**Citrus limetta** Peel-Derived Catalyst for Sustainable Production of Biodiesel

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ABSTRACT: To produce biodiesel from oleic acid (OA), the effectiveness of sweet lemon (*Citrus limetta*) waste peels as an acidic catalyst in an esterification process is examined in the current work. A biowaste-derived sulfonated carbon-based catalyst is fabricated without high temperatures via a simple one-pot process. Several techniques are used to investigate the chemical components and morphology of the catalyst, including Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), and N₂ adsorption–desorption. The biodiesel conversion is observed by gas chromatography–mass spectrometry (GC–MS), proton nuclear magnetic resonance (¹H NMR), and carbon nuclear magnetic resonance (¹³C NMR). The excellent biodiesel conversion of 96% was obtained using optimized conditions, i.e., 1:20 of OA/MeOH, 5 wt % catalyst loading, 70 °C temperature, and 3 h. The catalyst shows 87% conversion in just 1 h, and the maximum conversion was found to be ≈96%. This high activity of the catalyst can be attributed to the presence of sulfonic groups and its porous nature. The formed catalyst shows excellent catalytic activity up to three cycles.

1. INTRODUCTION

The rise of the industrial revolution and a fast-growing population has resulted in a massive spike in fossil fuel consumption, resulting in abnormal depletion of fossil resources and climate change.¹,² Considerable increases in the use of fossil energy have put the world at risk of fossil fuel depletion, prompting a shift to alternative, sustainable, efficient, renewable, and cost-effective sources.³ A great deal of work has been done in the previous two decades to produce sustainable and renewable energy sources, including wind energy,⁴ tidal energy,⁵ solar energy,⁶ and biofuels.⁷ Since biofuels (such as diesel and ethanol) burn cleanly and are a viable alternative to fossil fuels, they have attracted the attention of a growing number of academicians.

The biochemical interaction of oily raw resources (edible, nonedible, or waste microalgal lipids, animal fats, and waste vegetable oils) with suitable alcohol yields biodiesel. Biodiesel, also known as fatty acid methyl ester (FAME), has superior performance and is renewable and nontoxic as compared to other petrodiesel fuels.⁸ For large-scale biodiesel production, homogeneous catalysts are widely accepted. The homogeneous catalysts such as potassium hydroxide and sodium hydroxide provide great advantages, including modest operating conditions,⁹ shorter reaction times,¹⁰ high catalytic activities,¹¹ and cheap feedstock materials.¹² However, homogeneous materials are very sensitive due to water and free fatty acid (FFA).¹³ Furthermore, the accumulation of soaps as a consequence of saponification and neutralization of side reactions would impede the purification and separation process, create a significant amount of wastewater, and impose extra operational costs. Along with this, homogeneous catalysts have caused equipment corrosion, emulsion formation, higher reactant consumption, and an increased alcohol–oil molar ratio.¹⁴ Because of this necessity, the homogeneous catalyst is harmful to the environment.¹⁰,¹² However, heterogeneous catalysts have garnered more interest due to their reusability, no soap formation, ease of handling, easy recovery, lower corrosiveness, and little waste from the reaction.¹⁵–¹⁷ Several basic and acidic catalysts, including hydrotalcite, mixed oxides, metal oxides, ion exchange resin, transition-metal oxides, zeolites, and carbon-based, are available for biodiesel synthesis. In the heteroge-
neous catalyst, the presence of a three-phase system causes the diffusion issue, which inhibits the reaction.\textsuperscript{9} The mass transfer efficiency is limited by three highly immiscible phases of solid catalyst—alcohol—oil, decreasing the reaction rate.\textsuperscript{18} Moreover, additional problems include leaching, high cost, toxicity, fewer active sites, microporosity, and environmental unfriendliness.\textsuperscript{19,20} As a result, to prepare an effective solid acid catalyst, the catalyst must have a wide pore diameter and greater specific surface area (exterior catalytic sites, hydrophobicity, etc.).\textsuperscript{13} and from this perspective, heterogeneous catalysts generated from biomass materials have the potential to overcome these drawbacks.\textsuperscript{21,22} Since from biomass, we can develop a very effective biobased solid catalyst. Biomass-based solid catalysts provide an environmentally favorable alternative since they are noncorrosive, nontoxic, and do not generate effluent. Heterogeneous catalysts are derived from biomass, which is an inexpensive and plentiful resource. Additionally, the catalyst’s biodegradability means that it will not provide an immediate challenge for disposal. Using biomass waste, biodiesel production is done effectively, including the biomass of banana,\textsuperscript{23} orange,\textsuperscript{24} sugarcane,\textsuperscript{25} areca nut husk,\textsuperscript{26} plantain peels,\textsuperscript{27} wood,\textsuperscript{27} and coconut husk.\textsuperscript{28}

\textit{Citrus limetta} or sweet lemon is a variety of the citrus family. India is among the top three countries in the production of sweet lemon. \textit{C. limetta} is widely used for fruit juice, and so a large number of peels are generated as waste. Peels as waste, particularly seasonal and perishable, is a concern to the pollution monitoring authorities and processing industry. The pursuit of repurposing waste materials to create useful goods is an ever-increasing focus. Various applications of \textit{C. limetta} peel, such as sensing, biomedical, and photoelectrocatalytic, are revealed.\textsuperscript{29} However, catalytic applications of \textit{C. limetta} for biodiesel production have not been tested yet, despite the fact that its chemical composition implies its potential use as a catalyst.

In this paper, sulfonated \textit{C. limetta} peel biomass (SCLPB) as the catalyst is manufactured successfully using a one-step sulfonation process. The primary criteria are to use lower temperatures (60–100 °C) than those reported in the previous literature. \textit{C. limetta} peel biomass was sulfonated with concentrated sulfuric acid to generate a solid acid catalyst, which was then tested for its possible use in the synthesis of biodiesel from OA. The introduction of SO\textsubscript{3}H by an easy process significantly enhanced the esterification reaction. To test the potential of the novel SCLPB catalyst, we apply the esterification process to produce FAME. The conversion of biomass into a catalyst is a simple, nontoxic, and cheap process. The formed catalyst is characterized by various techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy—energy-dispersive X-ray spectroscopy (SEM–EDS), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller ( BET). And biodiesel is characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and gas chromatography—mass spectrometry (GC–MS). The application of \textit{C. limetta} peel biomass as a catalyst has not been reported for biodiesel production, but it might provide another dimension to the exploration of ecologically friendly feedstock for catalysts for converting OA to biodiesel.

2. MATERIALS AND METHODS

2.1. Materials. \textit{C. limetta} was obtained from the local market of Silchar, India. OA having a purity of ≥99% was acquired from Sigma-Aldrich. BaCl\textsubscript{2} (99%), MeOH (99%), and H\textsubscript{2}SO\textsubscript{4} (98%) were purchased from Merck. Deionized water was taken from a UV water purification system (Merck). No additional purification was performed on any of the compounds before they were employed.

2.2. Catalyst Preparation. The ripe \textit{C. limetta} was peeled manually and cut into pieces. The peels that were obtained were washed 3–4 times with distilled water to remove impurities and dried in an oven at 100 °C. The dried peels were crushed and sieved. The obtained peel powder was dissolved in concentrated H\textsubscript{2}SO\textsubscript{4} in a ratio of 1:10 in a borosilicate bottle and kept in an oven at 80 °C for 24 h. After cooling to ambient temperature, the solution was diluted with 40–50 mL of deionized water and washed with deionized water until no residual sulfate particles were found in the filtration. The material was kept in an oven at 70 °C overnight to dry.

2.3. Process of FAME Production. An ACE pressure tube was filled with a homogeneous mixture of methanol/OA (5:1–20:1 M ratio) and a heterogeneous catalyst (3–9 wt % of OA) and heated up to 50–80 °C in an oil bath for 60–180 min with the help of a digital magnetic stirrer at a speed of 300 rpm. The progress of the reaction was measured by thin-layer chromatography. Excess MeOH was removed from the solution using a rotary vacuum evaporator to obtain the product. Following the conclusion of the process, the catalyst was filtered out of the mixture. NMR and GC–MS were used to examine the separated products. To conduct catalyst regeneration studies, the used catalyst that had been extracted by filtering was rinsed with MeOH (5 × 20 mL) and dried for 5 h at 80 °C in a vacuum. Prior to reusing the dried catalyst, it was weighed again. There was no evidence of a substantial decrease in mass in any of the cases. The experiments were all conducted three times.

2.4. Catalyst Characterization. Various techniques are used to characterize the as-synthesized catalyst for elemental and chemical composition. The KBr pellets were used with a Bruker 3000 Hyperion Microscope with Vertex 80 for FTIR instrumentation. Powder XRD was carried out using the Phillips X’pert Pro MPD (multipurpose diffractometer) with Cu Kα radiation (2Θ = 10–90) at a scan speed of 2°/min. SEM–EDS was performed on a JEOI6390LA/OXFORD XMX N with a tungsten filament and an accelerating voltage ranging from 0.5 to 30 eV. SEM has a resolution of 300000, whereas EDS has 136 eV and a detector area of 30 mm\textsuperscript{2}. HRTEM was carried out using Jeol/JEM 2100 with a voltage of 200 kV and LaB6 as an electron gun. XPS with Auger electron spectroscopy was performed on the PHI 5000 Versa Prob II FEI Inc. with Ar ion and a C60 sputter gun. TGA simultaneously with differential thermal analysis (DTA) was carried out using a TGA–DTA PerkinElmer STA6000, PerkinElmer Diamond, at a temperature range of −150 to 600 °C. The material was degassed at 80 °C for 6 h before BET measurement on a QuantaChrome Nova 2200e Surface Area & Pore Size Analyzer.

2.5. Biodiesel Characterization. NMR spectroscopy was used to verify and identify the purity of the esterification product. \textsuperscript{1}H and \textsuperscript{13}C NMR were performed on a Bruker Avance III series equipped with a frequency of 500 MHz and
Figure 1. (a) XRD and (b) FTIR pattern of the SCLPB catalyst.

Figure 2. SEM–EDS images of the SCLPB catalyst at different magnifications: (a) 10 μm, (b) 5 μm, (c) 2 μm, and (d) 1 μm. (e) Spectrum showing carbon, oxygen, and sulfur.
tetramethylsilane (TMS) as a reference standard to investigate the chemical structure and synthesis of FAME. The chemical composition of FAME was investigated by GC−MS. GC was performed on an Agilent model 8890 with polar columns (DB-WAX & HP-5 MS), UI Agilent column (30 m × 250 μm × 0.25 μm), and split/splitless injectors. The initial temperature of the oven was 50 °C, and it was increased at the rate of 5 °C/min until 350 °C. The MS component of the GC−MS experiment was carried out using an Agilent 5977 MSD apparatus with a mass range of 1.6−1050 amu.

3. RESULTS AND DISCUSSION

3.1. Effect of Sulfonation. The introduction of sulfonic acid into biomass was affected by temperature in terms of activity and stability. The constrained sulfonation resulted in a low connection of sulfonic acid groups, forming unstable and
easily decomposed compounds. High temperatures may result in undesirable multisulfonated groups and reduce the catalytic activity. Lower S-content was obtained by increasing the sulfonation temperature to 100 °C and subsequently to 120 °C. This was ascribed to cracking of the carbon network, which reduced the amount of surface sites for sulfonation, as well as high-temperature acid group dehydration.

3.2. Catalyst Characterization. The XRD pattern of the synthesized SCLPB catalyst is shown in Figure 1a. The catalyst shows a broad peak at a 2θ of 16−26°, which indicates the amorphous character of the catalyst in which carbon is oriented randomly. Catalysts have randomly oriented aromatic carbon sheets, which are responsible for the large diffraction peak at 2θ from 16 to 26°. FTIR spectroscopy is done to determine the presence of functional groups. The FTIR study (Figure 1b) revealed a peak at 1024 cm⁻¹, which corresponded to the symmetric stretching mode of SO₃H. It was analyzed from the spectra that the 1600 and 1700 cm⁻¹ peaks were attributed to the C=C and carbonyl stretching in the aromatic rings. A series of peaks between 2921 and 3245 cm⁻¹ belongs to the group of aldehydes and sp³ C−H atoms. Peaks in the range of 3486−3754 cm⁻¹ correspond to O−H stretching modes.

Scanning electron micrographs showed an uneven, porous surface that is constituted of particles of irregular size and discrete pores on the surface of the catalyst (Figure 2a−d). EDS mapping revealed the sample’s compositional homogeneity, revealing abundant C, O, and S. EDS data show the presence of carbon (61.28%), oxygen (35.74%), and sulfur (2.98 wt %) (Figure 2c). It was sulfur that served as the catalysts’ principal active ingredient in the form of sulfonic acid groups, which contributed to their performance and activity. At a higher resolution, TEM results of the SCLPB catalyst indicate that the structure incompletely formed carbonaceous sheetlike frameworks (Figure 3).

TGA and DTA were used to determine the thermal response of SCLPB catalysts in the range of 28−750 °C to determine the stability (Figure 4). Primarily, from 30 to 100 °C, the mass loss is due to adsorbed water. However, since −SO₃H is hydrophilic and promotes water adsorption, the mass loss of SCLPB occurs at a high temperature. A major percentage of the weight reduction was attributable to the breakdown of lignin, hemicelluloses, and celluloses at 150−750, 210−315, and 310−400 °C, respectively. A temperature range of 400−750 °C was reported by Luque et al. as the decomposition temperature range for the majority of carbon species. The XPS survey spectrum confirms the presence of carbon, oxygen, and sulfur (Figure 5a−d). The C−O−C and COOH peaks at 286 and 288 eV (Figure 5a) were clearly seen throughout the time-domain spectra of the C 1s area. Concurrently, the C−O and C≡O maxima in the O 1s area were 533 and 534 eV, respectively (Figure 5b). At ≈170 eV (Figure 5c), the S 2p area showed only one prominent signature that could be linked back to sulfur in SO₃H’s high-oxidation state, which is also closely associated with FTIR data.

BET analysis was used to analyze the surface area and pore volume of the SCLPB catalyst. For N₂ adsorption data, the
Figure 6. (a) Barrett–Joyner–Halenda (BJH) pore size distribution. (b) N$_2$ adsorption–desorption isotherm curve of the SCLPB catalyst.

Figure 7. GC–MS data of biodiesel obtained through OA esterification.

Figure 8. $^1$H NMR data of the synthesized FAME.
pore size distribution (PSD) and surface area were computed (Figure 6a,b). According to the BET study, the surface area of the catalyst was 32.310 m²/g. As seen in Figure 6b, N₂ adsorption–desorption follows a type IV isotherm and has a broad hysteresis loop, showing the catalyst is mesoporous. The estimated pore diameter was determined to be 2.217 nm. Oleic acid readily diffuses into and out of the catalyst’s core via these mesopores, enhancing catalytic activity. The textural quality of the porous structure, as assessed by the N₂ adsorption isotherm, confirmed its presence.

3.3. Biodiesel Characterization. To see whether our approach can provide good FFA esterification catalysts, we used the SCLPB catalyst to test the production of methyl oleate from OA. The formed biodiesel product has 24 components as analyzed by GC−MS (Figure 7), with the primary elements being methyl esters of 9,12-octadecadienoic acid (Z,Z) (4.07%), methyl stearate (5.00%), 2-decanoic acid (6.60%), hexadecanoic acid (8.49%), 9-octadecenoic acid (62.22%), octanoic acid, methyl ester (0.12%), decanoic acid, methyl ester (0.40%), nonanoic acid, 9-oxo-, methyl ester (0.21%), nonadecanoic acid, dimethyl ester (0.32%), decanedioc acid, dimethyl ester (0.20%), methyl tetradecanoate (2.85%), heptadecanoic acid, methyl ester (0.16%), 8,11-octadecadienoic acid, methyl ester (0.19%), 6,9,12-octadecatrienoic acid, methyl ester (0.11%), methyl 9,12-epithio-9,11-octadecanoate (1.75%), eicosanoic acid, methyl ester (0.83%), 10-methyl-8-tetradecc-1-ol acetate (0.45%), ethyl stearate, 9,12-diepoxy (0.30%), linoleic acid ethyl ester (0.38%), octadecanoic acid, 9,10-dihydroxy-, methyl ester (0.32%), docosanoic acid, methyl ester (0.47%), octadecanoic acid, 9,10-dibromo-, methyl ester (0.11%), and tetracosanoic acid, methyl ester (0.24%). On the other hand, the percentage conversion of FAME was calculated using eq 1.

\[
\text{biodiesel yield} = \frac{\text{weight of FAME}}{\text{weight of OA}} \times 100
\]

The presence of a signal at 3.67 ppm in the ¹H NMR spectra (Figure 8), ascribed to methoxy protons, demonstrates the successful synthesis of FAME. Further, FAME was investigated using ¹³C NMR to validate its formation (Figure 9). The emergence of a signal at 51.388 ppm (referred to as OCH₃) confirms FAME synthesis and hence validates the ¹H NMR results. The precise numerical spectroscopic statistics for 9-octadecenoic acid methyl ester is as follows: ¹³C NMR (125 MHz, CDCl₃, 25 °C): 174.2, 130.2, 129.8, 51.38, 34.09, 31.91, 29.75–29.07, 27.21, 27.15, 25.0, 14.1; ¹H NMR (500 MHz CDCl₃, 25 °C): 5.345 (m, 13H), 3.665 (s, 1H), 2.302 (t, 3H), 2.028 (m, 7H), 1.619 (m, 5H), 1.302 (m, 6H), 0.881 (q, 3H). From ¹H NMR data, the percentage yield was calculated using eq 2.

\[
\text{conversion (\%)} = 100 \times \frac{2A_{\text{ME}}}{3A_{\text{CH}_2}}
\]

Here, \(A_{\text{CH}}\) and \(A_{\text{ME}}\) are the integration value of methylene protons and methoxy protons.

3.4. Catalyst Activity. The esterification reaction is endothermic and reversible, and so high temperatures and excess methanol are required to carry out the reaction in the forward direction and boost the reaction rate. All experiments were conducted at a 20:1 molar ratio of methanol/OA and a temperature of 70 °C (Figure 10a–d). Moreover, a moderate stirring of 300 rpm and a moderate catalyst dosage of 5 wt %
was used. The excellent catalytic activity of the SCLPB catalyst is attributed to its high hydrophilicity, high concentration of the SO$_3$H group, and large surface area.

3.5. Influence of Reaction Parameters on the Formation of Biodiesel. 3.5.1. Effect of Catalyst Loading. The influence of reaction parameters was tuned for the SCLPB catalyst for esterification. Esterification of OA was observed for four varied amounts of catalyst in the range of 3–9 wt % using the methanol/OA ratio of 20:1, temperature of 80 °C, and reaction time of 3 h. Figure 10a shows that on increasing the catalytic dosage, the percentage amount of biodiesel increased due to the increase in active sites present on the catalyst surface. The catalyst shows 93% conversion when the dosage is increased from 3 to 5 wt %. Biodiesel conversion and yield were reduced as a result of increasing the quantity of the SCLPB catalyst. However, increasing the catalyst quantity further resulted in a decrease in biodiesel output and conversion. This can be attributed to the fact that as the reaction mixture approaches the optimal catalyst level, it gets more viscous, disrupting the dispersion of reactants into the acid–catalyst–methanol system. As a result, the optimal catalyst concentration is 5 wt %.

3.5.2. Effect of the Methanol/OA Ratio. The esterification reaction is reversible, and so the reaction rate of the process may be accelerated by the employment of excess methanol. The effect of a molar ratio of 5:1 to 20:1 of methanol to OA on biodiesel synthesis under experimental parameters including 5 wt % catalysts for 3 h, and 20:1 methanol/OA molar ratio is increased from 5:1 to 20:1. The lower yield in the 5:1 methanol/OA molar ratio was due to the decrease in the amount of mass transfer barrier between the catalyst and reactants. Esterification in the forward direction is encouraged by the high methanol ratio, as shown in Figure 10b. Consequently, the ideal ratio of 20:1 is achieved.

3.5.3. Effect of Temperature. The three-species/phase system (catalyst, OA, and methanol) involved in the esterification process makes the diffusion of reactants from one phase to another very challenging. The temperature may be used to reduce the diffusion resistance in the reaction system. Experiments were conducted to determine the effect of reaction temperature on OA esterification in the range of 50–80 °C, 5 wt % catalysts for 3 h, and 20:1 methanol/OA molar ratio. Because the esterification process is endothermic, increasing the temperature makes it easier for the reaction to achieve a maximum conversion of 96%. This was achieved by increasing the reaction temperature from 50 to 70 °C. The miscibility of the three species/phases system is further increased by high temperatures, which cause a violent collision between the systems. However, when methanol vaporizes at high temperatures, the yield drops as the temperature increases, i.e., over 70 °C, because the mixture has less methanol available. Therefore, the ideal temperature for the reaction is 70 °C (Figure 10c).

3.5.4. Effect of Time. The reaction period was adjusted from 60 to 180 min at 70 °C (MeOH/OA = 20:1, 5% catalyst loading). In just 1 h, the reactions achieved 87% biodiesel production (Figure 10d). After which, the reaction proceeded...
slowly, which may be due to a reduction in the number of active sites with increasing time. At 180 min, the maximum yield of 96% was achieved, after which conversion stagnated (Table 1).

Table 1. Comparison of the Formed Catalyst with Reported Catalysts

| s. no. | catalyst | conditions and dosage | conversion (%) | time (h) | references |
|--------|----------|-----------------------|----------------|---------|------------|
| 1      | 12-tungstosilic acid-Hβ | 1:20, dose-100 mg | 86 | 10 | 46 |
| 2      | aminophosphonic acid resin D418 | 1:14, dose-10 wt % | 92 | 10 | 47 |
| 3      | Fe₃O₄@ZIF-8/TiO₂ | 1:30, dose-6 wt % | 93 | 1.25 | 48 |
| 4      | E-260-20-SO₃H | 1:15, dose-5 wt % | 95.5 | 5 | 49 |
| 5      | HZSM-5 | 1:45, dose-10 wt % | 83 | 4 | 50 |
| 6      | [HMIM]HSO₄ | 1:15, dose-14 wt % | 95 | 8 | 51 |
| 7      | biochar | 1:30, dose-5 wt % | 48 | 3 | 52 |
| 8      | SCLPB | 1:20, dose-5 wt % | 96 | 3 | present study |

Figure 11. (a) XRD spectra and (b) FTIR spectra of the reused catalyst.

Figure 12. EDS spectrum of the reused SCLPB catalyst.
3.6. Reusability of the Catalyst. The catalyst reusability plays a crucial role in the utilization of catalysts on a large scale. The catalyst recycling was done by filtration, followed by washing with methanol, and kept in an oven at 70 °C for 4 h. The reusability of the catalyst was determined using optimized conditions (20:1, 5 wt %, 70 °C, 180 min). The catalyst showed efficient biodiesel production of 96, 92, and 82% for three cycles, respectively. In the fourth cycle, the conversion of biodiesel decreased to 59%. The reused catalyst was characterized again with XRD, FTIR, and EDS. The XRD pattern of reused catalyst shows decreases in the intensity, as shown in Figure 11a, and also the FTIR spectra of reused catalyst clearly indicate the shift in the position of SO\textsubscript{4}H active species, that is, 1026–1096 cm\textsuperscript{-1} (Figure 11b). The sulfur content of the reused catalyst was confirmed by EDS data (Figure 12), which indicates that there are decreases in the sulfur content during the process of esterification.

4. CONCLUSIONS
In our study, SCLPB was successfully synthesized by a simple one-pot process. The presence of the SO\textsubscript{4}H group in the SCLPB catalyst shows high stability and enhancement of biodiesel production. The synthesized SCLPB catalyst offers excellent FAME conversion with the help of oleic acid. The sulfonic group presence shows high acid density, which results in a high esterification yield. The biobased catalyst offers reusability for up to three cycles. Additionally, the utilization of biowaste resources as a catalyst reinforces the possible regeneration of biological waste resources while also lowering the overall expense and adverse ecological effects of industrial-scale biodiesel synthesis.

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Notes
The authors declare no competing financial interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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