Box–Behnken Design for Hydrogen Evolution from Sugar Industry Wastewater Using Solar-Driven Hybrid Catalysts

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ABSTRACT: Hydrogen is a clean and green fuel and can be produced from renewable sources via photocatalysis. Solar-driven hybrid catalysts were synthesized and characterized (scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), photoluminescence (PL) spectroscopy, and UV–vis diffuse reflectance spectroscopy (DRS)), and the results implied that graphene-supported LaRuO$_2$ is a more promising photocatalyst to produce hydrogen and was used to produce hydrogen from sugar industry wastewater. To investigate the main and interaction effects of reaction parameters (pH, catalyst amount, and [H$_2$O$_2$]$_0$) on the evolved hydrogen amount, the Box–Behnken experimental design model was used. The highest hydrogen evolution obtained was 6773 μmol/g cat from sugar industry wastewater at pH 3, 0.15 g/L GLRO, and 15 mM H$_2$O$_2$. Based on the Pareto chart for the evolved hydrogen amount using GLRO, among the main effects, the only effective parameter was the catalyst amount for the photocatalytic hydrogen evolution from sugar industry wastewater. In addition, the squares of pH and two-way interaction of pH and [H$_2$O$_2$]$_0$ were also statistically efficient over the evolved hydrogen amount.

INTRODUCTION

Hydrogen evolution from various renewable sources such as biomass and wastewater streams using solar energy to provide a simultaneous solution for current global energy and environment problems has recently gained great attention because it is considered to be a promising and green fuel in future. One of the most promising hydrogen evolution processes is photocatalysis since it involves green processes and also it is a simple and relatively low-cost process. Various semiconductors with different band gap energies were used to produce hydrogen from alcohol, glycerol, and wastewater. Kuang and Zhang synthesized carbon-doped TiO$_2$ (C-TiO$_2$) and reduced graphene-decorated C-TiO$_2$ (C-TiO$_2$/rGO) to produce hydrogen from water using methanol as an electron donor under visible light irradiation. The amount of hydrogen produced was 0.67 ± 0.12 to 1.50 ± 0.2 mmol g$^{-1}$ h$^{-1}$ using C-TiO$_2$ and C-TiO$_2$/rGO, respectively. Graphene has a large surface area and provides better electron transfer, thus enhancing the obtained hydrogen amount. Additionally, the band gap energies of C-TiO$_2$ and C-TiO$_2$/rGO were reported to be 2.5 and 2.2 eV, respectively. Hence, the introduction of rGO causes a decrease in the band gap energy, and so the utilization of visible light becomes a feasible option. Cheng et al. synthesized a hybrid catalyst (TiO$_2$–graphene nanocomposite) via a solvothermal reaction to produce hydrogen from the mixture of methanol and water by photocatalytic oxidation, and the mass ratio of graphene was optimized to be 0.5 wt % and almost 6000 μmol of H$_2$ was produced using this catalyst. Graphene served as an acceptor of the photogenerated electrons of TiO$_2$ and as a transporter to separate the photogenerated electron–hole pairs effectively. The hybrid catalysts had enhanced light absorption ability and a lower recombination rate of photogenerated electron–hole pairs and hence showed higher photocatalytic activity toward hydrogen production from the methanol and water mixture under visible light illumination than raw TiO$_2$. Sekar et al. studied hydrogen production from Bisphenol A, which is an endocrine-disrupting chemical and has severe toxic effects on human health, using a hierarchical bismuth vanadate (h-BiVO$_4$)/reduced graphene oxide (rGO) composite. While 11.5 μmol g$^{-1}$ h$^{-1}$ of hydrogen was produced in the presence of h-BiVO$_4$/rGO, 0.03 μmol g$^{-1}$ h$^{-1}$ of hydrogen was obtained using BiVO$_4$. While 57% Bisphenol A removal was achieved in the presence of BiVO$_4$, a 72% removal was obtained using h-BiVO$_4$/rGO. Hence, the...
introduction of graphene causes an increase in the produced hydrogen amount and Bisphenol A removal since graphene has outstanding properties. For instance, it behaves as a cocatalyst, charge transfer mediator, photosensitizer, and electron trap. In addition, perovskite-type catalysts (i.e., LaCoO$_3$, LaFeO$_3$, CaTiO$_3$) could be used to produce hydrogen by photocatalysis. For instance, Acharya et al. examined water decomposition reaction using the LaFeO$_3$ nanotubes/graphene oxide (GO) composite via photocatalytic oxidation and using methanol as a sacrificial agent, and the maximum hydrogen production ($611.3 \text{ mmol h}^{-1} \text{ g}^{-1}$) was obtained in the presence of LaFeO$_3$ nanotubes/(1% by mass)GO. Furthermore, it has been found that the addition of reduced GO to LaFeO$_3$ reduces band gap, and it was found that the reduced GO provided a more active surface for adsorption and photocatalytic reaction because of the wide surface area and that the reduced GO layer could efficaciously collect and transport electron, which reduced the probability of electron–hole recombination and increased the efficiency of separation. Therefore, considering the wide band gap range of perovskite-type catalysts (BiFeO$_3$ and LaRuO$_3$) and the outstanding properties of graphene, in this study, solar-driven hybrid catalysts, i.e., graphene-supported BiFeO$_3$ (GBFO) and graphene-supported LaRuO$_3$ (GLRO), were synthesized to produce hydrogen from sugar industry wastewater.

In the literature, various photocatalysts were tested to produce hydrogen from sucrose solution. For instance, noble-metal (Pd, Pt, Au, Rh, Ag, and Ru) loaded TiO$_2$ and La-doped alkali tantalate were used. To the best of our knowledge, GBFO and GLRO have not been used to produce hydrogen from sucrose solution and/or sugar industry wastewater, and so in this study, hydrogen evolution from sucrose solution and sugar industry wastewater was performed using these solar-driven photocatalysts. Additionally, the Box–Behnken statistical model was used to investigate the impacts of reaction parameters (pH, catalyst amount, and $[\text{H}_2\text{O}_2]$) on the evolved hydrogen amount, and their main impacts and interactions were statistically analyzed.

## RESULTS AND DISCUSSION

**Characterization of Hybrid Catalysts.** The surface morphology of hybrid catalysts was investigated via scanning electron microscopy (SEM) analysis, and the results are shown in Figure 1. SEM images showed that they are agglomerated nanocrystals and have a porous structure. The perovskite structure did not change after the introduction of graphene to obtain hybrid catalysts. In addition, graphene was homoge-

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**Figure 1.** SEM images of GBFO (a) and GLRO (d); SEM-energy-dispersive spectrometry (EDS) spectra of GBFO (b) and GLRO (e); TEM images of GBFO (c) and GLRO (f).
neously distributed on the surface of hybrid catalysts, and in the literature, similar results were reported in many studies.\textsuperscript{14,15} Transmission electron microscopy (TEM) images of hybrid catalysts, shown in Figure 1, showed polycrystallinity and BFO and LRO covered in a layer of graphene, and the incorporation of graphene did not lead to any change in the structure of BFO and LRO. Brunauer–Emmett–Teller (BET) areas of perovskite and hybrid catalysts were determined. The BET area of BFO was 1.2 m\textsuperscript{2}/g; however, it increased to 2.6 m\textsuperscript{2}/g after the incorporation of graphene. On the other hand, LRO and GLRO had higher BET areas compared to BFO and GBFO. BET areas of LRO and GLRO were determined to be 22.7 and 27.6 m\textsuperscript{2}/g, respectively. In the literature, the BET area of LRO was reported to be 2 m\textsuperscript{2}/g by Pietri et al.;\textsuperscript{16} however, in the present study, it had a relatively higher BET area. Perovskite catalysts have characteristic peaks at certain 2\theta values (22.63, 32.22, 39.73, 46.21, 57.45, 67.42, 72.12, and 76.69°), and the observation of these peaks at given 2\theta values is attributed to the orthorhombic structure of perovskite-type catalysts.\textsuperscript{14,15,17} To confirm the presence of these characteristic peaks, X-ray diffraction (XRD) analysis was performed, and the results are shown in Figure 2. The results showed that all catalysts had characteristic peaks of perovskite structure, and similar results were reported in the literature.\textsuperscript{18–20} Additionally, the nanocrystalline nature of perovskite and hybrid catalysts was proved by the broadness of these peaks. Graphene has a characteristic peak around 21° and it has an amorphous structure,\textsuperscript{21} and the results showed that graphene was successfully synthesized. If the peak in the photoluminescence (PL) diagram of a photocatalyst has a reduced intensity, then it indicates a slower charge pair recombination and a longer life period of e\textsuperscript{−} and h\textsuperscript{+} pairs.\textsuperscript{11,22–24} Therefore, PL analysis was performed to comprehend the recombination process of photoexcited charge carriers and the life span of electron–hole pairs, and the results are shown in Figure 2. The peaks of BFO, GBFO, LRO, and GLRO were observed at 552, 550, 536, and 534 nm, respectively. Hence, the graphene incorporation led to a small shift and it could be concluded
that lower photon energy is necessary to produce hydrogen using hybrid catalysts. Therefore, the highest hydrogen production should be observed in the presence of GLRO, while the lowest value should be observed using BFO.

UV–vis DRS analysis of GBFO and GLRO was carried out in the range of 200 and 800 nm, and their band gap energies were calculated by the Kubelka–Munk method. The results of this analysis are shown in Figure 3, and the band gap energies of GBFO and GLRO were determined to be 2.05 and 2.61 eV, respectively. In the literature, the band gap energy of BFO was reported to be between 2.2 and 2.8 eV. Additionally, the separation process of electron−hole pairs and the photocatalytic process for these hybrid catalysts and XPS results were reported in our previous study.23

In our previous study, the energy levels of calculated valence band edge (\( E_{VB} \)) for BFO, LRO, and graphene were reported to be 2.58, 3.26, and 1.99, respectively. Additionally, the energy levels of calculated conduction band edge (\( E_{CB} \)) for BFO, LRO, and graphene were reported to be 0.50, 0.45, and −1.79, respectively. Considering the results, it could be concluded that the CB position of BFO and LRO is lower than that of the graphene, which reduces the recombination of electron−hole pairs and enhances the photoactivity of GBFO and GLRO.25 A schematic diagram of the separation process of electron–hole
pairs of GBFO and GLRO is shown in Figure 4. In this study, the introduction of graphene into the perovskite structure led to fast charge transfer, thereby enhancing the hydrogen evolution from sucrose model solution and sugar factory wastewater. Additionally, electrons are transferred through the graphene sheets to react with absorbed $\text{H}^+$ into wastewater for hydrogen evolution. Various composite photocatalysts were used to produce hydrogen via photocatalysis. For instance, Chang et al. studied photocatalytic hydrogen evolution from lactic acid solution using MoS$_2$/graphene under visible light. Similarly, they reported that the electrons can be transferred to the edge of MoS$_2$ through the graphene sheets and then react with adsorbed $\text{H}^+$ at the edges of MoS$_2$ to form hydrogen.\textsuperscript{26}

**Photocatalytic Hydrogen Evolution.** Photocatalytic hydrogen evolution from sucrose solution and sugar industry wastewater was studied in the presence of GBFO and GLRO, and to examine the impact of reaction parameters (pH, catalyst amount (CA), and $[\text{H}_2\text{O}_2]_0$) the Box–Behnken model was used. Additionally, the same experimental matrix was used for sucrose solution and sugar industry wastewater. The uncoded values of these parameters are 3–7.5, 0.1–0.2 g/L, and 0–15 mM for pH, catalyst amount, and initial hydrogen peroxide concentration, respectively. The uncoded design table of this experimental study and evolved hydrogen amounts (response) are presented in Table 1.

| reaction conditions | evolved hydrogen (μmol/g$_\text{cat}$) | sucrose solution | sugar industry wastewater |
|---------------------|--------------------------------------|------------------|-------------------------|
| pH                  | catalyst amount [g/L]                | initial $\text{H}_2\text{O}_2$ concentration [mM] | GBFO | GLRO | GBFO | GLRO |
| 3                   | 0.15                                 | 0                | 2717 | 3031 | 5490 | 5521 |
| 7.5                 | 0.15                                 | 15               | 2580 | 3179 | 4472 | 4687 |
| 5.25                | 0.15                                 | 7.5              | 2701 | 3383 | 3564 | 3895 |
| 7.5                 | 0.15                                 | 0                | 2756 | 2805 | 6089 | 6645 |
| 3                   | 0.1                                  | 7.5              | 2552 | 2679 | 6617 | 6758 |
| 5.25                | 0.15                                 | 7.5              | 3102 | 3410 | 3245 | 3237 |
| 7.5                 | 0.1                                  | 7.5              | 2569 | 2866 | 5429 | 5686 |
| 5.25                | 0.2                                  | 15               | 2591 | 3047 | 3674 | 3588 |
| 5.25                | 0.1                                  | 15               | 3515 | 3135 | 4032 | 4354 |
| 3                   | 0.2                                  | 7.5              | 2729 | 3086 | 3339 | 3527 |
| 5.25                | 0.15                                 | 7.5              | 2739 | 3339 | 3823 | 4186 |
| 5.25                | 0.15                                 | 7.5              | 2673 | 3416 | 3124 | 3892 |
| 5.25                | 0.10                                 | 0                | 2970 | 2899 | 4296 | 4391 |
| 5.25                | 0.15                                 | 7.5              | 3460 | 3405 | 4208 | 4076 |
| 5.25                | 0.15                                 | 7.5              | 2662 | 3350 | 3075 | 4794 |
| 7.5                 | 0.2                                  | 7.5              | 2783 | 2888 | 2778 | 2914 |
| 5.25                | 0.2                                  | 15               | 2508 | 3322 | 3174 | 3124 |
| 3                   | 0.15                                 | 15               | 3025 | 3256 | 6436 | 6773 |

The evolved hydrogen amounts from sucrose solution in the presence of GBFO varied between 2778 and 6617 μmol/g$_\text{cat}$, and the mean value was determined to be 2846 ± 21 μmol/g$_\text{cat}$. The mean value of evolved hydrogen from sugar industry wastewater using GBFO was 3507 ± 469 μmol/g$_\text{cat}$. The highest hydrogen production achieved was 6617 μmol/g$_\text{cat}$ from sugar industry wastewater at pH 3 and using 0.1 g/L GBFO catalyst and 7.5 mM $\text{H}_2\text{O}_2$. This value was more than twice the amount of hydrogen obtained from the sucrose solution under the same reaction conditions. The mean value of evolved hydrogen from sucrose solution using GLRO was 3139 ± 34 μmol/g$_\text{cat}$. The highest hydrogen evolution from sucrose solution was achieved at 3416 μmol/g$_\text{cat}$ under the following reaction conditions: 5.25 pH, 0.15 g/L GLRO, and 7.5 mM $[\text{H}_2\text{O}_2]_0$. The evolved hydrogen amounts from sugar industry wastewater using GLRO varied between 2914 and 6773 μmol/g$_\text{cat}$. The mean value of evolved hydrogen from sugar industry wastewater using GLRO was 4013 ± 530 μmol/g$_\text{cat}$. The highest hydrogen evolution obtained was 6773 μmol/g$_\text{cat}$ from sugar industry wastewater at pH 3, 0.15 g/L GLRO, and 15 mM $\text{H}_2\text{O}_2$. This value was more than twice the amount of hydrogen obtained from sucrose solution under the same reaction conditions. Furthermore, the results were in consistence with the results of PL analysis of these catalysts.

The ANalysis Of Variance (ANOVA) table of this experimental design that was carried out using GBFO is presented in Table 2 to consider the interactions between factors based on the $p$-values of each factor. Based on the results, the most significant term was the $[\text{H}_2\text{O}_2]_0$ and the main effects of reaction parameters (pH, catalyst amount, and $[\text{H}_2\text{O}_2]_0$) were highly effective over the evolved hydrogen amount from sucrose solution using GBFO. Additionally, CA$^*$[H$_2$O$_2$] was also efficient. The other terms did not have any impact on the evolved hydrogen statistically. The value of $R^2$ for this model was calculated to be 98.82%, and hence it could be deduced that the model is a good fit to the observed response (evolved hydrogen amount). The main impact of pH and CA did not affect the evolved hydrogen amount from sugar industry wastewater; however, CA showed a main effect on the evolved hydrogen amount. Moreover, the square of pH was also statistically effective. Other parameters were not statistically effective on the evolved hydrogen amount from sugar industry wastewater using GBFO. In addition, the $p$-value (probability value) of lack-of-fit (0.079) was found to be higher than the value of $α$ (0.05). Hence, it could be deduced that the model was well fitted to obtained experimental data. Furthermore, the $R^2$ of the model was determined to be 86.35%, and thus it could be deduced that the model was a good fit to the observed response.

The normal probability plot and histogram diagram are shown in Figure 5a and b, and the Pareto chart is shown to comprehend the individual and interaction effects of factors in Figure 5c for evolved hydrogen amount from sucrose solution using GBFO. In addition, the probability plot, histogram diagram, and Pareto chart for evolved hydrogen amount from sucrose solution using GBFO are shown Figure 5d–f, respectively.

Experimental points were reasonably aligned, suggesting normal distribution between −60 and +60 in Figure 5a. In Figure 5b, the $t$-value was 2.31 in a confidence level of 95%. Hence, $[\text{H}_2\text{O}_2]_0$ was the most important parameter. In addition, all main factors also had a major effect on the photocatalytic hydrogen evolution from sucrose solution using GBFO. Moreover, CA$^*$[H$_2$O$_2$] had a synergistic effect on the evolved hydrogen amount from sucrose solution using GBFO. The normal probability plot (Figure 5d) implies that the data were normally distributed. Additionally, Figure 5e shows that the experimental points were aligned in the range of −600 and +800. The normal distribution range extended in a larger interval compared to the results of sucrose solution. The main and interaction effects of the reaction parameter were elucidated via Pareto chart, and the minimum statistically

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important impact magnitude for 95% confidence level was shown with the vertical line in Figure 5f. Thus, the parameter which has a higher magnitude than this vertical line was statistically effective over hydrogen evolution from sugar industry wastewater using GBFO. In addition, the $t$-value is equal to 2.306 in this confidence level. Therefore, among the main effects, the only effective parameter was CA for the photocatalytic hydrogen evolution from sugar industry wastewater using GBFO.

Table 2. ANOVA Table for Evolved Hydrogen Amounts Using GBFO

| source                  | DF | Adj SS | Adj MS | F-value   | P-value  | DF | Adj SS | Adj MS | F-value   | P-value  |
|-------------------------|----|--------|--------|-----------|----------|----|--------|--------|-----------|----------|
| model                   | 9  | 960 091| 106 677| 74.18     | 0.000001 | 9  | 22 089| 149 | 2 454 350 | 5.62     | 0.012 |
| linear                  | 3  | 506 630| 168 877| 117.43    | 0.000001 | 3  | 8 331| 329 | 2 777 110 | 6.36     | 0.016 |
| pH                      | 1  | 354 132| 354 132| 246.25    | 0.000000 | 1  | 1 211| 588 | 1 211 588 | 2.78     | 0.134 |
| CA                      | 1  | 121 179| 121 179| 84.26     | 0.000016 | 1  | 6 862| 106 | 6 862 106 | 15.73    | 0.004 |
| $[\text{H}_2\text{O}_2]$ | 1  | 31 319 | 31 319 | 21.78     | 0.001609 | 1  | 257 634 | 257 634 | 0.59      | 0.464    |
| square                  | 3  | 433 900| 144 633| 100.57    | 0.000001 | 3  | 12 002| 961 | 4 000 987 | 9.17     | 0.006 |
| pH*pH                   | 1  | 74     | 74     | 0.05      | 0.825932 | 1  | 8 933| 569 | 8 933 569 | 20.47    | 0.002 |
| CA*pH                   | 1  | 3301   | 3301   | 2.30      | 0.168244 | 1  | 686 803 | 686 803 | 1.57      | 0.245    |
| $[\text{H}_2\text{O}_2]$* $[\text{H}_2\text{O}_2]$ | 1  | 414 035| 414 035| 287.90    | 0.000000 | 1  | 2 042| 335 | 2 042 335 | 4.68     | 0.062 |
| 2-way Interaction       | 3  | 19 561 | 6520   | 4.53      | 0.038800 | 3  | 1 754| 859 | 584 953  | 1.34     | 0.328 |
| pH*CA                   | 1  | 4 728  | 4 728  | 3.29      | 0.107381 | 1  | 98 302 | 98 302  | 0.23      | 0.648    |
| $\text{CA}*[\text{H}_2\text{O}_2]$ | 1  | 12 102 | 12 102 | 8.42      | 0.019863 | 1  | 1 398 | 668 | 13 986  | 0.03     | 0.862 |
| error                   | 8  | 11 505 | 1438   |           |          | 8  | 3 490| 951 | 436 369  |          |
| lack-of-fit             | 3  | 9 447  | 3149   | 7.65      | 0.025725 | 3  | 2 494| 876 | 83 1625  | 4.17     | 0.079 |
| pure error              | 5  | 2057   | 411    |           |          | 5  | 996 075 | 199 215 |          |
| total                   | 17 | 971 596|        |           |          | 17 | 25 580| 099 |          |

Figure 5. Normal probability plot (a), histogram (b), and Pareto chart (c) for evolved hydrogen amounts from sucrose solution using GBFO. Normal probability plot (d), histogram (e), and Pareto chart (f) for evolved hydrogen amounts from sugar industry wastewater using GBFO.

important impact magnitude for 95% confidence level was shown with the vertical line in Figure 5f. Thus, the parameter which has a higher magnitude than this vertical line was statistically effective over hydrogen evolution from sugar industry wastewater using GBFO. In addition, the $t$-value is equal to 2.306 in this confidence level. Therefore, among the main effects, the only effective parameter was CA for the photocatalytic hydrogen evolution from sugar industry waste-
water using GBFO. In addition, the squares of pH affected the evolved hydrogen amount. However, other parameters were not statistically effective.

The ANOVA table of this experimental design that was carried out using GLRO is presented in Table 3 to comprehend the main effects of factors and the interactions between them based on p-values of each factor. The main

| source        | DF | Adj SS | Adj MS | F-value | P-value |
|---------------|----|--------|--------|---------|---------|
| model         | 9  | 874 526| 97 170 | 75.60   | 0.00000 |
| linear        | 3  | 210 295| 70 098 | 54.54   | 0.0001  |
| pH            | 1  | 871 4   | 871 4  | 6.78    | 0.03143 |
| CA            | 1  | 67 910  | 67 910 | 52.84   | 0.00009 |
| $[\text{H}_2\text{O}_2]_0$ | 1  | 133 671 | 133 671| 104.00  | 0.00001 |
| square        | 3  | 630 624 | 210 208| 163.55  | 0.00000 |
| pH*pH         | 1  | 284 963 | 284 963| 221.72  | 0.00000 |
| CA*CA         | 1  | 255 119 | 255 119| 198.50  | 0.00000 |
| $[\text{H}_2\text{O}_2]_0$*[$\text{H}_2\text{O}_2]_0$ | 1  | 7344    | 7344   | 5.71    | 0.04383 |
| 2-way interaction | 3  | 33 607  | 11 202 | 8.72    | 0.00668 |
| pH*CA         | 1  | 31 958  | 31 958 | 24.87   | 0.00107 |
| CA*[H$_2$O$_2$]$_0$ | 1  | 1 275 058| 1 275 058| 1.91  | 0.01907 |
| $[\text{H}_2\text{O}_2]_0$*[H$_2$O$_2$]$_0$ | 1  | 1 229 470| 1 229 470| 5.48  | 0.04704 |
| error         | 5  | 53 607  | 13 402 | 5.30    | 0.05781 |
| lack-of-fit   | 3  | 49 327  | 16 444 | 1.53    | 0.31423 |
| pure error    | 5  | 53 500  | 10 700 | 1.54    | 0.31423 |
| total         | 17 | 884 808 |        |         |         |

**Table 3. ANOVA Table for Evolved Hydrogen Amounts Using GLRO**

**Figure 6.** Normal probability plot (a), histogram (b), and Pareto chart (c) for the evolved hydrogen amount from sucrose solution using GLRO. Normal probability plot (d), histogram (e), and Pareto chart (f) for the evolved hydrogen amount from sugar industry wastewater using GLRO.
effects and the square of all factors were significant over the evolved hydrogen amount from sucrose solution using GLRO. Among two-way interaction terms, pH × CA had a synergistic effect and the other terms did not affect the amount of evolved hydrogen from sucrose solution statistically. The main effect of pH and [H₂O₂]₀ did not affect the evolved hydrogen amount; however, CA showed a main effect. Moreover, the square of pH was also statistically effective. Among the two-way interactions, pH × [H₂O₂]₀ had a significant effect over the evolved hydrogen amount from sugar industry wastewater using GLRO. Therefore, the pH and [H₂O₂]₀ showed a synergetic effect during the degradation of organic compounds in the sugar industry wastewater and concomitant hydrogen evolution. The synergetic effect of pH and [H₂O₂]₀ depends on various parameters such as TOC and concentration of organic substances in the wastewater stream, and if their synergetic effect is observed, it implies that appropriate reaction conditions were provided. Therefore, the reaction conditions were appropriate to produce hydrogen and degrade organic substances in the wastewater. However, other parameters did not have a statistically significant effect over the evolved hydrogen amount using GLRO. The p-value of lack-of-fit (0.15S) is higher than the value of α (0.05), and thus it could be inferred that the model was well fitted to the experimental data. In addition, the R² values for this model were determined to be 98.84 and 87.26% for sucrose solution and sugar industry wastewater, respectively. Therefore, the model showed a good fit to the observed response data.

Based on the residual plots, it could be deduced that the experimental points for evolved hydrogen from sucrose solution (Figure 6a) and from sugar industry wastewater (Figure 6d) were reasonably aligned with normal distribution between −40 and +30 and in the range of −800 and +800, respectively. Pareto charts of evolved hydrogen from sucrose solution and from sugar industry wastewater are shown in Figure 6c and f, respectively. In these graphs, the t-value is equal to 2.31 with a confidence level of 95%. Therefore, the square of pH and the square of CA were the most important parameters for the photocatalytic hydrogen evolution from sucrose solution using GLRO. Additionally, the square of [H₂O₂]₀ was also an effective parameter. Moreover, all main factors also had a major effect over the evolved hydrogen amount. Moreover, the two-way interaction of pH and CA had a synergistic effect over the produced hydrogen amount. On the other hand, among the main effects, the only effective parameter was CA for the photocatalytic hydrogen evolution from sugar industry wastewater using GLRO. Although the squares of pH and the two-way interaction of pH and [H₂O₂]₀ affected the evolved hydrogen amount, other factors were not statistically effective.

CONCLUSIONS

Photocatalytic oxidation is a feasible process to produce hydrogen, which is a clean and green fuel from renewable sources. In this context, first, solar-driven hybrid catalysts (graphene-supported BiFeO₃ and graphene-supported LaRuO₃) were synthesized. Then, the characterization study consisting of SEM, TEM, BET, XRD, PL, and UV–vis DSR analyses was conducted, and based on PL results, GLRO was the most promising photocatalyst to produce hydrogen. The Box–Behnken experimental design model was used to investigate the main and interaction effects of reaction parameters (pH, catalyst loading, and [H₂O₂]₀) on the evolved hydrogen amount from sucrose solution and sugar industry wastewater via photocatalysis. The lowest evolved hydrogen amount was 2508 μmol/g-cat at the following reaction conditions: a pH of 5.25, 0.2 g/L catalyst (GBKFO) loading, and 15 mM [H₂O₂]₀ while the highest hydrogen evolution achieved was 6773 μmol/g-cat from sugar industry wastewater at pH 3, 0.15 g/L catalyst (GLRO) loading, and 15 mM [H₂O₂]₀. The most effective parameter over evolved hydrogen amount using GLRO was found to be the square of pH, and the other effective parameters were catalyst amount and two-way interaction of pH and [H₂O₂]₀. It could be deduced that pH and [H₂O₂]₀ showed a synergetic effect over the evolved hydrogen amount from sugar industry wastewater using GLRO.

MATERIALS AND METHODS

Materials. Sucrose (Merck) and sugar industry wastewater (supplied from Eskişehir Sugar Factory, Turkey) were used to produce hydrogen. Graphite, sodium nitrate, hydrogen peroxide, lanthanum nitrate hexahydrate, bismuth nitrate pentahydrate, iron nitrate nonahydrate, hydrazine hydrate, and sodium hydroxide were purchased from Merck to conduct the study. Citric acid and ethylene glycol were purchased from Isolab, and potassium permanganate was purchased from Tekkim. Lastly, ruthenium chloride and hydrochloric acid were purchased from Sigma.

Synthesis of Hybrid Catalysts. First, graphene was produced from graphite via the chemical decomposition method. In this context, 1 g of graphite was mixed with NaNO₃ (0.5 g) and sulfuric acid (25 mL) and then the mixture was kept in an ice bath to control the temperature (T < 20 °C) during the addition of KMnO₄ (3 g) into this mixture. After that, this solution was still kept in the ice bath and stirred at 35 °C for 40 min. After completing this step, 45 mL of distilled water (DW) was put in a beaker and the obtained solution was added into DW and stirred for 20 min. Then, a mixture of H₂O₂ and DW (140:10, v/v) was prepared and preprepared graphite-containing solution was added into this H₂O₂ and DW solution. The final solution was kept at room temperature for 1 day and then it was filtered, and hence graphene oxide (GO) was obtained. Then, to remove the impurities (i.e., metal ions, sulfate, etc.), it was washed with 5% HCl solution and the solid residue was calcinated at 300 °C for 15 min. After this step, hydrazine hydrate (HH) was used to reduce GO to graphene; 1 mL of HH was added to 100 mg of GO (on basis), and the mixture of HH and GO was stirred at 80 °C for 6 h. Then, the obtained solid residue was dried under vacuum at 50 °C to afford graphene. ²⁷

Second, perovskite-type catalysts (BiFeO₃ and LaRuO₃) were synthesized and detailed synthesis steps were given. To prepare BiFeO₃, bismuth nitrate and iron nitrate were used as precursors and they were separately dissolved in DW considering their stoichiometric ratio. Afterwards, they were mixed together and stirred to obtain a precursor solution at room temperature for 1 h. A mixture of citric acid (1.5 times of total moles of precursors) and ethylene glycol (25 mL for 0.1 mol of each precursor) in DW was prepared and added into the obtained precursor solution. Then, it was heated up to 80 °C by stirring, and it was kept at 80 °C until the gel formation was observed. Thereafter, the gel was dried at 150 °C for 6 h, and then it was calcinated at 700 °C for 4 h to obtain BiFeO₃ (BFO). ²⁸ To synthesize LaRuO₃ (LRO), lanthanum nitrate and ruthenium chloride were used. First, citric acid, ruthenium
chloride, and ethylene glycol were mixed at the given ratios (citric acid/ruthenium chloride = 4 and ethylene glycol/citric acid = 1.38). Then, lanthanum nitrate was added considering the stoichiometric ratio between lanthanum and ruthenium into this solution and kept at 50 °C and complete evaporation was achieved after 2 days. Then, the remaining residue was dried at 150 °C for 6 h, and then it was calculated at 700 °C for 4 h to obtain LaRuO$_3$ (LRO).$^{16}$

Last, hybrid catalysts (GBFO and GLRO) were synthesized using previously prepared graphene and perovskite catalysts. To prepare 20 wt % graphene-containing hybrid catalysts, first, the required amount of graphene was added into the ethanol/water mixture and then sonicated for 2 h. After sonication, the perovskite catalyst (i.e., BFO) was added into this solution and stirred for 2 h. Then, the solid residue was separated via centrifugation and dried at 70 °C for 12 h.$^{28,29}$ Consequently, the hybrid catalysts were obtained.

**Characterization of Hybrid Catalysts.** SEM-EDS analysis with the FEI QUANTA 250 FEG model was performed to investigate the surface morphology of hybrid catalysts. Also, TEM (JEOL 2100F 200 kV RTEM) analysis was performed. The BET areas of hybrid catalysts were determined using a Micromeritics ASAP 2010. The crystalline structure of hybrid catalysts was analyzed via XRD (Philips X’Pert diffractometer with Cu Kα radiation, 2θ = 5–80°, step length: 0.02°). PL (Edinburgh Instruments FLS920) was carried out to determine the photocatalytic activities of hybrid catalysts. UV–vis DSR (UV–vis, Shimadzu UV 2600) was used to calculate the band gap energies of hybrid catalysts.

**Experimental Setup and Procedure.** Photocatalytic hydrogen production setup consists of a cylindrical glass reactor (V = 1000 mL) with a jacket, a pump for circulation of solution, a stimulated solar lamp placed in the middle of a glass reactor, and a gas analysis system (ABB Advance Optima, AO2000) connected to the gas outlet of the reactor to measure the amounts of produced gases (CO, CO$_2$, H$_2$, and CH$_4$) throughout the experiments. A typical experimental procedure started with introducing the sucrose solution or sugar industry wastewater at desired pH value (adjusted using HCl or NaOH solution) in the reactor. After that, the desired amount of hybrid catalyst and hydrogen peroxide were introduced, and then the stimulated solar lamp was turned on to start the reaction to produce hydrogen via photocatalysis. The amounts of produced gases throughout the reaction were measured with a gas analysis system and the experiments lasted up to 4 h.

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**Funding**

This study was financially supported through the project of The Scientific and Technological Research Council of Turkey-TUBITAK (Project No. 217M272).

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank İzmir Institute of Technology Integrated Research Centres, Ege University Central Research Test and Analysis Laboratory Application and Research Centre, Dokuz Eylül University Electronic Materials Production and Application Centre, and Çanakkale Onsekiz Mart University ÇOBILTUM—Science and Technology Application and Research Centre for the product analyses of catalyst characterization studies. Additionally, they thank Prof. Dr. Şerife Şerif Helvacı for UV–vis DRS analysis.

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