnO$_2$ or WO$_3$ to have a more efficient electron-hole separation [71,72].

Hematite ($\alpha$-Fe$_2$O$_3$), is considered a very promising metal oxide photoanode since it has a narrow bandgap of around 2 eV, allowing to absorb light beyond 600 nm [59]. Therefore, its maximum theoretical STH conversion efficiency is around 15% [19]. Moreover, $\alpha$-Fe$_2$O$_3$ presents a good chemical stability and it is inexpensive and abundant. Its conduction band is situated at positive potentials of around 0.4 V vs NHE [19], therefore, it is necessary to apply a bias to drive hydrogen
production. Nevertheless, it has a very low hole diffusion length of around 2-4 nm and a low electron mobility which limits its performance [60]. Strategies to improve α-Fe₂O₃ conductivity and activity include, doping with elements as W, Mo and Nb [73–75], loading of co-catalysts as Co-Pi or Ni(OH)₂ [55,76] or surface passivation with Al₂O₃ [77].

3.2.2 Photocathodes

Contrary to the case of photoanodes, the choice of p-type materials for photocathodes is limited due to their low stability in contact with the electrolyte [78]. Some strategies to improve the performance of the photocathode include the use of protective layers that improve stability and the deposition of co-catalysts to enhance the reduction ability[79–81].

Cuprous oxide (Cu₂O), is a popular photocathode choice, it has a band gap of 2 eV and a theoretical STH conversion efficiency of 18% [80]. Its conduction band is well positioned for water reduction, around 0.7 V vs NHE more negative than hydrogen evolution potential [22]. However, the potentials for reduction from Cu₂O to Cu and oxidation to CuO are within the band gap, reducing its stability [82]. There are several research studies that had improved its stability adding protective layers as ZnO [79]. Moreover, co-catalysts as Pt had been added to enhance the reduction activity [80].

Copper based chalcogenide semiconductors have also been proposed as promising photocathodes for hydrogen production [83]. One of them is CuInₓGa₁₋ₓSe₂ (CIGS) which has a tuneable composition, with a band gap ranging from 1 eV to 1.7 eV and a large absorption coefficient [81]. Their activity have been enhanced adding protective layers and co-catalysts such as Pt [84]. However, CIGS include In and Ga which are scarce and expensive elements. Another type of chalcogenide photocathode is Cu₂ZnSnS₄ (CZTS), which has earth abundant elemental constituents, high absorption coefficient and small band gap, however; it suffers from low long-term stability [85]. The research to improve its activity has also focused into surface modification, adding protecting layers as TiO₂ and co-catalysts as Pt [81].

3.2.3 Dark cathode electrocatalysts

The selection of a cathode for hydrogen evolution reaction benefits from an extensive research in the electrochemistry field. HER involves the adsorption of a proton on the electrocatalyst surface and the desorption of hydrogen. For this reason, following Sabatier principle, the optimal catalytic activity will be achieved with a catalyst that achieves intermediate binding energy between the
substrate and the catalyst [86]. The catalyst activity is as well dependent on the pH of the electrolyte, and in general, HER activities in alkaline electrolyte are lower than in acid. Consequently, the majority of the research is done in acid environment. For HER, the catalyst closer to the optimum intermediate binding energy is Pt. Platinum has generally the best performance as hydrogen production catalyst, it has a low overpotential and high reaction rates in acidic environment [61]. Pt foil and wires, together with Pt supported carbon are the most common cathodes used in the studies for H₂ production from driven photoelectrochemical oxidation of substances in wastewater.

Other catalysts with a good performance are Ru, Rh, Ir and Pd. However, all these noble metal catalysts, together with Pt, have a high cost and they are scarce, which makes challenging their large-scale application. Different approaches have been widely researched to find electrocatalysts with low cost and good performance. Two strategies that have been used to improve activity and reduce the cost of using noble metal catalysts are nanostructuring the catalyst to achieve a large surface to volume ratio, and forming alloys which reduce the catalyst loading [87,88].

Non-noble metal alloys have also been used for HER. Ni-based electrodes are preferred cathodes for hydrogen production in basic environment as Ni-Mo [88]. Transition metals chalcogenides as carbides and phosphides have also showed HER activity. Chalcogenides as MoS₂ showed activity for HER due to their sulphided Mo-edges with and overpotential close to Pt [89]. Similarly, WS₂ also demonstrates HER activity [90] as well as their selenides forms MoSe₂ and WSe₂ [91]. Tungsten carbides such as WC and W₂C, exhibit promising potential as HER catalysts [92]. Phosphides as CoP and Ni₂P are among the most HER active non-noble electrocatalysts [93,94]. Alternatively, non-metals electrocatalysts options have also been explored as heteroatom doped graphene nanosheets [94] or carbon nitride [95].

3.3 Efficiency

When evaluating the performance of photoelectrochemical cells, the external quantum efficiency is also referred as Incident Photon to Current Efficiency (IPCE), and the number of successful events can be evaluated by the photo-electrical current generated. This expression is given in (5), where λ is the wavelength of irradiation in nm, J is the photocurrent density given in mA cm⁻², P is the photon flux in mW cm⁻² at a particular λ, h is Plank’s constant and c is the speed of light in vacuum [53].
Moreover, when evaluating the performance of photoelectrochemical cells, $\eta_{STH}$ can also be determined from the photocurrent density generated. This expression is shown in (6) where $J$ is the photocurrent density given in mA cm$^{-2}$, $V$ is the required potential in V derived from Gibbs free energy, $\eta_f$ is the HER faradaic efficiency and $P$ is the light power in mW cm$^{-2}$ measured with a light source with a spectra equal to air mass global (AM) 1.5 [51]. It is important to note that $J$ needs to be measured between the working and counter electrode in a 2 electrode PEC configuration. No bias potential should be applied in the evaluation of $\eta_{STH}$. Whenever a bias potential is applied between working and counter electrode to drive the reaction, the Applied Bias Photon to Current Conversion Efficiency (ABPE) can be derived, as shown in (7) [51]. In this expression $V_{bias}$ is the applied voltage in V, which is subtracted from the required potential derived from Gibbs energy.

$$EQE(\lambda) = IPCE(\lambda) = \frac{\Phi_e}{\Phi_{pi}} = \frac{J \cdot h\nu}{\lambda \cdot P\lambda}$$

(5)

$$\eta_{STH} = \left[ \frac{J \cdot V \cdot \eta_f}{P} \right]_{AM\ 1.5G}$$

(6)

$$ABPE = \left[ \frac{J \cdot (V - V_{bias}) \cdot \eta_f}{P} \right]_{AM\ 1.5G}$$

(7)

For wastewater treatment applications, an UV source is commonly used as oppose to solar irradiation; therefore the power coming from the sun should be replaced by the power of the UV source.

4. H$_2$ production from wastewater

Wastewater includes every water stream that has been polluted by human utilization, therefore, its chemical composition varies greatly depending on its origin. Domestic wastewater, which derives from urban areas, is generally rich in microorganism, organic materials, metals, and nutrients as phosphorous or nitrogen [96]. These effluents are usually treated at municipal wastewater
treatment plants. On the contrary, industrial effluents are diverse, being originated by very different processes. Some industrial wastewaters have a similar chemical composition than domestic wastewater and can be treated in urban wastewater treatment plants, while other industrial effluents contain substances that need a specific and complex treatment process, as persistent organics, antibiotics or metals [97]. Finally, agricultural activities generate wastewater with a high content of nitrogen compounds, due to excessive use of fertilizers and intensive farming [98], although agricultural wastewater normally cannot be collected and treated.

These wastewaters, originated by human activities, need to be treated to avoid pollution and protect the ecosystems. Therefore, coupling the production of hydrogen with the removal of pollutants represents a promising option to recover energy from wastewater and at the same time managing the water pollution issue. This section describes the studies that produced hydrogen coupled to the degradation of wastewater compounds, including the materials used and the possible mechanisms. The reviewed wastewater substances include nitrogen compounds, saccharides, phenolic compounds, alcohols, organic acids, aldehydes, and complex mixtures from oil mill wastewater, juice production wastewater and sludge from wastewater treatment plants.

4.1 Nitrogen compounds

Ammonia and urea, along with nitrates and nitrites, contribute to nitrogen pollution. Nitrogen pollution of water has deleterious effects including eutrophication and toxicity to the organisms living in the water body. The hazardous concentration of nitrogen in wastewater originate from diverse sources, as intensive farming and excessive fertilizer use [98]. Additionally, high nitrogen concentrations can also be found in either domestic and municipal sewage sludge and in wastewater from some industries [99].

In water, un-ionized ammonia (NH₃) exists in pH dependent equilibrium with ionized ammonium (NH₄⁺), having a pKa of 9.25, when the pH is lower than the pKa, NH₄⁺ is the major form and when the pH is higher than the pKa is NH₃ the major form. Therefore, one of the research focuses has been to determine which of the forms would have a higher photocatalytic oxidation rate. Several studies have revealed that ammonia in neutral form presents better oxidation rates compared to ionized ammonium [23,100,101]. Nemoto et al. investigated the pH effect in the photocatalytic ammonia oxidation, testing a pH range from 0.68 to 13.7 [23]. The study reports that the evolution of gaseous products (N₂ and H₂) increased between the pH 9 and 10 and peaked
at pH around 11, due to higher oxidation rates with neutral ammonia. Zhu et al. reported how the oxidation rates obtained were proportional to the initial concentration of NH$_3$ and not the total content of NH$_3$ and NH$_4^+$ [100]. From this study, it was concluded that high oxidation rates are obtained when ammonia is in neutral form, even if better photocatalytic activity could be expected with positively ionized NH$_4^+$ and a negative photocatalyst surface charge, which occurs when the pH is higher than the photocatalyst point of zero charge and lower than the ammonium pKa. Wang et al. compared the photocatalytic activity in acidic, basic and neutral environment using g-C$_3$N$_4$ as photocatalyst and reported higher rate of photocatalytic ammonia oxidation in basic solutions [101].

The most studied photocatalyst for ammonia oxidation has been TiO$_2$ [23,102–104], covering how the co-catalyst material affects the activity and product selectivity [23,102–104] and determining the possible reaction mechanism on H$_2$ production from ammonia decomposition [103]. Nemoto et al. compared the activity of TiO$_2$ loaded with RuO$_2$, Pt and both RuO$_2$ and Pt as co-catalysts for photocatalytic ammonia oxidation and hydrogen production [23]. The results showed that the N$_2$ gas produced was similar for all the co-catalysts; however, the H$_2$ production varied significantly. The photocatalyst loaded with Pt achieved the highest H$_2$ production and an external quantum yield of 5.1 % at 340 nm, while the system with both co-catalysts produced a small amount of H$_2$. The system loaded with RuO$_2$ did not produce any H$_2$, showing that RuO$_2$ cannot reduce protons to form hydrogen. Altomare and Selli studied how the conversion and selectivity of ammonia oxidation to N$_2$ would be affected by the deposition of noble metals (Pt, Pd, Au and Ag) on the TiO$_2$ photocatalyst [102]. The experiments showed that all the metal-modified photocatalysts had better catalytic performance that the bare TiO$_2$, with the exception of Au/TiO$_2$. The loaded photocatalyst that showed higher ammonia removal was Ag/TiO$_2$ and the one that showed better selectivity towards N$_2$ was Pd/TiO$_2$. This latter study did not link the oxidation of ammonia to H$_2$ production. Yuzawa et al. studied the mechanism of decomposition of ammonia to produce dinitrogen and hydrogen using TiO$_2$ photocatalyst loaded with Pt, Rh, Pd, Au, Ni and Cu [103]. Pt presented the best activity with high production rate of H$_2$ and N$_2$ and Cu the worse. The study concluded that the metal with larger work function would easily accept the photo-excited electrons to produce hydrogen. The mechanism proposed consisted in the predominant adsorption of ammonia to the Lewis acid site and some to the hydroxyl groups in TiO$_2$. The TiO$_2$ is irradiated generating holes and electrons, where the holes migrate to the surface and the electrons to the Pt
The photogenerated holes oxidize the adsorbed NH$_3$ to form amide radicals and protons, while the amide radicals can produce hydrazine. The hydrazine could produce diazene that would be decomposed to form N$_2$ and H$_2$. The photogenerated electrons reduce the protons to form hydrogen in Pt [103]. This mechanism is represented in figure 5. Shiraishi et al. investigated the photocatalytic hydrogen production from ammonia using TiO$_2$ loaded with Au and Pt [104]. Pt-Au/TiO$_2$ showed a growth in hydrogen production rate compared to Pt/TiO$_2$, suggesting that alloying Au to Pt resulted in a decrease of the Schottky barrier height at the interface between metal and TiO$_2$. The catalyst with the highest H$_2$ production rates consisted in a homogeneous mixture of 10 % mol of Au and 90 % mol of Pt loaded on TiO$_2$.

Figure 5. Suggested mechanism for photocatalytic ammonia degradation using Pt loaded on TiO$_2$. Figure has been reprinted from reference [103] with permission from the American Chemical Society.

Photocatalytic ammonia oxidation has also been reported using metal free photocatalyst. Wang et al. used an atomic single layer g-C$_3$N$_4$ as photocatalyst, achieving an ammonia removal of 80% of the initial concentration [101]. Both hydroxyl radicals and photogenerated holes were suggested
to be responsible for the ammonia oxidation; in this study ammonia oxidation was not coupled to H₂ production.

The number of research papers reported on ammonia oxidation using photoelectrochemical cells is reduced compared to photocatalysis [54,105]. Wang et al. used highly ordered TiO₂ nanotube arrays as a photoanode and Pt foil as cathode [105], reporting an ammonia removal of 99.9% under an applied bias of 1.0 V (not coupled to H₂ production). Kaneko et al. used nanoporous TiO₂ film as photoanode, formed by P25 deposited on FTO glass and a Pt foil as a cathode [54]. The experiments showed a 150 µA cm⁻² photocurrent and a production of 194 ml of H₂ and 63 ml of N₂ after 2 hours with no bias applied under a pH of 14.1.

The reported studies of H₂ production driven by photocatalytic or photoelectrochemical oxidation of urea are scarce and their main focus is proving the feasibility of the process [24,55,106]. They include the study of surface modification and co-catalyst loading. Moreover, a comparison of the H₂ production rate from oxidation of urea, ammonia and formamide has also been studied [56].

Kim et al. investigated the effect of dual surface photocatalyst modification in the production of hydrogen and oxidation of urea [24]. TiO₂ modified with both a noble metal, Pt, and an anion adsorbate [24]. The results showed that F-TiO₂/Pt achieved higher H₂ production rates than Pt/TiO₂, besides, F-TiO₂ did not show any H₂ production, highlighting the combined effect of surface anions and metal deposits to reduce charge recombination and improve electron transfer. Moreover, the effect of other anions as Cl⁻, ClO⁻ and Br⁻ was studied, resulting in only F⁻ to have an enhancement effect, Cl⁻ and ClO⁻ had no effect and Br⁻ inhibited the hydrogen production. These results were explained by the surface complexation among acidic Ti(IV) sites and basic anions, which is dependent on the hardness of the anions, being only F⁻ the one that has higher hardness than OH⁻. Furthermore, experiments with deuterated urea were performed, showing than H₂ production comes mainly from water molecules while urea acts as an electron donor.

Wang et al. studied the feasibility of hydrogen production driven by urea or urine oxidation in a photoelectrochemical cell [55]. In this work, the suitability of two photoanodes was studied, TiO₂ nanowires and α-Fe₂O₃ nanowires, both loaded with Ni(OH)₂ as urea oxidation co-catalyst. Pt was used as counter electrode. The viability of solar driven urea oxidation with Ni/TiO₂ as photoanode was reported using an unbiased cell, producing a current density of 0.35 mA cm⁻². Moreover, the feasibility of using directly urine was also studied, resulting in comparable results to urea,
highlighting the possibility of driving the production of hydrogen with the oxidation of urine. The effect of loading \(\alpha-\text{Fe}_2\text{O}_3\) with Ni(OH)\(_2\) was studied, showing a negative shift in the onset potential of 400 mV, suggesting that Ni(OH)\(_2\) is an efficient catalyst for urea oxidation. However, the use of \(\alpha-\text{Fe}_2\text{O}_3\) as photoanode required an external bias due to the low position of its conduction band.

Xu et al. investigated as well the role of Ni(OH)\(_2\) as a co-catalyst in the photoelectrochemical oxidation of urea, not coupled to the production of hydrogen [106], by using a photoanode formed by Ti-doped \(\alpha-\text{Fe}_2\text{O}_3\) and loaded with Ni(OH)\(_2\). The addition of Ni(OH)\(_2\) reduced the onset potential by 100 mV and increased the photocurrent density by 4 times, showing the enhanced effect of the use of Ni(OH)\(_2\) as urea oxidation co-catalyst.

Pop et al. focused their study in the comparison of the hydrogen production rates driven by oxidation of three nitrogen compounds found in wastewater: ammonia, urea and formamide [56]. The cell configuration combined a nanoparticulate TiO\(_2\) photoanode and a mixture of carbon paste dispersing platinum nanoparticles as cathode in the same electrode. This configuration was unbiased and used under UV illumination. The detected hydrogen production after 4 hours was about 30, 140 and 240 \(\mu\text{mol}\) in presence of ammonia, formamide and urea, respectively. From these results, urea proved to be the best choice for photoelectrochemical hydrogen production. Additionally, a cell configuration with a separated photoanode and cathode, applying 0.5 V bias was also tested. The results from the two configurations were compared after 50 min, in which the biased configuration reported a \(\text{H}_2\) production rate of 2.7 \(\mu\text{mol min}^{-1}\) while the unbiased configuration reported a rate of 1.4 \(\mu\text{mol min}^{-1}\), highlighting the improved charge separation induced by the use of a bias.

4.2 Saccharides

Different saccharides compounds can be found wastewater; among them, cellulose is commonly found in domestic wastewater and effluents from industries as the paper industry [107].

Kawai and Sakata demonstrated the feasibility of producing hydrogen from Saccharides (\(\text{C}_n\text{H}_{2n}\text{O}_n\)\(_m\)), as saccharose (\(n=2\)), starch (\(n \approx 100\)) and cellulose (\(n \approx 1000\) to 5000), using a photocatalyst formed by RuO\(_2\)/TiO\(_2\)/Pt. A quantum yield of 1 % at 380 nm was reported for cellulose in 6 M NaOH [108]. Moreover, Kondarides et al. studied the hydrogen production from the photocatalytic reforming of several compounds including cellulose using an Pt/TiO\(_2\) photocatalyst, proving the potential of cellulose for \(\text{H}_2\) production [25]. Speltini et al. investigated
the photocatalytic hydrogen production from cellulose using a Pt/TiO$_2$ photocatalyst [109]. The study showed higher H$_2$ production rates with neutral pH and reported a H$_2$ production of 54 µmol under UV-A irradiation. A degradation mechanism was also reported suggesting that cellulose depolymerizes and converts into glucose and other water-soluble products. Caravaca et al. researched the photocatalytic H$_2$ production from cellulose using different metals as co-catalysts loaded in TiO$_2$. The H$_2$ production was reported highest with Pd and lowest with Ni and Au, following the trend Pd > Pt > Ni ~ Au [110]. Even the H$_2$ production using Ni as co-catalyst was lower compared to the noble metals Pd and Pt, it was in the same magnitude, highlighting the possibility of using a no noble metal as co-catalyst. Moreover, the study suggested the possibility of the hydrolysis of cellulose taking place during photo irradiation to produce glucose, which could follow different pathways to produce hydrogen.

The photoreforming of glucose, which is proposed to be an intermediate in the cellulose photoreforming process has been reported in several studies [25,26,111–113]. Kondarides et al. studied the hydrogen production from the photocatalytic reforming glucose using an Pt/TiO$_2$ photocatalyst, reporting an external quantum efficiency of 63 % at 365 nm [25]. Fu et al. studied the effect of different parameters as pH and co-catalyst material and proposed a mechanism for the hydrogen production from photocatalytic reforming of glucose using a metal loaded photocatalyst [26]. The study reported the effect of different co-catalysts loaded in TiO$_2$, showing all of them a better activity than the bare TiO$_2$; the best activity was obtained using Pd and Pt and the worse with Ru and Au, following the trend Pd > Pt > Au ≈ Rh > Ag ≈ Ru. Moreover, the variation of pH over a wide range resulted in an increasing H$_2$ production rate with increasing pH, with a plateau region from pH 5 to 9 and maximum peak at pH 11. The pKa of glucose is around 12.3; therefore, higher rates of glucose oxidation are produced with glucose in its molecular form. In the proposed mechanism, the glucose is adsorbed preferentially in the uncoordinated Ti atoms through its hydroxyl group, it dissociates and then it is oxidized by a photogenerated hole. The radicals generated attack other glucose molecules, forming R-CHOH, which are deprotonated and further oxidized to [R-COOH]$^-$ by the radical •OH. Lastly, [R-COOH]$^-$ species are photo-oxidized by a hole to generate CO$_2$ via a photo-Kolbe reaction [26]. This mechanism is presented in figure 6. Chong et al. investigated the glucose photoreforming mechanism using Rh/TiO$_2$ photocatalyst, reporting the production of arabinose, erythrose, glyceraldehyde, gluconic acid and formic acid (together with CO and CO$_2$ gas) [111]. In the suggested mechanism, glucose is oxidised into
arabinose, then further oxidised into erythrose and ultimately into glyceraldehyde. These oxidation reactions take place through \( \cdot OH \) radicals, which leads to the generation of formic acid and hydrogen. Subsequently, formic acid is converted into CO or CO\(_2\). Imizcoz and Puga studied photocatalytic hydrogen production from glucose using TiO\(_2\) loaded with different metals as Au, Ag, Pt and Cu [112]. The study reported a catalyst efficiency following the trend Pt\(>\)Au\(>\)Cu\(>\)Ag, without significative differences between Cu and Au, proposing Cu as an inexpensive co-catalyst for hydrogen production. Bahadori et al. researched the hydrogen production from glucose photoreforming using CuO or NiO loaded TiO\(_2\) as photocatalyst [113]. The highest hydrogen production yield reported was 9.7 mol g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\) using 1 wt\% CuO on P25.

Other semiconductor materials as WO\(_3\) and \(\alpha\)-Fe\(_2\)O\(_3\) have also been studied using a photoelectrochemical cell for hydrogen production from photoreforming of glucose. Esposito et al. reported how a thin film WO\(_3\) photoanode presented a good photocatalytic activity for H\(_2\) production from glucose photoreforming using a tandem cell device [114]. Wang et al. investigated the possibility of using Ni(OH)\(_2\) as co-catalyst for glucose oxidation (not coupled to H\(_2\) production) in a photoelectrochemical cell, reporting an increased activity for Ni(OH)\(_2\) loaded in \(\alpha\)-Fe\(_2\)O\(_3\)[62].

Figure 6. Proposed mechanism for photoreforming of glucose on Pt loaded TiO\(_2\). This figure has been reprinted from reference [26] with permission from Elsevier.
4.3 Phenolic compounds

Phenolic compounds are found in significant quantities in wastewater from effluents of several industries as oil refining, petrochemicals, resin manufacturing and pulp, but also in agricultural and domestic wastewaters [97,115]. Phenolic compounds are considered toxic and its discharge without treatment produces harmful effects in the aquatic systems [116]. The photocatalytic degradation of phenolic compounds has been widely studied [117]. However, only few cases coupled the photocatalytic oxidation of phenolic compound to H\textsubscript{2} production [24,27,33,57,118–120], demonstrating the feasibility of this process.

Hashimoto et al. investigated the photocatalytic H\textsubscript{2} production in presence of different aliphatic and aromatic compounds with suspended Pt/TiO\textsubscript{2} [27], demonstrating the production of hydrogen in presence of phenol. Moreover, the study showed an increased rate of H\textsubscript{2} production in presence of phenol in alkaline conditions over acidic conditions. Languer et al. reported that the photocatalytic phenol degradation over TiO\textsubscript{2} nanotubes produced hydrogen at a rate of about 0.06 \textmu mol h\textsuperscript{-1} cm\textsuperscript{2} [119]. Kim et al. demonstrated the feasibility of hydrogen production coupled to photocatalytic degradation of 4-chlorophenol [24]. The study involved the activity comparison of the following photocatalysts: TiO\textsubscript{2}/Pt, F-TiO\textsubscript{2}/Pt and P-TiO\textsubscript{2}/Pt. The highest H\textsubscript{2} production rate was obtained with F-TiO\textsubscript{2}/Pt and the lowest with TiO\textsubscript{2}/Pt. However, the good activity of F-TiO\textsubscript{2}/Pt was limited to acidic region since the fluorides desorb at the alkaline region. P-TiO\textsubscript{2}/Pt had higher H\textsubscript{2} production range than TiO\textsubscript{2} for all the pH range. Lv et al. used S doped two-dimensional g-C\textsubscript{3}N\textsubscript{4} for the photocatalytic hydrogen production from phenol, achieving a H\textsubscript{2} production rate of 127.4 \textmu mol/h and an external quantum efficiency of 8.35 % at 400 nm [33].

In photoelectrochemical cells, several photoanodes materials have been tested. Wu et al. studied the effect of the photoanode and photocathode materials on the voltage and current generated in the phenol degradation and hydrogen production [57]. Different photoanode and photocathode nanostructures, as nanorods (NRs), nanoparticles (NPs) and nanowires (NWAs) were tested from TiO\textsubscript{2}, CdS, CdSe and Cu\textsubscript{2}O. It was demonstrated that the open circuit voltage depends not only on the Fermi level between the photoelectrodes, but also on crystal facet for the same semiconductor materials with different microstructures. The best phenol removal efficiency was achieved with the combination of the photoanode TiO\textsubscript{2} NRs/FTO-C/Cu\textsubscript{2}O and the photocathode C/Cu\textsubscript{2}O NWAs/Cu. This combination reached a phenol removal rate of 84.2 % and an overall hydrogen
production rate of 86.8 µmol cm$^{-2}$ in 8 hours. Park et al. demonstrated the feasibility of hydrogen production driven by the photoelectrochemical degradation of phenol using improved multi-layered BiO$_x$-TiO$_2$/Ti electrodes [118]. The electrodes were formed by an under layer of TaO$_x$-IrO$_x$, a middle layer of BiO$_x$-SnO$_2$, and an upper layer of BiO$_x$-TiO$_2$ which covered on both sides of Ti foil. The study showed that bismuth doping, even at high concentration, increased TiO$_2$ conductivity, while preserving the original photoelectrochemical properties. Li et al. studied the photoelectrocatalytic hydrogen production in presence of phenol using Bi/BiVO$_4$ as photoanode [120]. The study reported a hydrogen production rate of 27.8 µmol cm$^{-2}$ h$^{-1}$.

4.4 Alcohols

Although alcohols are not expected to be abundant and common substances in municipal wastewater, they may be present in some industrial wastewater [121]. The production of H$_2$ from photocatalytic oxidation of alcohols has been extensively studied, mainly methanol, ethanol, and glycerol oxidation.

Kawai and Sakata demonstrated the feasibility of producing hydrogen by photoreforming of methanol [122]. The study reports the highest H$_2$ production rate Pt and an apparent quantum yield of 44 % at 380 nm with a photocatalyst formed by RuO$_2$/TiO$_2$/Pt. In the proposed reaction mechanism, methanol forms an intermediate, formaldehyde, which further oxidises to formic acid and finally decomposes to CO$_2$ and H$_2$. Chiarello et al. studied the effect of loading different noble metal co-catalysts to a TiO$_2$ photocatalyst in the photoreforming of methanol [123]. Among the investigated co-catalysts (Ag, Au and Pt), Pt showed the highest hydrogen production rate. Moreover, Naldoni et al. studied the difference between loading TiO$_2$ photocatalyst with Au or Pt, concluding that photogenerated electrons are more easily transferred to the Pt nanoparticles to reduce protons, than to Au [124]. Chen et al. studied the mechanism of the photocatalytic reaction of methanol for hydrogen production on Pt/TiO$_2$ [125]. The proposed mechanism (figure 7) involves the formation of H$_2$ on Pt sites, in which the proton transfer to the Pt sites is mediated by the adsorbed water and methanol molecules. Most of the protons that form H$_2$ in the Pt sites come from water and not methanol. The study demonstrates that the surface species of CH$_2$:O, CH$_2$:OO and HCOO were formed. Moreover, an increase in Pt loading generated a decrease on methanol adsorption, which suggest that Pt atoms occupy sites for methanol adsorption [125]. Ismail studied the use of a Ru doped TiO$_2$ photocatalyst for the hydrogen production from methanol, reporting an
enhancement on the activity due to the decrease in the band gap and a larger surface area. The highest activity was reported doping with of 0.1 % mol of Ru. In another study, Chen et al. reported the possibility of using a low cost photocatalyst formed by carbon coated Cu/TiO$_2$ (C/Cu/TiO$_2$) for hydrogen production from methanol [126]. This photocatalyst produced a H$_2$ yield of 269.1 µmol h$^{-1}$ which is comparable to 290.8 µmol h$^{-1}$, the yield produced with Pt/TiO$_2$.

Liu et al. investigated the interaction between CuO$_x$-TiO$_2$ and its effect on the photocatalytic production of hydrogen from methanol [127]. The highest H$_2$ production was reported with CuOx/TiO$_2$-{0 0 1} which has the highest Cu$_2$O dispersion and strongest interaction. Jiménez-Rangel et al. study the performance of g-C$_3$N$_4$/NiOOH/Ag as photocatalyst for the photoreforming of methanol, obtaining a maximum H$_2$ yield of 350.6 µmol/h. The hydrogen yield of the combined g-C$_3$N$_4$/NiOOH/Ag photocatalyst resulted significantly higher compared to the yield of g-C$_3$N$_4$, g-C$_3$N$_4$/NiOOH or g-C$_3$N$_4$/Ag alone [34]. Hojamberdiev et al. studied the use of a photocatalyst composed of g-C3N4 Ni(OH)$_2$ and halloysite nanotubes for the production of hydrogen from methanol [128]. This photocatalyst presented a higher H$_2$ production rate (18.42 µmol h$^{-1}$) than g-C$_3$N$_4$/Ni(OH)$_2$ (9.12 µmol h$^{-1}$) or g-C$_3$N$_4$ (0.43 µmol h$^{-1}$). This enhancement was attributed to charge separation being the holes trapped by the halloysite nanotubes and the electrons transferred to Ni(OH)$_2$.

Figure 7. Proposed mechanism for the photoreforming of methanol on Pt loaded TiO$_2$. This figure has been reprinted from reference [125] with permission from the American Chemical Society.
Ethanol has been extensively studied as a sacrificial agent for H\(_2\) production [25,31,32,129–135]. Kawai and Sakata studied the photocatalytic production of hydrogen from ethanol [129]. The study reports the production of hydrogen, methane, and acetaldehyde. Moreover, different co-catalyst loaded in TiO\(_2\) were studied as Ni, Pd, Pt and Rh, being Pt the one with the highest H\(_2\) production rate and with a reported external quantum yield of 38 % at 380 nm. Kondarides et al. studied the hydrogen production from the photocatalytic reforming of ethanol with an Pt/TiO\(_2\) photocatalyst, reporting an external quantum efficiency of 50 % at 365 nm [25]. Yang et al. researched the photocatalytic production of hydrogen from ethanol using metal loaded TiO\(_2\) as photocatalyst and compared it to the H\(_2\) production from other alcohols [130]. Pt and Pd presented higher H\(_2\) production rates than Rh. Moreover, it was suggested that the hydrogen production over Pt/TiO\(_2\) is governed by the solvation of the alcohol, following the H\(_2\) production the following trend: methanol ≈ ethanol > propanol ≈ iso-propanol > n-butanol. Sola et al. investigated the effect of the morphology and structure of Pt/TiO\(_2\) photocatalysts on the hydrogen production from ethanol [131]. The study showed an improved performance for the Pt/TiO\(_2\) photocatalysts with higher surface area and lower pore size. The best performing photocatalyst was found to be Pt/TiO\(_2\) with an average pore size of 29.1 nm and a surface area of 51 m\(^2\) g\(^{-1}\), reporting an apparent quantum yield of 5.14%. Acetic acid, 2-3 butanediol and acetaldehyde were the main products in the liquid phase, finding a higher concentration of 2-3 butanediol with lower pore size. Puga et al. studied the hydrogen production from photocatalytic ethanol oxidation over Au/TiO\(_2\), obtaining as main products acetaldehyde in the liquid phase and H\(_2\) in the gas phase with a volumetric proportion of 99%, while the other gaseous product detected were CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), CO and CO\(_2\) [132].

Deas et al. used Au loaded on TiO\(_2\) nanoflowers as photocatalyst for hydrogen production from ethanol, reporting a hydrogen production rate of 24.3 mmol g\(^{-1}\) h\(^{-1}\), compared to only 12.1 mmol g\(^{-1}\) h\(^{-1}\) obtained with Au/P25 [133]. This enhancement was ascribed to the thin and crystalline anatase sheets of the nanoflower petals which reduce the bulk recombination. Pajares et al. investigated the use of WC as TiO\(_2\) co-catalyst for the photocatalytic hydrogen production from ethanol, reporting an enhancement of 40% the H\(_2\) yield compared to P25 [134]. Zhang et al. investigated the effect of Ti\(^{3+}\) defects of Au/TiO\(_2\) on the hydrogen production from ethanol [135]. The study reported an increased activity with higher defects, concluding that oxygen vacancies on TiO\(_2\) rich in defects, facilitates the adsorption of ethanol and hole transfer. Ryu et al. studied the
photoreforming of ethanol using CdS attached on microporous and mesoporous silicas as photocatalyst. The study suggests that the photoactivity was dependent on the silica cavity size, which partially controls the CdS particle size [31]. Cebada et al. studied the use of Ni/CdS as photocatalyst for the hydrogen production from ethanol, proving that higher Ni content resulted in increased hydrogen production [32].

Antoniadou et al. studied the hydrogen production from ethanol using a photoelectrochemical cell chemically biased [136]. The cell had two compartments, with a TiO$_2$ photoanode in an acidic electrolyte compartment and a Pt cathode in alkaline electrolyte compartment. The study reported an IPCE of 96 % at 360 nm and proved that the photoreforming of ethanol is more efficient than photocatalytic water splitting. Adamopoulos et al. investigated the effect of adding a top layer of TiO$_2$ to a WO$_3$ photoanode in the hydrogen production from ethanol using a biased photoelectrochemical cell [137]. Carbon black loaded on carbon paper was used as cathode. Increased current density and hydrogen production were reported when using the TiO$_2$/WO$_3$ bilayer photoanode; this improvement was ascribed to the lower number of recombination sites.

H$_2$ production from photoreforming of glycerol has also been widely studied [25,138–143]. Kondarides et al. studied the hydrogen production from the photocatalytic reforming of glycerol, reporting an external quantum efficiency higher than 70 % at 365 nm with a Pt/TiO$_2$ photocatalyst and 1 M of glycerol [25]. Fu et al. studied the mechanism of photoreforming polyols as glycerol using a Pt/TiO$_2$ photocatalyst, proposing that just the H atoms connected to hydroxyl C atoms can form H$_2$ while the C atoms are oxidized to CO$_2$ [138]. For non-OH bonded C atoms, the bond H and C atoms form products in the form of alkanes as CH$_4$ or C$_2$H$_6$. Bowker et al. investigated the photocatalytic reforming of glycerol using Pd and Au modified TiO$_2$ and proposed a possible mechanism [139]. Hydrogen production rate from Pd was four times larger than the one of Au. The mechanism suggests that H$_2$ is produced through the dissociation of adsorbed glycerol molecules with the associated production of CO, when using Pd/TiO$_2$. Subsequently, the CO reacts with oxygen radical at the metal surface to produce CO$_2$ freeing sites. Montini et al. studied the hydrogen production from glycerol using Cu/TiO$_2$ photocatalyst [140]. Hydrogen and carbon dioxide were the main products in gas phase, and 1,3-dihydroxypropanone and hydroxyacetaldehyde in liquid phase. Moreover, Chen et al. reported a quantum efficiency of
24.9% at 365 nm and hydrogen production rate of 17.6 mmol g\(^{-1}\) h\(^{-1}\) from glycerol using Cu/TiO\(_2\) as photocatalyst [141]. Daskalaki and Kondarides studied the hydrogen production from photoreforming of glycerol over Pt/TiO\(_2\), reporting H\(_2\) and CO\(_2\) as the only products in gas phase and methanol and acetic acid as intermediates in liquid phase [142]. Naffati et al. reported a hydrogen production rate of 2091 \(\mu\)mol g\(^{-1}\) from glycerol using a photocatalyst consisting of TiO\(_2\) loaded with Pt and carbon nanotubes (CNT) [143].

Hydrogen production from glycerol has been also demonstrated using photoelectrochemical cells using a TiO\(_2\) photoanode [144], or a TiO\(_2\) photoanode functionalized with CdS [145].

4.5 Organic acids and aldehydes

Other compounds that can be part of the organic waste contained in wastewater are organic acids and aldehydes [146,147]. Patsoura et al. studied the hydrogen production and simultaneous degradation of formic acid, acetic acid and acetaldehyde over a Pt/TiO\(_2\) photocatalyst [148]. The study reported a hydrogen production after 20 hours of 183.2 \(\mu\)mol from acetic acid and 72.5 \(\mu\)mol from acetaldehyde.

Li et al. researched the photocatalytic hydrogen production in presence of oxalic acid, formic acid and formaldehyde using a Pt/TiO\(_2\) photocatalyst [28]. The study reported that the photocatalytic activity of these electron donors follows the trend of oxalic acid > formic acid > formaldehyde which agrees with the order of adsorption affinity of these electron donors on TiO\(_2\).

Imizcoz and Puga investigated the photoreforming of acetic acid using Cu/TiO\(_2\) as photocatalyst [149]. Hydrogen production from acetic acid was enhanced by including a photoreduction step to control the oxidation stage of Cu. On the contrary, when Cu was used directly, its passivation resulted in a high decarboxylation, producing mainly CH\(_4\) instead of H\(_2\).

4.6 Wastewater mixtures

The feasibility of photocatalytic H\(_2\) production from wastewater mixtures such as olive mill wastewater, juice production wastewater and waste activated sludge has been demonstrated [29,50,112,150].

Olive mill wastewater (OMW) contains a high load of organics varying from 40 to 220 g L\(^{-1}\) [151]. The main components found on this wastewater are oil, grease, polyphenols and sugars [150].
Badawy et al. studied the photocatalytic degradation of OMW with simultaneous hydrogen production using nanostructured mesoporous TiO$_2$ as photocatalyst [29]. TiO$_2$ loading and pH were the main factors affecting the photocatalytic degradation and H$_2$ production in this study. The maximum hydrogen production was 38 mmol after 2 hours at a pH of 3 and a photocatalyst concentration of 2 g L$^{-1}$. The organic pollutants contained in OMW enhanced the H$_2$ production, by scavenging holes and decreasing the electron hole recombination. Speltini et al. investigated the effects of factors as photocatalyst concentration, pH and OMW concentration in H$_2$ production, using Pt/TiO$_2$ as photocatalyst and UV-A irradiation [150]. The study reports an apparent quantum yield of 5.5 $10^{-3}$ at 366 nm and the production of 44 µmol of H$_2$ after 4 hours of UV-A irradiation, using a photocatalyst concentration of 2 g L$^{-1}$, OMW concentration of 3.35 v/v, and a pH of 3. Moreover, the H$_2$ yield produced by OMW was compared to glucose, which have been considered a good sacrificial donor for H$_2$ production, and similar production rates were obtained.

Imizcoz and Puga demonstrated the feasibility of photocatalytic hydrogen production using wastewater from a juice production industry, which contains high amounts of saccharides [112]. The study reported a H$_2$ yield of 115 mol g$_{cat}^{-1}$ h$^{-1}$ using Au/TiO$_2$ as photocatalyst.

The simultaneous H$_2$ production and degradation of waste activated sludge from wastewater treatment processes was investigated by Liu et al., using Ag/TiO$_2$ as photocatalyst, proving the possibility of this process [30].

All the materials used in the reviewed works for H$_2$ production by photocatalytic and photoelectrochemical oxidation of each wastewater component are summarize in table 1 and table 2.

Table 1. Summary of the materials used in the H$_2$ production from photocatalytic degradation of wastewater compounds.

<table>
<thead>
<tr>
<th>Waste</th>
<th>Photocatalyst</th>
<th>Co-Catalyst</th>
<th>Maximum Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>TiO$_2$</td>
<td>Pt or RuO$_2$</td>
<td>EQE($340$ nm) = 5.1</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt, Rh, Pd, Au, Ni or Cu</td>
<td>-</td>
<td>[103]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt-Au</td>
<td>-</td>
<td>[104]</td>
</tr>
<tr>
<td>Urea</td>
<td>F-TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[24]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>RuO$_2$/TiO$_2$</td>
<td>Pt</td>
<td>EQE($380$ nm) = 1</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
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<td>Pt</td>
<td>-</td>
<td>[25]</td>
</tr>
<tr>
<td>Chemical</td>
<td>Surface</td>
<td>Active Metal</td>
<td>EQE (nm)</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
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<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Pd, Pt, Ni or Au</td>
<td>-</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>EQE$_{(365 nm)}$ = 63</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pd, Pt, Au, Rh, Ag or Ru</td>
<td>-</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Rh</td>
<td>-</td>
<td>[111]</td>
</tr>
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<td></td>
<td>TiO$_2$</td>
<td>Pt, Au, Ag or Cu</td>
<td>-</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>CuO</td>
<td>-</td>
<td>[113]</td>
</tr>
<tr>
<td>Phenol</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>-</td>
<td>-</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>S-g-C$_3$N$_4$</td>
<td>-</td>
<td>EQE$_{(400 nm)}$ = 8.35</td>
<td>[33]</td>
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<tr>
<td>4-chlorophenol</td>
<td>F-TiO$_2$ or P-TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[24]</td>
</tr>
<tr>
<td>Methanol</td>
<td>TiO$_2$/RuO$_2$</td>
<td>Pt or Pd</td>
<td>EQE$_{(380 nm)}$ = 44</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Ag, Au or Pt</td>
<td>-</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Au or Pt</td>
<td>FQE = 14</td>
<td>[124]</td>
</tr>
<tr>
<td></td>
<td>Ru-TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[127]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>EQE$_{(355 nm)}$ = 2.9</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$/C</td>
<td>CuC</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td></td>
<td>g-C$_3$N$_4$</td>
<td>NiOOH/Ag</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>g-C$_3$N$_4$</td>
<td>Ni(OH)$_2$(Al$_2$Si$_2$O$_4$(OH)$_4$</td>
<td>-</td>
<td>[128]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>EQE$_{(365 nm)}$ = 50</td>
<td>[25]</td>
</tr>
<tr>
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<td>TiO$_2$</td>
<td>Ni, Pd, Pt or Rh</td>
<td>EQE$_{(380 nm)}$ = 38</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt, Pd or Rh</td>
<td>FQE = 10</td>
<td>[130]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>EQE = 5.14</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Au</td>
<td>-</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Au</td>
<td>-</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Au</td>
<td>-</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>WC</td>
<td>-</td>
<td>[134]</td>
</tr>
<tr>
<td></td>
<td>Cds</td>
<td>-</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td>Ni</td>
<td>-</td>
<td>[32]</td>
</tr>
<tr>
<td>Glycerol</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>EQE$_{(365 nm)}$ = 70</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[138]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pd or Au</td>
<td>-</td>
<td>[139]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Cu</td>
<td>-</td>
<td>[140]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Cu</td>
<td>EQE$_{(365 nm)}$ = 24.9</td>
<td>[141]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[142]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>CNT-Pt</td>
<td>-</td>
<td>[143]</td>
</tr>
<tr>
<td>Formic acid</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>-</td>
<td>[148]</td>
</tr>
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</table>
Table 2. Summary of the materials used in the H₂ production from degradation of wastewater compounds using photoelectrochemical cells.

<table>
<thead>
<tr>
<th>Waste</th>
<th>Photoanode</th>
<th>(Photo)Cathode</th>
<th>Maximum Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>TiO₂</td>
<td>Pt</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>Pt/C</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Urea</td>
<td>Ni(OH)₂ loaded on TiO₂ or α-Fe₂O₃</td>
<td>Pt</td>
<td>-</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>Pt/C</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Formamide</td>
<td>TiO₂</td>
<td>Pt/C</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Glucose</td>
<td>WO₃</td>
<td>WC</td>
<td>EQE(600 nm) = 80</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td>Ni(OH)₂ loaded on α-Fe₂O₃</td>
<td>Pt</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td>Phenol</td>
<td>TiO₂ NRs, TiO₂ NTs/Ti, CdS and BiO₃·TiO₂·Ti</td>
<td>C/Cu₂O/Cu and Cu₂O</td>
<td>IPCE(380 nm) = 68</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>Bi/BiVO₄</td>
<td>SS</td>
<td>-</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Bi/BiVO₄</td>
<td>Pt</td>
<td>-</td>
<td>[120]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>TiO₂</td>
<td>Pt</td>
<td>IPCE(360nm) = 96</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>TiO₂/WO₃</td>
<td>Carbon black</td>
<td>-</td>
<td>[137]</td>
</tr>
<tr>
<td>Glycerol</td>
<td>TiO₂</td>
<td>Pt</td>
<td>-</td>
<td>[144]</td>
</tr>
<tr>
<td></td>
<td>TiO₂/CdS</td>
<td>Pt</td>
<td>-</td>
<td>[145]</td>
</tr>
</tbody>
</table>

5. Conclusions

This review has described the potential of wastewater as source for energy recovery, using photocatalytic oxidation of pollutants coupled to hydrogen production. The production of
hydrogen from pollutants and wastes is energetically more favourable than the production of hydrogen from water splitting.

Using suspensions of photocatalytic particles has been the most common approach to date, while only a limited number of works have adopted the use of photoelectrochemical cells. PEC represent a promising option since this configuration reduces the recombination losses within the system. Up to now there has been limited research focused on the optimization of the design of photocatalytic reactors or photoelectrochemical cells to improve the overall system efficiency. More research is needed on materials that have already shown promising results for water splitting and which might show improved efficiencies as compared to pure TiO$_2$ for hydrogen production from wastewater.

Only a few studies investigate hydrogen production coupled to the treatment of real or simulated wastewater and more studies are needed to assess the real application. It is extremely challenging to compare the performance from the different published works. Hydrogen production rates, when given, are measured under very different operating conditions and the quantum efficiencies are sometimes not reported. Therefore, following a systematic procedure in reporting photocatalytic performance would be beneficial for the evaluation of the different compounds. Nevertheless, hydrogen production linked to the treatment of pollutants in wastewater is an exciting area for research and may have true potential for scale up in niche applications.

**Acknowledgements**

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