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Energy recovery from tannery sludge wastewaters through photocatalytic hydrogen production

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ABSTRACT

The presented work focuses on energy recovery through the photocatalytic conversion of sulfide-rich tannery sludge into hydrogen using CdS as a photocatalyst, platinum as a co-catalyst and visible light. Four reaction parameters were evaluated through a multivariate experimental design that included investigations of the mass of the photocatalyst (CdS), sacrificial reagent (tannery sludge) concentration, pH and amount of co-catalyst (Pt). The results demonstrated that the tannery sludge concentration and pH were the most important factors in producing the highest hydrogen levels. The strong interaction between these two factors is associated with the consumption of hydrogensulfide ions during the reaction, which can be replenished in basic medium. In contrast, the Pt content and mass of CdS were less relevant factors. The hydrogen production rate under optimal reaction conditions was only 12% lower than that obtained under simulated conditions after the first 5 h of irradiation. However, this rate decreased with longer reaction times.

1. Introduction

Leather is a natural product with special features that arise from animal rearing conditions and the industrialization process. Animal hide gives unique characteristics to leather, making it irreplaceable. Brazil is one of the world's leading leather producers and processes more than 40 million hides annually [1]. According to the Center of the Leather Industries of Brazil (CICB), the leather industry currently employs more than 50,000 workers throughout the country, but part of them are dedicated on actions aimed to mitigate the environmental damage that is currently caused by tanneries. It is estimated that the environmental impact of the leather industry is equivalent to the pollution generated by 1000–4000 Brazilian citizens for each ton of animal hide treated [2]. Thus, the use of new environmentally friendly technologies is necessary to alleviate these environmental effects.

During the tanning process to produce wet blue leather, the hides are treated with chemical products such as sodium hydroxide, ammonium hydroxide, nonionic tenso-active compounds, bactericides, proteolytic enzymes, hydrated lime, sodium sulfide, ammonium chlorite, ammonium sulfate, sulfuric acid, formic acid, and chromium salts to transform them into unalterable and imputrescible products [3–5]. Of these chemicals, Na_2S causes the most discomfort in tanneries due to its characteristic odor. Na_2S is used to remove hair from the hides and to destroy the epidermis by breaking the cysteine-disulfide bridges (keratolysis) via reductive division through a step known as liming. This process generates emissions with high chemical oxygen demands (COD), biological oxygen demands (BOD), and total suspended solid (TSS) loads in the resulting industry effluent [6].

Currently there are many physical, chemical and biological methods for treatment of waste streams [7–13]. Among these methods, it is worth mentioning photocatalysis due to its low cost, sustainability and high efficiency in the degradation of environmental hazardous substances [11,12]. In general, this process includes oxidation of organic species and reduction of inorganic. Most studies on the photocatalytic treatment of tannery waste investigate the advanced oxidation process of organics and the removal of hexavalent chromium via photoreduction [4,14–16]. On the other hand, the photocatalytic degradation of organic compounds under non-aerated conditions takes place with the simultaneous production of hydrogen over irradiated

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semiconductor photocatalyst suspensions [17]. Based on this principle, some studies have focused on energy recovery by photocatalytically converting waste into hydrogen [18–21].

It has been reported that photocatalytic activity of hexagonal CdS for hydrogen evolution is higher in the presence of sulfide ions instead of organic compounds [22]. Liming bath sludge is rich in sulfide, and therefore this wastewater can be used for photocatalytic hydrogen generation, since sulfide ions in aqueous solutions act as efficient hole scavengers when metal sulfide-based photocatalysts are employed [6,22,23]. In these systems, sulfide (S^{2-}) and hydrogensulfide (HS^-) are readily oxidized to SO_4^{2-} and polysulfide ions (S_n^{2-}), such as S_4^{2-} and S_5^{2-}, on hydrous CdS surfaces at pH 14. These polysulfide ions impart a yellow hue to the aqueous suspensions and may act as optical filters and effectively compete in the photoreduction of protons [22]. The formation of yellow polysulfide ions can be suppressed by adding sulfite ions to the reaction media to generate HS^- and thiosulfate ($S_2O_3^{2-}$) [22].

In general, the presence of sulfide ions in a reaction medium increases the hydrogen production rate due to suppression of the recombination charge effect [22]. Moreover, the sulfide ions in solution stabilize CdS surfaces to eliminate surface defects created by photocorrosion. Several aspects regarding the surface chemistry of hydrous CdS have been studied previously [24–26]. Metal sulfides suspended in aqueous solutions have been shown to behave as diprotic acids, much like metal oxides. In the case of CdS prior to irradiation, hydroxyl and thiol (in protonated and deprotonated forms) groups are developed on photocatalyst surface and involved in the reaction equilibria that are strongly pH dependent (equations 1-4) [22,24]:

$$>CdSH_2^+ \rightleftharpoons >CdSH + H^+ \tag{1}$$

$$>CdSH \rightleftharpoons >CdS^- + H^+ \tag{2}$$

$$>CdOH_2^+ \rightleftharpoons >CdOH + H^+ \tag{3}$$

$$>CdOH \rightleftharpoons >CdO^- + H^+ \tag{4}$$

Bastos et al. [24] utilized an adsorption study to investigate which species were most prevalent on CdS surfaces under different pH and salinity conditions prior to irradiation. At a lower pH, the protonated functional groups were predominant (i.e., $>CdSH_2^+$ at pH 4.1–4.3, more acid groups, and $>CdOH_2^+$ at pH 5.8–7.7), while a higher pH generated more of the deprotonated forms (i.e., $>CdS^-$ at pH 7.3–7.7 and $>CdO^-$ at pH 8.9–9.9). During irradiation, the groups attached to the surface acted as reversible charge-carrier traps in the primary steps of the photoelectrochemical mechanism. For solutions rich in sulfide ions, it was necessary to maintain a strongly basic medium to prevent the loss of sulfide ions as H_2S.

In this work, the feasibility of using wastewater from a leather tannery'sliming bath to generate hydrogen was evaluated. In this study, sludge was treated photocatalytically with visible light irradiation, under anaerobic conditions, using CdS as a photocatalyst and Pt as co-catalyst. In general, the addition of a noble metal, mainly Pt, improves the photocatalytic activity, especially for hydrogen-involving reactions [27]. The main purpose is to investigate the influence of the parameters that traditionally affect quantum yields in this reaction. A multivariate experimental design was employed to decrease the total number of experiments required and evaluate the interactions between the parameters.

2. Experimental

2.1. Chemicals

All the reagents used in our experiments were of analytical purity and were used without further purification. Cadmium sulfide, CdS, and hexachloroplatinic acid solution, $H_2PtCl_6{\cdot}6H_2O$ wt. 8%, were purchased from Aldrich.

Table 1
Experiment matrix and results obtained from the 2^k factorial design.

Exp.	hex-CdS (mg)	pH	Residue (% v/v)	$H_2PtCl_6{\cdot}6H_2O$ (mg L^{-1})	nH_2 (μmol)/ Irradiation time		
					1 h	2 h	3 h
1	+(120)	+(13)	+(50)	+(20)	3.54	20.48	54.60
2	+	+	+	−(0)	3.91	21.07	52.53
3	+	+	−(10)	+	2.20	4.44	6.24
4	+	+	−	−	2.69	4.37	6.06
5	+	−(9)	+	+	4.32	7.58	11.04
6	+	−	+	−	4.42	7.34	10.62
7	+	−	−	+	1.00	1.58	2.16
8	+	−	−	−	0.64	1.16	1.57
9	−(60)	+	+	+	7.41	24.93	48.04
10	−	+	+	−	4.60	21.14	52.99
11	−	+	−	+	1.90	3.90	5.80
12	−	+	−	−	2.81	4.61	6.05
13	−	−	+	+	4.82	8.60	12.33
14	−	−	+	−	4.79	9.40	12.90
15	−	−	−	+	0.77	1.52	2.10
16	−	−	−	−	0.58	1.15	1.48
17 (CP)[a]	0(90)	0(11)	0(30)	0(10)	3.52	6.32	8.74
18 (CP)	0	0	0	0	3.74	6.42	8.80
19 (CP)	0	0	0	0	3.53	6.26	8.64
20 (CP)	0	0	0	0	3.80	6.51	8.88
21(CP)	0	0	0	0	3.48	6.35	8.70

+: top level, 0: central point, and −: lower level of the design. These signs are coded values, and the actual values are shown in brackets.
[a] (CP): Central point.