Article

Exploring the possibilities for reactions between SiW and alkaline solutions to be renewable energy sources

Hsuan-I (Ethan) Chou[1], Ching-Ching (Lara) Ku[2], Dino Ponnampalam[1]

[1] Kang Chiao International School, New Taipei City, Taiwan

[2] American School of The Hauge, Wassenaar, Netherlands

SUMMARY

The increasing concern over greenhouse gas emissions (GGE) has led to a search for cleaner energy sources, with hydrogen fuel cells being a promising alternative to fossil fuels. This study focused on the reaction between excess silicon (Si) and limiting alkaline solutions to produce hydrogen (H_2) gas, which can be consumed in an electrochemical cell to generate renewable energy. We investigated the effects of reaction temperature, concentration, and alkaline solution type on H_2 production rate because these variables are known to influence reaction kinetics and yield. By analyzing the correlation between H_2 production and reaction time and deriving the average H_2 production rate, we aimed to identify the most efficient conditions for H_2 generation. From the best-fit line of the volume-time profile, we deduced the average H_2 production rate. The results showed that higher temperatures, higher concentrations, and solutions with higher base dissociation constants (k_b) lead to a higher H_2 production rate. Along with this finding, the stable and consistent production of H_2 gas throughout all the trials demonstrated the viability of using Si waste as a source of renewable energy through hydrogen fuel cells.

INTRODUCTION

Greenhouse gas emissions (GGE) resulting from the combustion of fossil fuels are associated with significant environmental threats such as energy crises, pollution, and climate deterioration (1). As a result, the need for clean energy derived from renewable sources with minimal environmental impact has become widely recognized (2). In particular, the pursuit of energy sources with minimal GGE has gained importance in the search for renewable energy solutions in order to mitigate environmental impacts (1). Among the various options explored by past studies, hydrogen (H_2) fuel cells have shown particular promise in providing a sustainable pathway for development (3-6).

However, the widespread adoption of hydrogen fuel cells faces several challenges. Currently, the predominant method of hydrogen production is through steam methane reforming: a process that relies on natural gas, releases significant amounts of carbon dioxide, and undermines the environmental benefits of hydrogen use (7). Additionally, the catalysts used in fuel cells often contain rare and expensive materials like platinum, thus contributing to the high cost of fuel cell systems (8-9). Therefore, there is a pressing need to explore alternative methods of hydrogen production and fuel cell design that are both cost-effective and environmentally friendly.

Constituting 27.7% of the Earth's crust, silicon (Si) is the second most abundant element on our planet (10). Its natural abundance and prevalence as a waste product in various industries have made it an attractive candidate for renewable energy generation (11). In the semiconductor industry, an estimated 35–40% of silicon is lost as waste during the wafer production process, a procedure that slices pure silicon ingots into thin discs, generating substantial sawing waste (12). Through an etching reaction involving Si and an alkaline solution, which contains a higher concentration of hydroxide ions (OH^-) than hydrogen ions (H^+), silicon waste (SiW) can be selectively dissolved and removed (**Eqn. 1**). The reaction produces a Si compound and H_2 gas, the latter of which can be consumed in an electrochemical cell to generate electricity (13).

$$Si(s) + 2H_2O(l) + 2OH^-(aq) \rightarrow SiO_2(OH)_2^{2-}(aq) + 2H_2(g) \qquad \text{(Eqn. 1)}$$
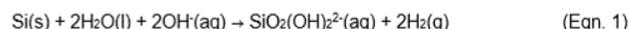
The etching process involves several key stages: the reactant molecules diffusing through the boundary layer to Si's surface; the surface absorbing the reactant molecules; the surface reaction and product desorption; and the by-products diffusing back across the boundary layer into the solution (14).

By using the etching reaction (**Eqn. 1**), it is possible to convert SiW into a source of H_2 production and contribute to the renewable energy cycle of hydrogen fuel cells (15). This conversion holds the potential to offer a cleaner and more efficient alternative to fossil fuels. This study aims to determine the optimal conditions for generating energy through reactions between Si and alkaline solutions by evaluating the effects of temperature, concentration, and alkaline solution type on H_2 production rate. We selected potassium hydroxide (KOH), sodium hydroxide (NaOH), and ammonium hydroxide (NH_4OH) solutions to evaluate the effects of solution on H_2 production rate due to their low costs and prominent roles in industrial production (16).

To better understand the underlying mechanisms that govern the rate of H_2 production, it is crucial to delve into the kinetic behavior of the gas itself. Based on the collision theory, the kinetic energy (K.E.) of a diatomic gas (such as H_2) can be expressed both in terms of mass, m, and the root-mean-square (RMS) speed, v, and in terms of the total number of molecules in the gas, N, the Boltzmann constant, k_B, and the absolute gas temperature, T, as shown in **Eqn. 2** (17-18).

$$K.E. = \frac{3}{2}Nk_BT = \frac{1}{2}mv^2 \qquad \text{(Eqn. 2)}$$

Since a higher temperature leads to a greater RMS speed, we expected that increasing the temperature would increase the particle collision frequency and thus the kinetic reaction rate. Hence, we hypothesized that there would be a positive correlation between H_2 production rate and temperature.

The effects of the concentration of KOH on reaction rate can be predicted using Seidel *et al.*'s proposed mechanism, where the etch rate is proportional to the concentrations of H_2O and KOH to the fourth and one-fourth powers, respectively (19). While there are currently no proposed equations for the reaction mechanisms of NaOH and NH_4OH, it can be reasoned that since one mole of both NaOH and NH_4OH yields four moles of water, their etching rate mechanisms may be generalized as in **Eqn. 3**, given in terms of a reaction rate constant k, an unknown exponent n, and an unknown cation X that can represent $[NH^{4+}]$ or $[Na^+]$. This indicates that H_2 production rate and concentration may be directly correlated.

$$Etch\ rate\ =\ k[H_2O]^4[XOH]^n \qquad \text{(Eqn. 3)}$$

The reaction rate may also be subject to the base dissociation constant, k_b, of the alkaline solution, as it provides information about the extent of each molecule's dissociation into the OH^- ion. Since the k_b value of NH_4OH is 1.8×10^{-5}, and those of KOH and NaOH are greater than 10, which indicate a complete dissociation in H_2O, it can be hypothesized that using the strong bases such as KOH and NaOH will yield a greater H_2 production rate than using a weak base like NH_4OH (20-21). Furthermore, KOH is a stronger base than NaOH due to the weaker bond of K-O than that of Na-O, which suggests KOH may generate H_2 gas at a higher rate than NaOH (17-18).

In summary, we hypothesized that the reaction rate would be positively correlated with temperature, concentration, and the base dissociation constant of the solution. To test these hypotheses, we recorded the time it took for specific volumes of H_2 gas to be produced in three experiments, in order to measure the approximate reaction rate at different temperatures, concentrations, and solution types. Our results suggest that reaction rate is indeed positively correlated with these variables, supporting our initial hypotheses.

RESULTS

We tested the effects of temperature (30°C, 40°C, 50°C, 60°C, and 70°C), concentration (1.0 M, 1.5 M, and 2.0 M), and solution type (KOH, NaOH, and NH_4OH) on the production of hydrogen gas through the reaction of silicon waste with alkaline solutions (**Figure 1**). For every experimental condition, we recorded the time it took to generate a specific volume of hydrogen gas. We then estimated the average reaction rate by deriving the slope of the best-fit line on a volume-time plot.

The Effects of Temperature on Reaction Rate

To explore the impact of temperature on the hydrogen production rate, we compared the reaction rates under varying temperatures (30°C, 40°C, 50°C, 60°C, and 70°C) at which the experiments were conducted. The solution type (KOH, NaOH, and NH_4OH) was used as a blocking variable. The KOH, NaOH, and NH_4OH solutions all exhibited a negative correlation between temperature and reaction time, with r^2 (coefficient of determination) values greater than 0.85 (**Figure 2**). We estimated the average rate of reaction, r, for
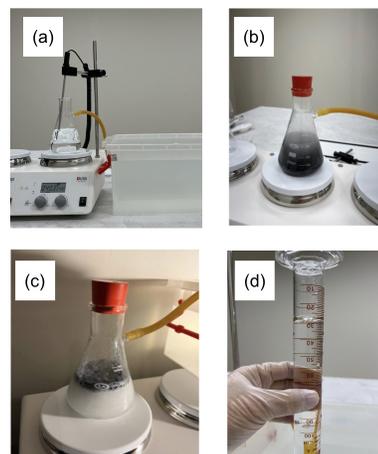

Figure 1. The setup of the experiment. (a) An Erlenmeyer flask on a stirrer with a hot plate, with the flask's opening connected to a plastic tube, leads the produced H_2 gas to a graduated cylinder under water. H_2 gas is collected through water displacement. **(b-c)** Si reacts with the alkaline solution, producing H_2 bubbles. **(d)** The H2 bubbles are observed in the graduated cylinder.

each experimental group by taking the slopes of the best-fit lines on the reaction rate versus H_2 gas volume graph and converting to mol s^{-1}.

Given the Arrhenius equation (**Eqn. 4**), an exponential relationship between k and the reciprocal of T can be reasonably expected (20):

$$k\ =\ Ae^{\frac{-E_a}{RT}} \qquad \text{(Eqn. 4)}$$

where A is a pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. To simplify analyses, Eqn. 4 can be linearized to give **Eqn. 5**:

$$ln(k)\ =\ -\frac{E_a}{R}\left(\frac{1}{T}\right) + ln(A) \qquad \text{(Eqn. 5)}$$

With the assumption that k is proportional to the reaction rate, r, if the concentration remains unchanged throughout the reaction (the reaction has not yet reached saturation), **Eqn. 6** can be derived, in which $C = [H_2O]^4[XOH]^n$ is a constant.

$$ln(r)\ =\ -\frac{E_a}{R}\left(\frac{1}{T}\right) + ln\left(\frac{A}{C}\right) \qquad \text{(Eqn. 6)}$$

By modeling the temperature with this equation and plotting $ln(r)$ against $1/T$, we found that the KOH, NaOH, and NH_4OH best-fit lines consisted of negative slopes, which aligned with the expected model, indicating that reaction rate increases as a function of temperature (**Figure 3**). The negative correlation between reaction temperature and reaction rate was significant for reactions in all three alkaline solutions ($r_2 > 0.98$, $p < 0.002$). The negative correlation supports the collision theory and kinetic energy hypothesis, as when T increases, $1/T$ would decrease, causing $ln(r)$ to increase and thus r to increase.

The Effects of Concentration on Reaction Rate

In order to determine the relationship between the concentration of various alkaline solutions and the rate of hydrogen gas production, we compared the reaction rates
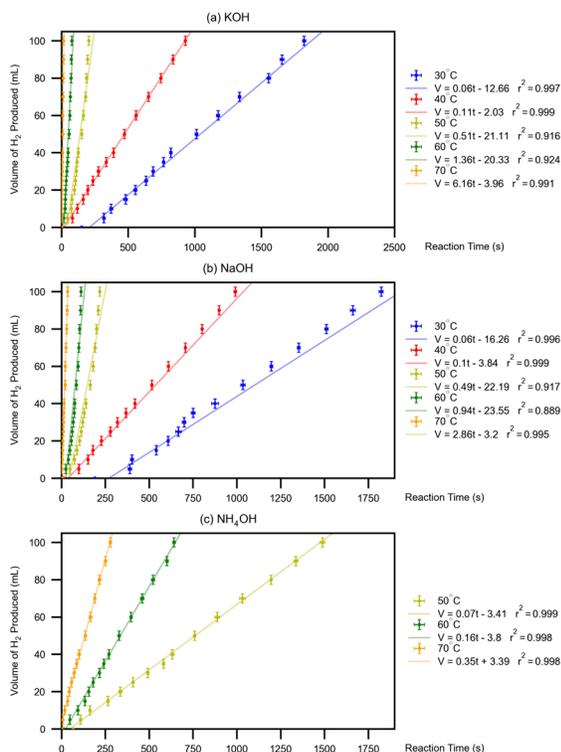
Figure 2. H₂ gas production over time at different temperatures.

Figure 2. H_2 gas production over time at different temperatures. **(a)** KOH**, (b)** NaOH, and **(c)** NH_4OH. Each marker denotes the average measured time across three experimental trials at the given volume. Horizontal error bars reflect the combined uncertainty from a 2-second timing error and the standard deviation across multiple trials. Vertical error bars correspond to a fixed measurement uncertainty of 2.5 mL for gas volume. No data were recorded for NH_4OH at 30°C and 40°C due to no signs of reaction after 5 minutes.

across the 1.0 M, 1.5 M, and 2.0 M solutions for each solution type (KOH, NaOH, and NH_4OH), using the solution type as a blocking variable. We found that reaction rates increase as a function of concentration, regardless of solution type (**Figure 4**). Assuming that the initial conditions (the reaction temperature and the concentration of H_2O) remained unchanged, combining $[H_2O]^4$ into the constant C and then taking the natural logarithm on both sides of **Eqn. 3** yield **Eqn. 7**, the linearized form. In **Eqn. 7**, [XOH] represents the concentration of the alkaline solution, *n*, the unknown exponent previously discussed, and *C*, a $[H_2O]^4$-dependent constant.

$$ln(r) = n \cdot ln([XOH]) + ln(C) \qquad \text{(Eqn. 7)}$$

By adopting this model, we found that the experimental values of *n* for KOH, NaOH, and NH_4OH were 0.35, 0.26, and 1.11, respectively (**Figure 5**). These derived exponent values quantitatively support that the hydrogen production rate is positively correlated with alkaline solutions' concentration.

The Effects of Solution Type on Reaction Rate

We investigated the reaction rates of 1.0 M solutions of KOH, NaOH, and NH_4OH at a controlled temperature of 50°C, whose means were determined to be 9.46×10^{-10} mol s⁻¹, 8.91×10^{-10} mol s⁻¹, and 1.18×10^{-10} mol s⁻¹,
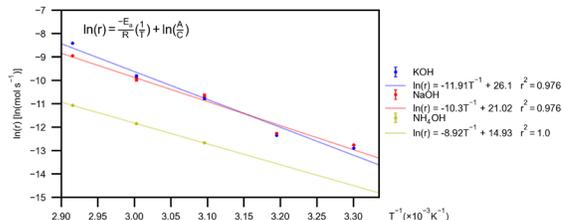

Figure 3. Natural logarithm of reaction rate as a function of the reciprocal of absolute temperature following the linearized Arrhenius equation. Error bars represent the propagated uncertainty from the one standard deviation errors associated with the best-fit slopes in **Figure 1.**

respectively (**Figure 6**). A Kruskal-Wallis test indicated a statistically significant variance among the three groups (p = 0.027), whose mean reaction rate ranks are 8, 5, and 2 for KOH, NaOH, and NH_4OH, respectively (where KOH has the greatest reaction rate and NH_4OH has the smallest reaction rate). Post hoc analysis with Dunn's test showed a significant difference between the KOH and NH_4OH groups (adjusted p = 0.022). On the other hand, we failed to find significant differences between the other solution pairs (KOH vs. NaOH: adjusted p = 0.36; NaOH vs. NH4OH: adjusted p = 0.36). The observed higher reaction rate for the KOH compared to the NH_4OH supports our hypothesis that solutions with higher dissociation constants correlate with faster reaction rates.

DISCUSSION

Our experiments have provided evidence supporting that higher temperatures, concentrations, and base dissociation constants can optimize hydrogen generation methods that utilize silicon waste. Based on our findings, we recommend the usage of 1.0 M KOH solutions at 70°C for optimizing H_2 production, which had the highest hydrogen production rate of 6.16 mL s⁻¹. Furthermore, our results demonstrated a stable trajectory for the cumulated H_2 gas volumes that may be linearly fitted, suggesting that if the reactions are implemented as sources of hydrogen fuel in an energy cell, the energy output would be stable and consistent.

We recognize a few potential sources of error in the experiments. For instance, small amounts of variance in temperature may account for slight deviations in RMS speed and thus H_2 production rate. While the sealing was considered sufficient by visual inspection, it is possible that any inadequacies in sealing could lead to gas leakage, possibly decreasing the total number of gas particles in a fixed volume and affecting the reaction rate. To address these potential sources of error, we suggest that future studies increase the number of trials conducted and the range of independent variables. For example, while our study examined temperatures at 30°C, 40°C, 50°C, 60°C, and 70°C, future experiments could investigate a more extensive temperature range, such as including lower temperatures like 10°C and 20°C, and higher temperatures beyond 70°C. Further, we noted an acceleration in hydrogen gas production towards the end of some trials. A possible explanation is a delayed onset of reaction due to kinetic barriers that were overcome as the reaction progressed. This may have affected certain trials, where at higher hydrogen volumes, the reaction progression is no longer strictly linear (**Figure 4a-b**). Consequently, the
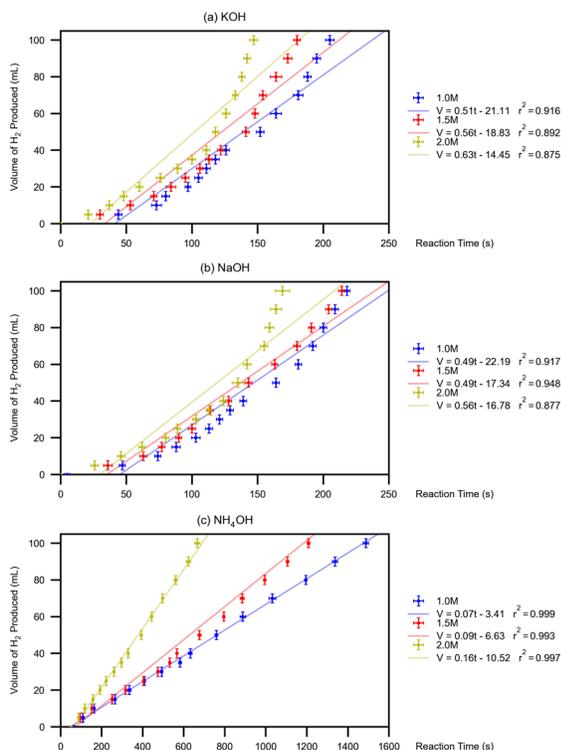
Figure 4. H₂ gas production over time at different concentrations. (a) KOH, **(b)** NaOH, and **(c)** NH₄OH. Each marker denotes the average measured time across three experimental trials at the given volume. Horizontal error bars reflect the combined uncertainty from a 2-second timing error and the standard deviation across multiple trials. Vertical error bars correspond to a fixed measurement uncertainty of ±2.5 mL for gas volume.

behavior may have resulted in lower-than-expected average reaction rates derived from the best-fit lines if we extrapolate over the entire course of the reaction.

In terms of practical application, KOH and NaOH are strong bases commonly used in the production line, which allows companies to easily generate hydrogen gas for renewable energy. Moreover, it was reported that GGE rose 6% each year in the decade 2010-2020, which has contributed significantly to global warming (22). Thus, implementing hydrogen fuel cells powered by the reactions tested in this study can potentially lessen the environmental burden of energy production. However, such ideas should also be implemented with caution due to the high flammability of H₂ gas, which brings some safety concerns (23).

Ultimately, though, hydrogen fuel cell technology holds the potential for significant environmental impact, mitigating the acceleration of climate change by replacing less sustainable forms of energy generation methods like the combustion of fossil fuels (1, 7). The advantage in stability, coupled with the high exergy efficiency of hydrogen cells, makes the production method discussed in this study likely favorable in the future (24). If the safety challenges associated with hydrogen production are addressed, hydrogen production from silicon waste could contribute to a future where energy sources are both sustainable and economically practical.
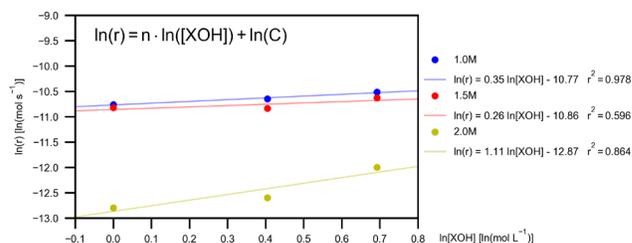

Figure 5. Natural logarithm of reaction rate plotted against the natural logarithm of [XOH]. Linear regression was performed based on the linearized form of the predicted reaction rate mechanism equation, as represented by the plotted lines.

MATERIALS AND METHODS

To test the three hypotheses regarding temperature, concentration, and type of solution, the following methodology was derived for this study. In the first experiment, the reaction was run at five temperatures (30°C, 40°C, 50°C, 60°C, and 70°C), controlled by a hot plate, using 1.0 M NH₄OH, NaOH, and KOH solutions to examine the effects of temperature on H₂ production rate. In the second experiment, concentration was represented by three experimental groups (1.0 M, 1.5 M, and 2.0 M) under the same controlled temperature of 50°C. In the final experiment, we compared the reaction rates across different solutions, specifically examining how each solution behaved at a concentration of 1.0 M and a temperature of 50°C. We derived the reaction rate for each treatment by determining the slope of the volume-time graph's best-fit line. Our experiments used Si powder with an average particle size of 0.125 ± 0.025 μm. In crystallized Si, the (111) plane, a specific arrangement of atoms in the Si crystal lattice, results in a self-limiting step, which slows down the reaction
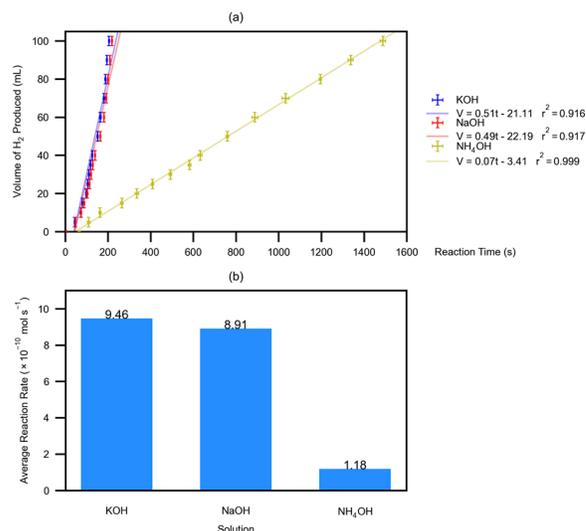

Figure 6. A comparison of H₂ production across the different alkaline solutions used. (a) H₂ gas production over time for each solution. Each marker denotes the average measured time across three experimental trials at the given volume. Horizontal error bars reflect the combined uncertainty from a 2-second timing error and the standard deviation across multiple trials. Vertical error bars correspond to a fixed measurement uncertainty of ±2.5 mL for gas volume. **(b)** Reaction rates (r) for 1.0 M KOH, NaOH, and NH4OH solutions under constant temperature (50°C).

rate (14). To overcome complications, we used Si powder so that the (111) plane was physically destroyed. Using Si powder also increases the substance's surface area, providing a greater chance for particle collisions so that all trials are conducted under the same optimal conditions for an accurate comparison (17). For all the trials in this study, the amount of Si added to the solution was controlled to 10 g, which ensured that the frequency of effective collisions (and thus the reaction time) was not affected by additional factors (17). To measure the volume of H_2 gas produced in each experiment, the water displacement method was employed. This involved submerging the opening of a gas collection tube attached to an Erlenmeyer flask; as H_2 gas was generated, it was directed into the tube, displacing the water within a water-filled container (**Figure 1**). The displaced water level was measured with a graduated cylinder, which provided us with a precise volume of the H_2 gas produced. This technique capitalizes on water's properties of conformity to the shape of the container and incompressibility, ensuring more accurate gas volume readings despite the irregular shapes of gases (18).

In our experimental setup, at least 500 mL of each alkaline solution was poured into a volumetric flask and diluted with water to the appropriate concentration. 200 mL of the desired alkaline solution was added to the Erlenmeyer flask and stirred at 500 rpm on a hot plate. A thermometer was placed in the Erlenmeyer flask to ensure thermal equilibrium before adding 10 g of Si powder. A stopwatch was started when the cap was placed on the Erlenmeyer. As the reaction proceeded (**Figure 1**), the amount of time for each corresponding volume of H_2 gas to be generated in the graduated cylinder was measured by the stopwatch and recorded. The above procedure was repeated for three trials to increase reliability; for each trial, the interior of the Erlenmeyer flasks was rinsed carefully to prevent contamination from previous trials.

To assess the statistical significance of the effect of solution type on reaction rate, we employed the non-parametric Kruskal-Wallis test, in case the obtained data do not follow normal distribution and equal variance. This test compared the reaction rates of three different 1.0 M solutions (KOH, NaOH, and NH_4OH) at 50°C. For each solution, linear regression was applied to volume-time plots, obtained from three experimental trials, to determine the slope. These slopes were treated as three independent observations of the reaction rate for each group. The null hypothesis tested was that the mean reaction rate ranks across the groups were equal, against the alternative hypothesis that at least one group's mean rank was different. The analysis was conducted at a significance level of $\alpha = 0.05$. Upon rejecting the null hypothesis, we carried out Dunn's post hoc test to identify the pairs of groups that differed significantly. P-values from these pairwise comparisons were adjusted using the Holm-Bonferroni method.

ACKNOWLEDGEMENTS

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