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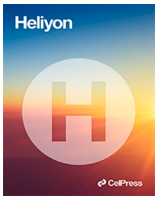

Research article

A cleaner and eco-friendly approach to simultaneous extraction and characterization of essential oil and pectin from Assam lemon peel and its application for energy generation through TENG devices

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ABSTRACT

Scientists have been working on developing a green bio-TENG for portable remote devices, including wearables in the biomedical sector. The process involves obtaining pectin, a green material with anti-microbial properties, as a Triboelectric material. This study focuses on the extraction of essential oil (EO) and pectin from Assam lemon peel simultaneously. A single-step strategy was optimized using a central composite design-based response surface approach. The extracted pectin yielded 4.19 ± 0.31 % and 11.53 ± 0.11 %, respectively. GC-MS analysis revealed 52 volatile components in the Assam lemon EOs, with limonin being 94.47 % and β-Bisabolene being 1.26 %. Only khusilal was found in the EOs, a rare discovery in the scientific domain. The extracted pectin showed good purity and antimicrobial properties. The *in vitro* activities of the citrus EO against microbial cultures revealed its activity in controlling and eradicating bacterial and fungal growth. Hydro distillation followed by enzyme treatment is a promising approach that combines two separate extraction procedures. The produced biopolymer showed the generation of electrical signals under minimal pressure and stretching and prevented microbial degeneration when applied to a nanogenerator.

1. Introduction

The northeastern region of India stands as a hub for various citrus varieties, among which the Assam lemon (*Citrus limon* L. Burm. f.) is a less-explored yet promising variant with multifaceted applications. Assam lemons, cultivated in the Kamrup district of Assam,

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exhibit a remarkable productivity of 70 t per hectare across 13,000 ha of cultivated land, and their processing generates waste that holds potential for valorization into diverse byproducts, aligning seamLessly with the concept of a circular economy [1]. Conversely, Mosambi, scientifically identified as *Citrus limetta*, plays a significant role in Indian citrus cultivation, especially thriving in tropical and subtropical climates. The harvest season, spanning from late October to early March, witnesses the ripening of these fruits, boasting glossy yellow-green skin and lusciously sweet flesh. Renowned for its rich vitamin C content and antioxidants, Mosambi is highly valued for promoting immune health, aiding digestion, and nurturing skin wellness. Its versatile nature allows for consumption as fresh fruit or extraction of its invigorating juice, epitomizing its widespread popularity in Indian cuisine and dietary preferences.

Citrus peels are recognized as repositories of valuable compounds, notably EO and pectin, the latter providing structural integrity and natural defense mechanisms. EO comprises a myriad of volatile substances, encompassing oxygenated by-products such as aldehydes (citral), alcohols, esters, and various terpenes. These active complexes contribute to the aroma of EOs and find diverse applications in personal care products, serving as natural antimicrobials, in food additives and flavoring, and within the pharmaceutical industry [2,3]. Multiple extraction methods are employed for EO extraction, including steam stripping, distillation, cold-pressing, supercritical-fluid, subcritical water, instantaneous controlled pressure drop, and microwave irradiation, each catering to specific needs [4]. However, some extraction methods like cold pressing or solvent extraction cannot be employed in pharmaceuticals or cosmetics due to phototoxic furocoumarins. Additionally, organic solvent extraction may not effectively extract monoterpenes and sesquiterpene compounds [5]. Hydro distillation, a process separating volatile aromatic compounds and water into an azeotropic mixture, allows for their subsequent separation in a Florentine flask after condensation due to the variance in density and immiscibility of oil and water [6]. The literature available in the scientific domain majorly focuses on wider pharmacological activities of citrus fruit extract and its constituents among them EOs possess a wide spectrum of biological activities like antimicrobial, antioxidant, anticancer, anti-inflammatory, embryo-fetotoxicity, and insecticidal properties because of the occurrence of compounds such as monocyclic monoterpene D-limonene, geraniol, terpene alcohol among others [7,8] On the other hand, Pectin is a natural, biocompatible, biodegradable, and hetero-polysaccharide constructed on α-(1,4)-linked D-galacturonic acid that is disturbed by L-rhamnose residues with sidechains accommodating D-galactose and L-arabinose [9] Pectin serves various essential functions as an emulsifier, gelling agent, glazing agent, stabilizer, and thickener and thus has a huge demand in food, pharmaceutical, and cosmetic industries. Marketable production of pectin relies on sources such as citrus peel and apple pomace constituting of white to light brown powdery compound. There are several established methods for the commercial production of pectin which comprise enzyme utilization, microwave, high pressure, subcritical water, ultrasound, and electromagnetic induction heating [10]. Considering several disadvantages of chemical pectin extraction, citrus peel is subjected to enzymatic extraction of pectin which is getting more impetus due to high pectin yield and mild process conditions (Sanadarani, 2017). Enzymatic extraction of pectin offers numerous advantages over traditional methods, making it a promising technique in the food industry. Firstly, it allows for higher yield and purity of pectin extraction compared to conventional methods. As highlighted in Teng and Chen [11], enzymatic hydrolysis facilitates the breakdown of cell walls, releasing more pectin from plant materials. This results in increased extraction efficiency and higher pectin yields. Moreover, enzymatic extraction offers selectivity, enabling the extraction of pectin with specific properties tailored to desired applications. For instance, enzymes can target specific linkages within the pectin structure, as discussed by Zheng et al. [12] leading to the extraction of pectin with desired functionalities such as gelling or thickening properties. Additionally, enzymatic extraction is environmentally friendly and energy-efficient, as it operates under mild conditions without the need for harsh chemicals or high temperatures, as noted in Teng et al. [13]. These advantages not only enhance the quality and functionality of extracted pectin but also contribute to sustainability in food processing. Therefore, enzymatic extraction holds great potential for improving pectin extraction processes in the food industry, paving the way for innovative applications in various food products.

The growing reliance on synthetic polymers has led to environmental worry because of their toxic compounds and toxic byproducts. Therefore, environment-friendly biopolymers are crucial for our daily life applications. In the last few years, interest in naturally available polymers or biopolymers has been increasing rapidly and replacing synthetic polymers in energy-efficient applications in the energy sector [14]. However, their exciting physical, chemical, and electrical properties have promoted their use as an alternative for several applications in the micro energy generation sectors for sensor development via triboelectric nanogenerator creation [15].

Conventionally, pectin and EOs extraction from the citrus peel consists of two separate procedures time bound with high manufacturing costs. Thus, it is necessary to establish a single procedure for a concurrent extraction of EOs and pectin from citrus waste. This study aims to create a predictive model for the concurrent separation of EOs and pectin from Assam lemon peel by integrating the two stages into one and making it more viable for industrial applications. To achieve this a response surface methodology (RSM) and designed experiments (DOE) based on a central composite design (CCD) were employed for the simultaneous extraction of EOs and pectin from peel where different physico-chemical process parameters were considered. Further biochemical characterization of EOs and pectin has been carried out. In addition, energy generation has been studied under different pressing and stretching conditions. Therefore, low-cost and non-toxic pectin can be a likely candidate for future energy applications in the biomedical sectors via triboelectric nanogenerators for powering small yet portable sensor-based devices that resist microbial degradation. Triboelectric generators (TEGs) are devices that generate electricity from the triboelectric effect, which is the result of two dissimilar materials being rubbed together and separated, causing a transfer of electrons between them. TEGs possess a range of favorable attributes, including simplicity, adaptability, and affordability, making them an attractive option for powering low-energy devices. Notably, recent times have seen an escalating interest in the utilization of sustainable biological materials for the development of TEGs, as they offer several advantages over traditional materials. For example, cellulose-based materials, such as paper and wood, exhibit substantial triboelectric charging capabilities and seamless integration potential into TEG systems. Similarly, silk and spider silk have also been investigated for their high strength, flexibility, and biocompatibility. Furthermore, various other sustainable

biological materials, including chitin, lignin, and keratin, have undergone exploration for their potential utility in TEG technology. Overall, the collective use of sustainable biological materials in TEGs offers a promising avenue for the development of environment friendly and economically viable energy harvesting devices [15].

2. Materials and methods

2.1. Substrate

Assam lemon, sourced from Assam, India (coordinates: 25°45′24″N 93°50′26″E), was chosen as the substrate for the extraction of EOs and pectin. Following the peeling of lemon and juice extraction, the peels were subjected to oven drying at 60 ± 2 °C and subsequently employed as the substrate.

2.2. Enzyme production and assay

Mosambi (*Citrus limetta*) peel was used as the substrate which was obtained from the nearby market at IIT Kharagpur. A predetermined amount of Mosambi peel was placed into an Erlenmeyer flask with basal salt media. Subsequently, the flasks were autoclaved at 121 °C for 15 min. After cooling, they were inoculated with 10 % (w/v) of *Aspergillus awamori* Nakazawa MTCC 6652 spore suspension. Fermentation was carried out for 3 days at 30 °C. The entire content was filtered using a cheesecloth and the resulting extracts were centrifuged for 15 min at 10,000 rpm. The supernatant obtained was collected as crude enzyme for further analysis [16]. Polygalacturonase activity was analyzed using the protocol as described by Miller [17].

2.3. Experimental procedure

To separate EO and pectin from Assam lemon peel, the peel was placed into an Erlenmeyer flask containing an enzyme of pH 4.5 and mixed properly. This amalgamation was then subjected to incubation at room temperature for varying time intervals. Following this, the mixture underwent a distillation process, commencing from the initial drop of distillate and continuing until the essential oil quantity reached a steady state. The extracted EOs were conserved at 4 °C for subsequent investigation. After the cooling period, the mixture underwent filtration, and the resultant filtrate was combined with twice its volume of ethanol. This composite was then placed in a refrigerated environment overnight to encourage the precipitation of pectin. The obtained pectin was gathered by passing the solution through cheesecloth and subsequently drying it in a well-ventilated oven at 40 °C [6,18]. A detailed experimental procedure has been depicted in Fig. 1.

2.4. Process optimization

After the investigation of single variables affecting the extraction of EOs and pectin, the optimization of process parameters became essential to enhance the yields of both EOs and pectin. Response surface methodology (RSM), which integrates statistical and mathematical techniques, was employed to anticipate, analyze, assess, and fine-tune responses based on the results of the designed experiments (DOE) [19–21] For the DOE, a two-level four-factor central composite design (CCD) was implemented. The total number

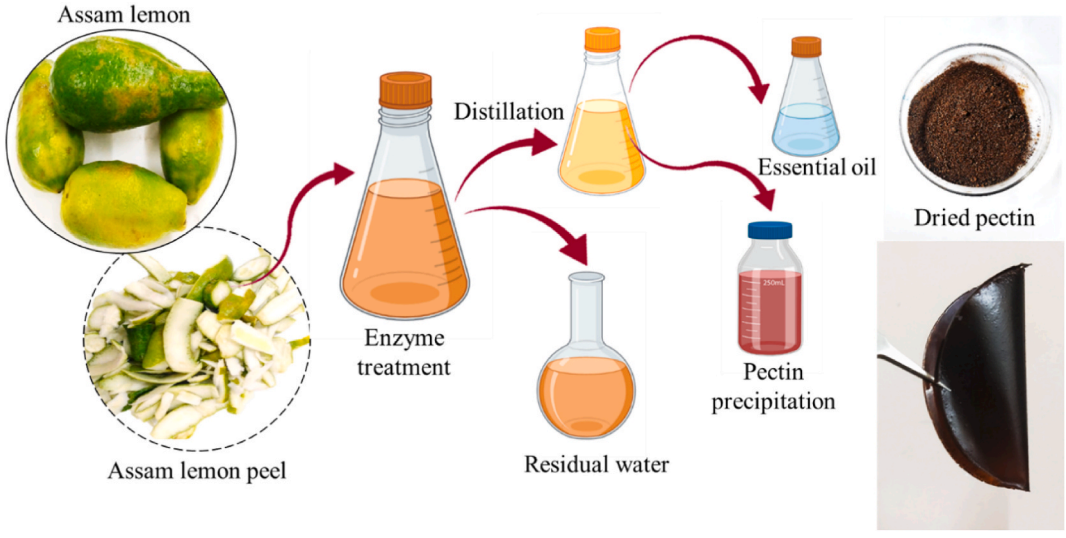

Fig. 1. Schematic representation of experimentation to construct pectin with EO film for use in TENG.

of experimental runs was calculated using the formula of 2^k+2k+7, where k represents the number of independent variables, this included 16 factorial points of 24 full factorial CCD along with 1 center point and 6 replicas of the center point in cubes. An empirical second-order polynomial quadratic model was employed for fitting the statistics in the following way (Eq. (1)).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j}^{k} \beta_{ij} x_i x_j + e \quad (1)$$

In equation (Eq. 1), Y is the response vector (debittering %), x_0, x_i, x_{ij} are coefficients for the linear, intercept, and interactions among all the factors. The response include the linear terms $x_1, x_2, \ldots, x_k$, square terms $x_1^2, x_2^2, \ldots, x_k^2$, and interaction terms $x_1x_2, x_1x_3, \ldots, x_{k-1}x_k$. The significance of the input factors was also determined by analysis of variance (ANOVA). A 3D response plot was utilized to assess the response, and the process parameters were fine-tuned to achieve maximum responses employing the point optimization technique with Design-Expert® 13.0.0 software.

2.5. Yield determination

The yield of the extracted EOs from Assam lemon peel was calculated as follows [22]:

$$\text{EO}\ (\%, \text{v}/\text{w}) = [\text{Volume of the collected oil}\ (\text{mL})\ /\ \text{Weight of the sample}\ (\text{g})]\text{x}\ 100 \quad (2)$$

The yield of the pectin was calculated as follows [23]:

$$\text{Pectin}\ (\%, \text{v}/\text{w}) = [\text{Volume of the collected oil}\ (\text{mL})\ /\ \text{Weight of the sample}\ (\text{g})]\text{x}\ 100 \quad (3)$$

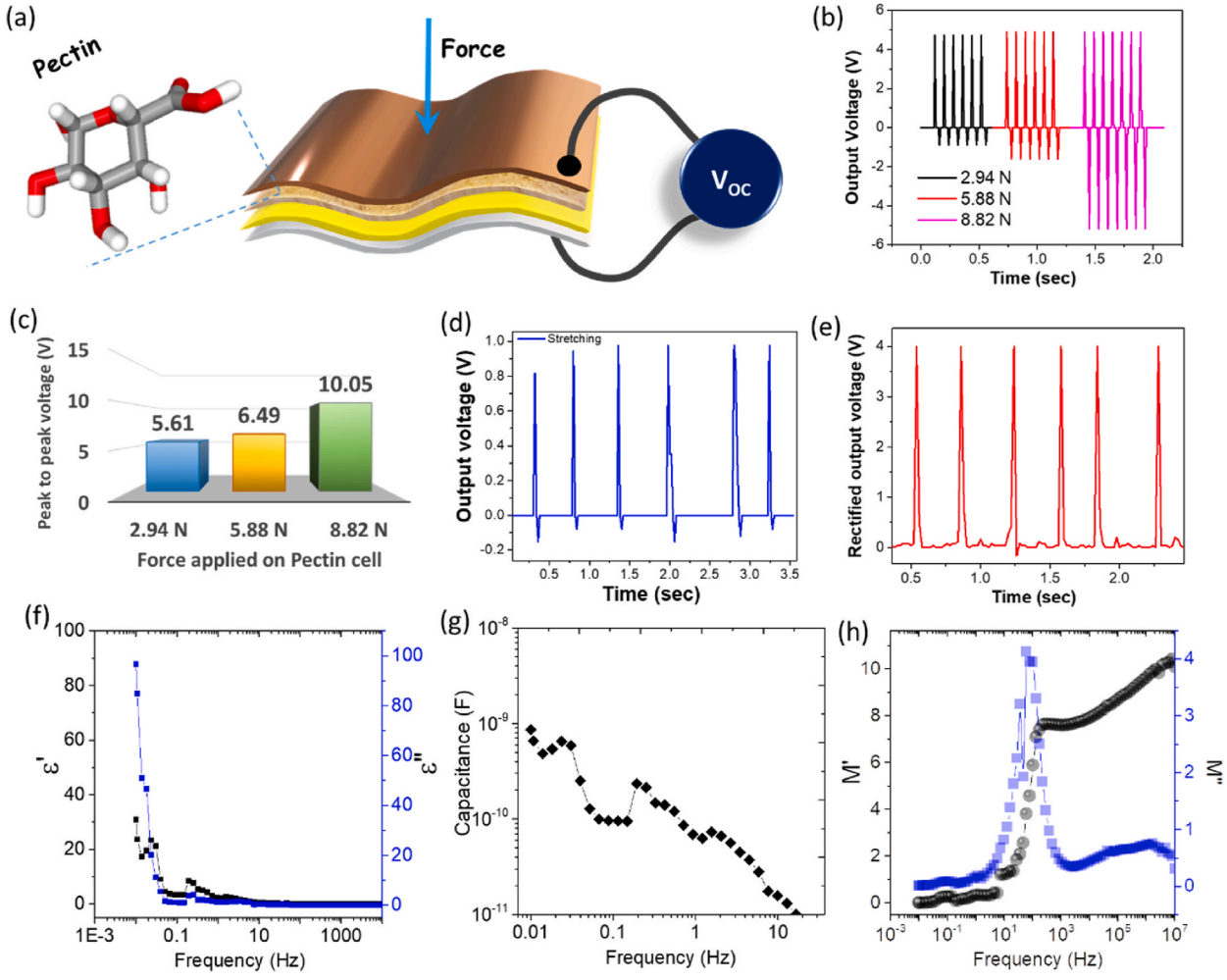

Fig. 2. (a) eco-TNG schematic diagram, (b) Voltage signal response towards different force applied, (c) calculated peak to peak voltage upon applied variable force, (d) Voltage output signal upon stretching the device, (e) Rectified DC voltage signal of the eco-TNG, (e) change in dielectric with respect to frequency, (f) Capacitance change with frequency, and (h) real and imaginary part of the Modulus (charge relaxation phenomena).

2.6. Characterization of EO

The composition of the EO extract underwent analysis through Gas Chromatography-Mass Spectrometry (GC-MS), employing a modified protocol outlined by Ref. [24]. Specific gravity determination followed the methodology detailed by Adepoju and Eyibio [25], while the analysis of Free Fatty Acids (FFA) was conducted as per the method described by Ref. [26]. Determination of the acid value in the EO was executed following the protocol established by Njoku and Evbuomwan [27]. The saponification value of the EO was determined using the procedure outlined by Ezejiofor et al. [28], and the iodine value was estimated via titration (AOCS, 1998 [29]). The assessment of the peroxide value in the Assam lemon EO adhered to the protocol outlined by Njoku and Evbuomwan [27].

2.7. Biopolymer preparation and energy production

The pectin biopolymer was formulated by combining 10 g of citrus peel pectin, 0.1 mL of glycerol, and 1 mL of Assam lemon EO. These components were added in 100 mL of distilled water and then mixed thoroughly with a homogenizer for 15 min at 70 °C. Subsequently, for the formation of films, 15 mL of the solution was poured into Petri dishes and allowed to dry overnight at 60 °C. The dried films that formed from this process were separated from the dishes and used in the following experimental procedures. A detailed illustration of this process and the corresponding experiment is provided in Fig. 2.

3. Results and discussion

3.1. Effect of single variables in oil and pectin extraction

3.1.1. Effect of solid to liquid ratio

The solid to liquid ratio is an important factor in the enzymatic reaction. Proper contact of the enzyme with targeted molecules facilitates proper bioconversion of the substrate. Increasing substrate concentration may enhance the rate of reaction up to a certain point. In saturated conditions when all of the free sites of enzymes are bound with the substrate, then further increment cannot affect the reaction rate [30]. A varied range of peel-to-enzyme ratios viz., 1: 10, 1: 20, 1: 30, 1: 40, and 1: 50 were taken to study its effect on EO and pectin extraction. Other parameters viz., enzyme treatment time (6 h), enzyme titer (15 IU/mL), and distillation time (1 h) were kept constant. Results exhibit that the maximum significant ($F_{4,10} = 11.28$; $p \leq 0.001$) yield of EO and pectin was observed at a 1: 20 substrate to enzyme ratio. Beyond that ratio, there was no noteworthy increase in the EO and pectin yield was found, the 1:20 substrate to enzyme ratio was kept constant for the subsequent set of experiments.

3.1.2. Effect of enzyme treatment time

After fixing the substrate to enzyme ratio, the time for enzyme and substrate reaction was evaluated. The efficiency of any enzymatic reaction is regulated by the interaction time of the substrate and the reactive site of enzymes [31]. As the duration of the reaction extends, the anticipated product formation is greater, but the rate of product formation does not follow a straightforward linear relationship. Over time the catalytic activity of the enzyme diminishes owing to the denaturation of its constituent proteins [32]. When determining an optimal incubation period, it may involve a certain trade-off among several factors but as time emerges as a pivotal factor of process feasibility in this context, it still holds significance. For the recent study, the time for enzyme and substrate reaction ranged from 6 h to 30 h to assess its effect on EO and pectin extraction. Other parameters viz., substrate to enzyme ratio (1: 20), enzyme titer (15 IU/mL), and distillation time (1 h) were kept constant. From Fig. S1 b it was inferred that no significant increase in EO and pectin concentration after 12 h of incubation can be found. From 6 h to 12 h a significant increase ($F_{4,10} = 11.28$; $p \leq 0.001$) in the product yield was found. Maximum EO and pectin were yielded at 12 h incubation. Thus 12 h incubation time was kept constant for the subsequent set of experiments.

3.1.3. Effect of enzyme titer

Enzyme titer assumes a decisive role in the bioconversion process, serving as a crucial factor in facilitating effective conversion of the substrate. This reaction occurs exclusively within the boundaries of designated active sites. The enzyme titer effectively signifies the pace at which the transformation of substrate to product occurs. Remarkably, a limited quantity of enzyme characterized by high titer has the potential to catalyse the required volume of reactants to desired yield of product [33] In this context a spectrum of enzyme titers spanning from 5 to 20 IU/mL was chosen to discern the impact of varying levels of enzyme on the extraction process of EOs and pectin from Assam Lemon peel. Other parameters *viz*., substrate to enzyme ratio (1: 20), enzyme treatment time (6 h), and distillation time (1 h) were kept constant. Application of 15 IU/mL enzyme titer resulted in significantly ($F_{3,8} = 15.83$; $p \leq 0.001$) highest yield of EOs and pectin. Further increment of enzyme titer did not exhibit any significant increase in EOs and pectin yield. Hence, 15 IU/mL enzyme titer was kept constant for the subsequent set of experiments.

3.1.4. Effect of distillation time

Distillation time may impact the yield of extracted compounds thus yield of EOs and pectin in the different time intervals during distillation was measured. For the determination of appropriate distillation time that can give maximum yield, a 1–5 h duration of distillation was considered. Other parameters viz., substrate to enzyme ratio (1: 20), enzyme treatment time (6 h), and enzyme titer (15 IU/mL) were kept constant. A significant increase ($F_{4,10} = 11.28$; $p \leq 0.001$) in EO and pectin yield was observed from 1 h to 2 h

distillation time Fig. S1 d. Further increment of distillation time up to 5 h, exhibit no significant increment in the yield. Therefore, 2 h distillation length was kept constant. Phuc et al. examined the impact of distillation time on Jasmine EO extraction by hydro distillation [34] Another research was conducted by Zheljazkov et al. to regulate the effect of distillation time of coriander oil yield [35]. The results exhibit the maximum yield of oil obtained at 160 min.

3.2. Optimization of simultaneous extraction of EO and pectin

3.2.1. Regression model development

Employing a single parameter study, the peel to enzyme ratio (×1), enzyme treatment time (×2), enzyme titer (×3), and distillation time (×4) were designated as factors for enhancing responses (EO and pectin content) within a two-level four-factor central composite design (CCD). The interactions among these factors were subsequently scrutinized through RSM. The variables ×1, ×2, ×3, and ×4 were selected within the ranges of 1:10–1:30, 6–18 h, 10–20 IU/mL, and 1–3 h, respectively. The outcome data were fit to second-order polynomial equations utilizing multiple regression analyses. Consequently, the mathematical regression equations for EO and pectin content, expressed in terms of coded factors, are as follows:

$$EO = 4.14 + 0.0594 \times 1 + 0.2744 \times 2 + 0.1256 \times 3 + 0.0944 \times 4 - 0.0381 \times 1B + 0.0281 \times 1C - 0.0306\ X1D - 0.1219\ BC + 0.0644\ BD - 0.0194\ CD - 0.4667 \times 1^2 - 0.6217 \times 2^2 - 0.7117 \times 3^2 + 0.1383 \times 4^2 \quad \text{(Eq. 4)}$$

$$Pectin = 11.19 + 0.4939 \times 1 + 1.02 \times 2 + 0.5700 \times 3 + 0.4594 \times 4 + 0.0406 \times 1 \times 2 - 0.0156 \times 1 \times 3 - 0.0644 \times 1 \times 4 + 0.1094 \times 2 \times 3 + 0.0256 \times 2 \times 4 - 0.1731 \times 3 \times 4 - 0.4060 \times 1^2 - 3.15 \times 2^2 - 2.66 \times 3^2 + 1.80 \times 4^2 \quad \text{(Eq. 5)}$$

From the equation, it was observed that the chosen parameters were found to positively influence the EO and pectin yield and were found to be significant.

3.2.2. Statistical analysis using ANOVA

ANOVA is an important statistical analytics tool employed to assess both significance and adequacy of the regression model, and individual model coefficient with lack of fit. The model's F-value surpassing the critical F-value rejects the null hypothesis. *p*-value indicates the significance of the *F* statistics. Remarkably, the linear, quadratic, and interaction influences of variables considered in the context of pectin extraction have shown exceptionally high levels of significance as indicated by their *p*-value ≤ 0.001. Regression coefficient (R^2) of 0.9593 (EOs) and 0.9849 (pectin) were obtained from the model which means that model could explain the 95.93 % and 98.49 % of process behaviour and only 4.07 % and 1.51 % variation could not be described by the model for EOs and pectin extraction, respectively. In addition, R^2 (Pred) of 0.9473 and 0.9623 of EOs and pectin extraction model is in good agreement with R^2 (Adj) of 0.9236 and 0.9716, respectively. The insignificant value for the Lack-of-Fit of the model for EOs ($p = 0.980$) and pectin extraction ($p = 0.173$) implies that the current model is valid.

3.2.2.1. Percentage contribution of the individual and interacting variables. The percent contributions of individual operating parameters on EO (%, v/v) and pectin extraction (%, w/w). The order of the percent contribution of the individual influencing variables on EO content was found to be: ×2 > ×3 > ×4 > ×1. Similarly, the percent contribution of the individual parameters on pectin extraction followed the order: ×2 > ×3 > ×1 > ×4.

The percentage contributions of the binary interactions among the various operating variables on EO (%, v/v) and pectin extraction (%, w/w). The order of the percent contribution of the interacting parameters on EO content was found to be: ×2 × ×3 > ×2 × ×4 > ×1 × ×2 > ×1 × ×4 > ×1 × ×3 > ×3 × ×4. Similarly, percent contribution of the interacting parameters on pectin content followed the order: ×3 × ×4 > ×2 × ×3 > ×1 × ×4 > ×1 × ×2 > ×2 × ×4 > ×1 × ×3.

3.2.3. 3D response surface analyses

Fig. S2 and S3 showcase the three-dimensional response surface curves, which vividly depict the interplay between paired factors across different combinations while maintaining the other two factors at a constant '0′ level. These response surfaces culminate in a prominent point that signifies the optimal output of the dependent variable, be it EO or pectin yield. Within Fig. S2 (a-c) and S3 (a-c), it becomes evident that an intermediate solid to enzyme ratio, closely aligned with the '0′ level, is the favoured operational point for amplifying EO and pectin yield, respectively. Furthermore, for achieving the highest EO and pectin yield, an intermediate enzyme treatment time is preferable, as observed in Fig. S2 (a, d, e) and S.3 (a, d, e). Similarly, the intermediate enzyme titer level emerges as the preferred operational point for attaining a notable rise in EO (Fig. S2(b, d, f)) and pectin (Fig. S3(b, d, f)) content. Additionally, it is noted that an intermediate distillation time benefits the enhancement of EO, while distillation has a less pronounced impact on pectin content improvement (Fig. S2(c, e, f) and S.3 (c, e, f)).

Fig. S2(g) and S3(g) provide insight into the percentage contributions of each individual operational parameter on EO (%, v/v) and pectin extraction (%, w/w), respectively. The ranking of percentage contributions of the individual influential variables on EO content was observed to be in the sequence of: ×2 > ×3 > ×4 > ×1. Likewise, the order of percentage contributions of individual parameters on pectin extraction followed: ×2 > ×3 > ×1 > ×4.

The proportional influences of the binary interactions between the different operational variables on EO (%, v/v) and pectin extraction (%, w/w) are depicted in Fig S2 (h) and S.2 (h) respectively. The hierarchy of the percentage contribution of the interacting parameters to EO content was determined as follows: X2X3 > X2X4 > X1X2 > X1X4 > X1X3 > X3X4. Similarly, the sequence of the percentage contribution of the interacting parameters to pectin content was observed as AC > X3X4 > X2X3 > X1X4 > X1X2 > X2X4 >

X1X3. Tables S2 and S3, Table S3 presents the analysis of variance (ANOVA) results for the quadratic equation pertaining to enzymatic delignification. An f-value and its related degrees of freedom (DF) are provided as the ANOVA outcome and p-value, respectively. In an analysis of variance (ANOVA), the f-value or f-ratio is the primary statistical measure used to test the hypothesis and determine the significance of the effects, along with the corresponding degrees of freedom. Moreover, when the p-value or probability value is determined to be less than the critical value (α), it is expected that the observed effect is statistically significant. Typically, a critical value of 0.05 is employed, whereby any value below this threshold yields statistically significant effects, while higher values yield non-significant effects.

In the analysis of variance (ANOVA), it was observed that the crucial f-value at degrees of freedom 14 and 10 was determined to be 4.69, which falls below the critical value of 26.96 and 74.35 as specified in the table. Therefore, it can be inferred that the regression analysis of the quadratic polynomial equation holds statistical significance in the context of pectin and EO isolation. Furthermore, the obtained p-values are below the significance level of 0.05, suggesting that the regression model for enzymatic extraction of pectin is statistically significant. The observed regression coefficient R2 was 98.66 %, whereas the adjusted R2 was 97.48 %, indicating a strong correlation with biological systems. The R2 and modified R2 values exhibit minimal disparity, suggesting the sufficiency of the regression model for enzymatic extraction. The p-value, which is more than 0.05, indicates that the null hypothesis is not supported.

The analysis of variance (ANOVA) table provides support for the aforementioned analysis and observations. This is further supported by the examination of 3D response surface plots in the regression equation, which highlight the significant interactions among different chosen parameters and their respective impacts on the enzymatic extraction of EO and Pectin. This suggests a substantial interaction among the different factors (Knawang et al., 2021). Georgiev et al. (2012) used orange peel used 0.5 % HA as extraction solvent and got a yield of 2.95 % thus our process is comparable at par with the findings.

3.2.4. Optimized conditions for maximized EO and pectin yields

For the extraction of EO, model-derived optimized conditions were peel: water 1: 20.29, enzyme treatment time 13.27 h, enzyme titer 15.35 IU/mL, and distillation time 2 h where the predicted and the observed value of EO was 4.17 % (v/v) and 4.12 % (v/v), respectively. For pectin extraction, the predicted value of peel: water, enzyme treatment time, enzyme titer, and distillation time were 1: 20.08, 13 h, 15.54 IU/mL, and 2 h, respectively. The predicted yield of pectin was 11.45 % (w/w) and the observed yield was 11.56 % (w/w). For the simultaneous extraction of EO and pectin model derived optimized conditions were peel: water 1: 20.91, enzyme treatment time 13.08 h, enzyme titer 15.47 IU/mL, and distillation time 2 h where the predicted yield of EO and pectin were 4.16 % (v/v) and 11.38 % (w/w). A total 3 times repetitions of the predicted optimized condition for simultaneous extraction of EO and pectin were evaluated. The yield of EO and pectin content under optimized conditions were 4.19 ± 0.31 % and 11.53 ± 0.11 %.

EOs from citrus, due to their fruity perfumes, are widely used as ingredients in the food, cosmetics, and pharmaceuticals industry. For the refreshing aroma of citrus EOs, it is also used as a room freshener. Insecticidal, antifungal, and antibacterial properties endorse EOs to apply as disinfectants (Bora et al., 2019, Othaman et al., 2017) the EO obtained from the Assam lemon peel was transparent. The total yield of extracted EOs from Assam lemon peel was 4.19 ± 0.11 % (v/w) [36]. Extracted EO from mandarin using xylanase treatment followed by hydro distillation where 5.06–5.46 % oil was obtained. Using the solar system as an energy source, the essential oil was extracted from orange peel waste through hydro-distillation and obtained a yield of 1.03 ± 0.02 % [37]. From the Washington Navel orange peel, 0.46–1.70 % oil was extracted after 3 h of the hydro-distillation process [38].

In the food, pharmaceutical, and cosmetic industries, pectin has wide applications as a thickener, texturizer, emulsifier, and stabilizer. It acts as a carrier polymer for the encapsulation of food ingredients. It is also used for the formation of anti-obesity, hypoglycemic, and cholesterol-lowering products [9,39] enzyme assisted extraction of pectin was carried out from the Assam lemon peel. The final value of extracted pectin from Assam lemon peel was 11.53 ± 0.31 (w/w). Enzyme-assisted extraction of pectin is more specific to some chemical bonds, which produces larger pectin molecules and facilitates a higher degree of esterification (Perssello et al., 2017) Extraction can be carried out under ambient temperature and thus reduces energy consumption. Furthermore, the mild process conditions eliminate equipment corrosion, which is frequently observed in conventional processes. It does not require any neutralization steps thus the waste generated can be used directly for any further valorization process. Yuliarti et al. reported a 4.5 % pectin yield when kiwifruit pomace was treated with a commercial enzyme named Celluclast 1.5L (cellulases, polygalacturonase, pectin lyase, and rhamnogalacturonan lyase) [40]. Using the same enzyme Wikiera et al. extracted 10.8 % and 19 % pectin from apple pomace by varying the process conditions [41,42] In the first treatment conditions were enzyme dose: 25 U/g; time: 18 h; temperature: 50 °C; pH 4.5 while in the second treatment conditions were enzyme dose: 25 and 75 μg/g; time: 18 h; temperature: 59 °C; pH: 4.5; stirring rate: 200 rpm. A 19.8 % pectin was extracted by using *endo*-β-1,4-glucanase and *endo*-β-1,4-xylanase from apple pomace [43]. Liew et al. [44] got 7.12 % pectin from passion fruit peels using Celluclast. It can be concluded that an improved recovery of the product was obtained which indicates the efficiency of indigenously produced cost-effective enzymes in the MBDSP laboratory.

3.3. Characterization of essential oils (EOs)

GC-MS analysis of the EO revealed the identification of 52 distinct components. The composition percentages of these compounds within citrus EOs are subject to variations based on both spatial and temporal factors. Notably, alterations in geographical and environmental conditions significantly influence the composition of EO components [45] Table S5 provides a comprehensive breakdown of the identified components, showcasing their respective percentage areas and retention times. Among these constituents, limonene emerged as the principal component, constituting a substantial 94.47 % of the total. Following limonene, β-Bisabolene held a presence of 1.26 %. Compounds found within the range of 0.1–0.9 % encompassα-pinene, *trans*-β-Ocimene, Decanal, 2,6-Dimethyl-1,3,5,7-octatetraene, Citral, 1,5-Heptadiene, 2,5-dimethyl-3-methylene, 3-Carene, n-Decanoic acid, α-Farnesene, Caryophyllene,

trans-α-Bergamotene, Khusilal, α-Cedrene, and n-Hexadecanoic acid. The remaining components were found in minimal proportions, each making up less than 0.1 % of the total composition.

More than 200 compounds have been documented as volatile and semi-volatile constituents, collectively comprising approximately 85–99 % of the total oil fraction. The composition of Assam lemon oil (Table S5.) prominently features hydrocarbon monoterpenes and sesquiterpenes. The prevalent constituents in EOs, as noted, are hydrocarbon and derivative mono- and sesquiterpenes, alongside other non-terpene entities like aldehydes, alcohols, ketones, esters, and acids. Non-volatile compounds encompass flavonoids, coumarins, diterpenoids, sterols, and fatty acids (González-Mas, 2019).

Much like other citrus species, Assam lemon essential oils (EOs) prominently showcase limonene as a major component. This hydrocarbon monoterpene stands out as the most abundant compound in EOs from different citrus species, constituting 60–95 % of the total oil content. In specific cases, such as in *C. bergamia* and *C. limon*, the limonin content has been recorded as 30 % and 48 %, respectively [46,47]. The compounds, originating from Assam lemon EO, are also present in several other citrus species, including *C. sinensis* (sweet orange), *C. reticulata* (mandarin), *C. paradisi* (grapefruit), *C. grandis* (pummelo), *C. limon* (lemon), *C. medica* (citron), *C. aurantifolia* (lime), *C. aurantium* (bitter orange), *C. bergamia* (bergamot orange), and *C. junos* (yuzu) (González-Mas, 2019). An intriguing exception is the compound khusilal, which is absent from the aforementioned 10 citrus EOs. The presence of khusilal components in citrus essential oil has not been reported yet by the scientific community. Khusilal, belongs to the uncommon C-14 class of terpenoids, is predominantly found in *Chrysopogon zizanioides* [48].

The essential oil exhibited a specific gravity of 0.816 g/mL, reflecting its weight. This value also serves as an indicative measure of the essential oil's purity, with specific gravity typically falling within the range of 0.696–1.88 g/mL for most essential oils [49]. Less than 1 specific gravity is due to the presence of oxygenated aromatic compounds like Monoterpene alcohol, Sesquiterpenes alcohol, Aldehydes, Ketones, Esters, Oxides, Lactones, and ether (Osagie et al., 1969 [50]). The specific gravity of Assam lemon EO implies that it is lighter than water and consequently will be insoluble in water.

Quantification of FFA is very important as it is associated with the degree of degradation of essential oil. With degradation acidity also increases which results in the production of FFA [51].

The presence of Free Fatty Acids (FFA), which have separated from oil molecules or triacylglycerols due to factors like moisture, temperature, and the action of the lipolytic enzyme lipase, indicates oil degradation. FFA are less stable and thus prone to oxidation, leading to the development of rancidity [10,52]. This factor plays a pivotal role in determining both the quality and commercial worth of oils, with lower FFA levels signifying superior oil quality. Assam lemon essential oil demonstrates a FFA content of 1.72 mg/KOH. The acceptable threshold for non-rancidity is a maximum of 5.00 mg KOH/g (Rehinam, 2003), indicating that the extracted essential oil falls well within the non-rancid range.

The Assam lemon essential oil exhibited an acid value of 3.02 mg KOH/g. Oils with diminished acid values are considered neutralized and suitable for the formulation of skincare products [10]. This reduced acid value also signifies an extended storage lifespan.

The saponification value of Assam lemon essential oil measured 175 mg KOH/g. This value serves as an indicator of the average molecular weight of the fatty acids present in the glycerides constituting the oil, thereby reflecting the chain length. It operates on an inverse relationship with oil molecular weight, with high saponification values suggesting a prevalence of shorter carbon chain lengths within the fatty acids of glycerides, and conversely.

Saponification is a chemical reaction involving the hydrolysis of triglycerides into glycerol and alkali salts of fatty acids. In this process, each glyceride molecule necessitates the involvement of three KOH molecules for complete saponification. This procedure holds significant importance, particularly within the soap-making industry [10,52].

The iodine value assesses the extent of unsaturation within an oil/fat by quantifying the quantity of double bonds present. A higher iodine value indicates a greater abundance of C═C double bonds, which in turn signifies heightened vulnerability to oxidation. Consequently, a lower iodine value signifies a reduced degree of unsaturation, and vice versa. The determined iodine value for the examined oil was 79 g/100 g, indicating the presence of relatively few unsaturated bonds and consequently a lower susceptibility to oxidative rancidity [53].

Quantification of peroxide value is crucial as it indicates the degree of primary oxidation in the oil sample, serving as the initial indication of rancidity in unsaturated fats and oils. Organic compounds of peroxides are considered as skin irritating, sensitizing and allergic elements, and even carcinogenic. Though the peroxides values < 20 are acceptable but for cosmetic industries, the preferred value is < 5 [54]. High peroxide values denote less stability of oil with shorter shelf life. In this regard the peroxide value (4.79 or 9.21 mEq O_2/kg oil) obtained from the extracted Assam lemon EO represents the stability and storability of the oil. The number of double bonds is proportional to the autoxidation of EO, which leads to degradation, and results in unpleasant taste and aroma [10].

3.4. Antimicrobial property of EO

Essential oil plays an important role in nature by protecting the plants in the form of antiviral, antibacterial, antifungal, and insecticidal agents. Other than antimicrobial activities they are recognized for their diverse application such as anti-inflammatory, analgesic, sedative, spasmolytic, and locally anaesthetic remedies. According to the study by Carson and Riley, it was observed that because of their bactericidal and fungicidal properties they are widely used as an alternative for chemical synthetic products to protect the ecological equilibrium without imparting the same secondary effects [55]. Advancement in the research for understanding the characteristics of essential oil as an antimicrobial agent has opened up a huge scope of application in different sectors such as the pharmacological industry, food industry, agriculture industry, cosmetic industry, and health care division.

The scientific literature based on essential oils suggests that the major components responsible for the antimicrobial activities are

geranyl acetate, eugenyl acetate, menthol, *p*-cymene, limonene, γ-terpenes. Lewis et al. in a study reported that particularly citrus essential oils seem to contain different terpenes which constitute the main chemical class compound with anti-tumor and anti-ulcerogenic activity [56]. The presence of bioactive compounds in the essential oils has also been recognized for pathogen inhibition covering a wide spectrum of gram-positive and gram-negative bacteria as well as fungi [7].

The present study was conducted to study the antimicrobial effect of the extracted citrus essential oil. Zone inhibition assay for antimicrobial activity and broth dilution assay for estimation of minimum inhibitory concentration (MIC) were performed using the agar well method and serial dilution strategy. It was observed that the citrus essential oil showed an antimicrobial effect against the test microorganisms i. e the diameter of the inhibition zone ranged from 10 to 15 mm for bacteria i.e. *Staphylococcus epidermidis* (11 mm), *Cornybacterium muruki* (13 mm), *Enterobacter cloacae* (15 mm), *Bacillus subtilis* (10 mm) and *Pseudomonas aeruginosa* (14 mm), whereas for fungi the diameter of the zone of inhibition was 13 mm, 12 mm, 10 mm and 8 mm for *Aspergillus awamori nakazava, Rhizopus oryzae, Aspergillus niger* and *Trichoderma ressie* respectively. It was observed from the above mentioned data that the MIC of essential oil mostly ranged from 0.62 to 0.15 mg/mL for bacterial and fungal strains. From the results obtained it is clear that the antimicrobial activity of essential oil varies with the type of strain of the microorganism used. Based on the literature it is known that in comparison to gram-positive bacteria, gram-negative bacteria are less susceptible. This can be due to the fact that gram-negative bacteria have an outer membrane layer that is rigid, rich in lipopolysaccharide (LPS) and more intricate structure, thus impede the hydrophobic compounds to diffuse through it, whereas in gram-positive bacteria which are surrounded by a less dense peptidoglycan layer, do not provide sufficient resistance to small antimicrobial molecules. This facilitates the access to the cell membrane thus resulting in disruption of structural integrity and an imbalance in cellular metabolism causing cell death Hyldgaard et al., 2012. In addition, gram-positive bacteria may ease the infiltration of the compounds of essential oils due to the lipophilic ends of lipoteichoic acid (LTA) present in the cell membrane [57].

Studies conducted on the characteristics of essential oil showed that citrus essential oil displays antifungal properties against a wide range of fungal species but the antifungal mechanism of compounds present in the essential oil is still getting explored by the researchers. From various reports, it was suggested that the terpenes and the phenolic compound target the cell membrane of fungi which results in loss of membrane permeability and subsequent leakage of cellular components [46]. In a study by Tao et al., it was reported that the monoterpenes present in the oil such as limonene, octanal, and citral were accountable for the antifungal activity of mandarin essential oil against *P. digitatum* and *P. italicum* [58]. Based on their research, they suggested that mandarin essential oil induces cytotoxicity by disrupting the integrity of the fungal cell membrane, ultimately leading to the release of cellular components.

Overall, the mechanism through which the bioactive compounds found in essential oils exert their antimicrobial effects typically involves disruption of the cell membrane or membrane proteins, which eventually results in the leakage of cytoplasm, cell lysis, and ultimately culminates in cell mortality [59]. However, the actual mode of action of these compounds present in the essential is yet to be understood and thus further studies on the antimicrobial activities of the bioactive compounds in citrus essential oil are particularly needed in the future.

3.5. Characterization of pectin

The characterization of pectin isolated from Assam lemon showed its moisture content to be 7.50 ± 0.71 % (w/w) and ash content to be 1.04 ± 0.01 % (w/w). Pectin obtained from Assam lemon peel demonstrated a notable low moisture content, which enhances its shelf life. The diminished moisture content makes it more resilient against degradation by pectinase enzymes, in comparison moisture content of pectin, extracted from different citrus peels lies in the range of 6.4–10 % [60]. In the context of pectin quality, ash content of less than 10 % is considered favorable for effective gel formation. Additionally, it is worth mentioning that an inverse relationship between ash content and pectin yield that exists in Assam lemon indicates less presence of sugar and other constituents within the pectin matrix [61]. In the present study, ash content was considerably low (1.04 ± 0.01 % (w/w)) which signifies the good pectin yield as well as the purity of the pectin.

Enzyme-assisted pectin extraction produces high equivalent weight pectin from Assam lemon peel whereas, the use of a significant amount of free acid in pectin extraction decreases the equivalent weight by partially degrading the pectin (RamLi and Asmawati, 2011). The equivalent weight of extracted pectin from Assam lemon peel was 961.54.

Three noteworthy attributes of the pectin, specially methoxyl content, total anhydronic acid content, and degree of esterification, were measured and documented as follows: 9.24 ± 0.38 %, 70.75 ± 2.14 %, and 74.11 ± 0.80, respectively. Pectin containing over 7 % methoxyl content is classified as high methoxyl pectin [60], and in this context, Assam lemon pectin is categorized as high methoxyl, containing >9 % methoxyl groups.

Degree of esterification serves as a criteria dividing pectin into two distinct groups: those with over 50 % degree of esterification are deemed high-ester pectin, while those with less than 50 % are categorized as low ester pectin [62]. Therefore, pectin derived from Assam lemon peel falls under the category of high ester pectin, with a degree of esterification of 74.11 ± 0.80 %. Anhydronic acid content serves as an indicator of pectin purity. An anhydronic acid content of less than 65 % is indicative of low purity. With an anhydronic acid content of 70.75 ± 2.14 %, Assam lemon pectin is considered pure from a purity perspective. Potential impurities in pectin may include proteins, starches, and sugars [60].

3.6. Energy generation from eco-friendly biopolymer-based triboelectric nanogenerator (eco-TENG)

For fabrication of the triboelectric device (eco-TENG), Pectin film, Copper tape, Aluminium foil, and Copper wires are used. The triboelectric cell fabrication was done by placing alternate positive and negative layers from the triboelectric series. A layer of copper

having a more negative nature was placed on top of pectin film (positive layer) as the top electrode, following the next negative layer was a dielectric material Kapton which has more negative tendency compared to pectin, and Aluminium foil was placed next to Kapton to give a positive electrode material to the cell. Finally, two copper lids were attached to the top (copper) and bottom (Aluminium) electrodes for the cell connection.

In Fig. 2a, we present our fabricated eco-TNG schematic diagram, according to the triboelectric series. The fabricated eco-TNG generates an output voltage under constant pressure and stretching. The generation of output voltage under constant pressure is depicted in Fig. 2b. It shows that up to ~10 V (peak to peak voltage) has been obtained under a periodic force of 8.82 N. In Fig. 2c, we have observed that the output voltage is linearly increased as the pressure increases. Fig. 2d illustrate the performance of eco-TNG under low stretching condition, and it shows an output voltage up to ~1 volt for stretching the eco-TNG device. This efficiency is due to the highly sensitive nature of the polymer in small stretching conditions. In the eco-TNG, dissimilar electrodes are in contact or separated, and they will produce charge due to the contact electrification [63,64].

To characterize the eco-TNG for future applications, we have measured the rectified signal using a full-wave bridge rectifier circuit (Fig. 2e). Since most of the self-charging devices work on DC mode, voltage output upon DC mode rectification was measured upon 2.94 N force application. It shows positive signals under pressure up to ~4 volts; this reveals that the fabricated eco-TNG can be used for electric energy generation for low-power self-charging devices. The electrical measurements have been used to explain the contact-electrification-based energy generation performance of the eco-TNG. However, the generation and transformation of charge in triboelectric materials are still under debate [63,64]. Here, we consider that, at the initial, both the electrodes are in a neutral state. As the compression starts, opposite charges will accumulate on each polymer surface (Kapton and pectin). During the compression, contact surfaces are in electrical equilibrium. After releasing the pressure, the contact surface will separate, and electrons follow through the top and bottom metal electrodes. To confirm the generation of surface charge on the polymer, we have measured the dielectric constant (real and imaginary) as a function of frequency (Fig. 2f). It shows that in the low-frequency region, the dielectric constant is ~30, which is very high. Therefore, during contact-separation mode, the surface charge will be generated due to the high dielectric nature of the bio-polymer [15,63,64]

Additionally, we have measured the property to store charge accumulated on both sides of the electrodes of the eco-TENG, and it shows the change in the capacitance value with frequency variation. At lower frequency (~0.01 Hz), higher capacitance is observed. This suggests that the device can not only generate charge but also it can store charge at low frequency. Here, we also studied the charge relaxation phenomena to analyze the dielectric behaviour of pectin, the real and imaginary part of the Modulus has been measured and shown in Fig. 2h. The plot reveals that the charge carriers are capable of moving one site to another site successfully. Therefore, electrical results are well confirmed for the charge generation capability of the eco-TENG. In their study, Khandelwal et al. (2019) examined the endurance and application test of their bio-TENG. Additionally, Kim et al. (2019) conducted a power generation test under varying circumstances to demonstrate and enhance power generation. This study serves as a proof of concept, indicating the suitability of the material for energy generation. This study demonstrates the applicability of the methodology and optimization of EO and Pectin in the production of biomaterials for TENG preparation. Furthermore, it suggests that this approach can be applied in other applications where an acceptable grade of Pectin is utilized, such as in various sectors of pharmaceutical, cosmetic and electronics.

4. Conclusion

During the examination of essential oils derived from Assam Lemon, a notable abundance of hydrocarbon monoterpenes and sesquiterpenes was observed. Assam lemon essential oils, similar to other citrus species, notably emphasise limonene as a key constituent. The hydrocarbon monoterpene in question emerges as the predominant chemical found in abundance across several citrus species. In addition, the utilization of enzyme-assisted pectin extraction yields a substantial quantity of elevated-quality extracted pectin. Therefore, the concurrent enzymatic extraction of essential oils (EOs) and pectin from Assam lemon peel presents itself as a feasible and auspicious approach for effectively utilizing resources derived from citrus waste. A triboelectric nanogenerator based on biopolymers has been successfully constructed and holds potential for application in energy storage and generating devices. The enhanced dielectric properties play a significant role in enhancing the triboelectric performance when subjected to low levels of pressure and stretching. Hence, it is our contention that this study has presented a novel approach to the development of an environmentally sustainable energy system that is compatible with biological systems. The extraction and purification of pectin have resulted in the creation of a biopolymer capable of efficiently supporting a nanogenerator for portable energy generation. This invention has the potential to facilitate further advancements in biopolymer production using environmentally friendly enzymatic methods within the expanding biopolymer sector.

CRediT authorship contribution statement

Subhodeep Banerjee: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Debajyoti Kundu:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Writing – original draft, Writing – review & editing. **Subhara Dey:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Partha Kumbhakar:** Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. **Preeti Lata Mahapatra:** Formal analysis, Investigation, Methodology. **Sandipan Karmakar:** Formal analysis, Investigation, Supervision. **Chandra Sekhar Tiwari:** Supervision. **Rintu Banerjee:** Conceptualization, Software, Supervision, Validation, Visualization.

Declaration of competing interest

The authors have declared that there is no conflict of interest in financial or personal relationships and would like to document the fact that they have not submitted this article elsewhere for publication. The authors declare that no generative AI was used in documenting the publication.

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Appendix A. Supplementary data

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