Production of bioadsorbent from phosphoric acid pretreated palm kernel shell and coconut shell by two-stage continuous physical activation via N₂ and air

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In the present study, agricultural biomass—palm kernel shell (PKS) and coconut shell (CS)—was used to produce high porosity bioadsorbent using two-stage continuous physical activation method with different gas carrier (air and N₂) in each stage. The activation temperature was set constant at 600, 700, 800 or 900°C for both activation stages with the heating rate of 3°C min⁻¹. Two parameters, the gas carrier and activation temperature, were determined as the significant factors on the adsorption properties of bioadsorbent. BET, SEM, FTIR, TGA, CHNS/O and ash content were used to elucidate the developed bioadsorbent prepared from PKS and CS and its capacity towards the adsorption of methylene blue and iodine. The novel process of two-stage continuous physical activation method was able to expose mesopores and micropores that were previously covered/clogged in nature, and simultaneously create new pores. The synthesized bioadsorbents showed that the surface area (PKS: 456.47 m² g⁻¹, CS: 479.17 m² g⁻¹), pore size (PKS: 0.63 nm, CS: 0.62 nm) and pore volume (PKS: 0.13 cm³ g⁻¹, CS: 0.15 cm³ g⁻¹) were significantly higher than that of non-treated bioadsorbent. The surface morphology of the raw...
materials and synthesized bioadsorbent were accessed by SEM. Furthermore, the novel process meets the recent industrial adsorbent requirements such as low activation temperature, high fixed carbon content, high yield, high adsorption properties and high surface area, which are the key factors for large-scale production of bioadsorbent and its usage.

1. Introduction

Used since the ancient times by Egyptians and Indians, activated carbon is a unique and versatile adsorbent to eliminate undesirable odour, taste, dyes, heavy metals and organic substances. In contemporary times, activated carbon has been extensively used by the chemical industries for removal, separation and preconcentration of both metallic and organic species from water and wastewater [1]. Today, coal-based activated carbon is the most prevalent adsorbent used; however, it is expensive and non-sustainable. This has led to a search for low-cost, easily available materials as alternative adsorbent materials.

Conversion of lignocellulosic biomass to high-efficiency bioadsorbent would boost its economic value, develop economical adsorbent materials and inspire diversion of the waste away from landfill and open burning. In Malaysia, enormous amounts of palm kernel shell (PKS) and coconut shell (CS) are still underused. Chiefly, both of this lignocellulosic biomass has the aptitude to be used as inexpensive adsorbents as it is not only an underused resource but practically at hand and sustainable resource [2,3]. Thence, the application of these inexpensive lignocellulosic biomass wastes as the carbon precursor through thermochemical conversion is very promising [4]. The adsorbent can present specific physico-chemical characteristics (i.e. surface area, porosity, pore-size distribution and surface functional groups) depending on the precursor and the method used in its preparation [5,6]. Industrially, cheap carbonaceous precursors with high carbon and low inorganic (i.e. ash) contents are preferred as raw material for the production of adsorbent [6]. High mineral (ash) content in agricultural biomass such as PKS and CS creates a significantly different challenge for preparing high-quality activated carbon. Currently, carbon from this high-ash agricultural biomass generated in thermochemical conversion has only been used as a soil amendment or low-grade fuel [7,8]; this inherently limits the market demand for this type of carbon. Ash leaching method with phosphoric acid prior to physical activation has been proven to remove a huge fraction of ash-forming elements in biomass and expose the mesopores of the carbon produced [9,10]. However, for high-ash agricultural biomass such as PKS and CS, the pores are majorly clogged by ash components such as silica or silicate derivatives, which are difficult to remove using the leaching method. To unclog the existing mesopores and create micropores, the biomass has to undergo further treatment, physical activation [11].

Physical activation using only nitrogen as the carrier gas to produce adsorbent has been carried out by many researchers [12–20]. Nitrogen is a small-scale molecule that can penetrate into narrow, smaller and deeper inside of particles to create micropores [21,22]. However, using nitrogen gas as carrier gas produced a very small surface area and enormous amount of ash, leading to inhibition of the activation especially on high-ash biomass due to the lack of open mesopores structure in the raw material itself [23]. While, using air as the carrier gas, it primitively modifies the bioadsorbent adsorptive affinity for organic compounds by opening up pores and introducing strong hydrogen bonding sites for ionizable compounds [11]. Thermal air activation of biomass can modify the pore size distribution and connectivity, and promote the oxygen functionality [11,24]. High-ash biomass might develop from this air activation as it may help open up pores that are clogged by major ash components such as silica or silicate derivatives and create the mesopores structure on the carbon produced. However, when air was present in activation process with high temperature and prolong period, the biomass might burn and cause the char yield to decrease [25].

Physical activation of high-ash biomass via air and N\textsubscript{2} help in creating different types of pores: mesopores and micropores, respectively. Thus, two-stage continuous physical activation was suggested in this study. Incorporating two-stage continuous physical activation via air and N\textsubscript{2} on phosphoric acid treated high-ash biomass will certainly increase the quality of the bioadsorbent produced. No similar work has been reported so far for bioadsorbent produced via two-step continuous physical activation with nitrogen and air as carrier gas which suggests a need for the present work. This study suggests that it is feasible to control the sequence of the gas and activation temperature by means of the experimental parameters. The phosphoric acid pretreated biomass was physically activated in two stages using air or N\textsubscript{2} as the gas carrier in each stage (Air > N\textsubscript{2} or N\textsubscript{2} >
Air). The variations in properties of the bioadsorbent produced were analysed. One-stage physical activation using only N\textsubscript{2} or only air as the gas carrier was also conducted to create a comparison between one-stage and two-stage continuous physical activation of phosphoric acid treated PKS and CS. As a novelty, we include the significant difference in bioadsorbent characteristics of bioadsorbent prepared via one-stage and two-stage physical activation. Analysis of variance (ANOVA) was used to test the main effects of the suggested physical activation method (one-stage physical activation: Air or N\textsubscript{2}, and two-stage continuous physical activation: Air > N\textsubscript{2} or N\textsubscript{2} > Air) and activation temperature on the characteristics of adsorbent derived from phosphoric acid treated CS and PKS. Furthermore, the determination of the BET (Brunauer–Emmett–Teller) internal pore surface area and volume, structural analysis of the carbon crystals and pore bodies from the scanning electron microscope (SEM), chemical composition through CHNS/O and ash content while the surface chemical characteristics determined by Fourier transform infrared (FTIR) and thermal behaviour through thermogravimetric analysis (TGA) were also taken as responses. Thus, this study not only provides the adsorption capabilities of biomass from the suggested physical activation methods but also insight into the design and performance of bioadsorbent from high-ash biomass with high adsorption value.

2. Material and methods

2.1. Preparation of samples prior to physical activation (H\textsubscript{3}PO\textsubscript{4} pretreatment)

CS and PKS were collected, cleaned and dried in an oven at 105°C for 48 h. The dried raw materials were then crushed and sieved to 2–5 mm size range. Specified mass of the dried PKS and CS were impregnated with 30% phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) with impregnation mass ratio of 1:1 at 80°C for 2 h. The pretreated particles were filtered and washed with distilled water. The washed pretreated particles were dried at 105°C for 48 h.

2.2. Physical activation process

The process of physical activation was performed in a horizontal laboratory tube furnace. For one-stage physical activation, the H\textsubscript{3}PO\textsubscript{4} pretreated samples were activated for 75 and 105 min with air or N\textsubscript{2} gaseous (flow rate = 100 ml min\textsuperscript{-1}) at temperature 600, 700, 800 and 900°C, respectively. After, the one-stage physical activation, the activated samples were kept in desiccators for further analysis.

For two-stage continuous physical activation, the H\textsubscript{3}PO\textsubscript{4} pretreated samples were activated continuously in two stages of different gas carrier: air and N\textsubscript{2}. The activation temperature was set constant at 600, 700, 800 or 900°C for both activation stages with the heating rate of 3°C min\textsuperscript{-1}. For ‘N\textsubscript{2} > Air’ activation, the pretreated samples were activated in N\textsubscript{2} (flow rate = 100 ml min\textsuperscript{-1}) for 75 min before undergoing air activation (flow rate = 100 ml min\textsuperscript{-1}) for 30 min. While, for ‘Air > N\textsubscript{2}’ activation, H\textsubscript{3}PO\textsubscript{4} pretreated samples were activated with air (flow rate = 100 ml min\textsuperscript{-1}) for 75 min and followed by N\textsubscript{2} activation (flow rate = 100 ml min\textsuperscript{-1}) for 30 min. Samples were then cooled to room temperature by flowing N\textsubscript{2} through the activated samples (flow rate = 100 ml min\textsuperscript{-1}). After, the two-stage continuous physical activation, the activated samples were kept in desiccators for further analysis.

2.3. Characterization

The detail of the standard method testing process and calculation for the performance of bioadsorbent included BET surface area, specific surface area characteristics and iodine adsorption number was mentioned in our previous study [26]. In this study, methylene blue adsorption number was determined on the basis of Standard Method JIS K 1470–1991 [27,28]. The surface chemical characteristics of CS and PKS were determined by FTIR in the range of 700–4000 cm\textsuperscript{-1}. TGA was done using Perkin Elmer, USA, equipment. The experiments were performed in an inert atmosphere with a continuous flow of argon at the rate of 50 ml min\textsuperscript{-1} and heated at a heating rate of 10°C min\textsuperscript{-1}. About 10 mg of samples was placed on a balance located in the furnace tube and heat was applied over the temperature range from 0 to 1000°C. In addition, the ultimate analysis of the bioadsorbent was performed in CHNS/O analyser (Perkin Elmer PE2400 Series II). TAPPI standard method, T211 om-85 was used to determine the ash content. The oven-dried sample (2 g) was burned
(dry oxidation) in a muffle furnace at 575 ± 25°C for 4 h. This standard test method was used to determine the volume of ash remaining after dry oxidation of the sample [29].

2.4. Data analysis

Statistical package for the social science (SPSS) was applied to evaluate the data of adsorption properties of bioadsorbent for ANOVA at 95% confident level (p ≤ 0.05). Tukey-Kramer multiple comparison test was applied to analyse the differences of the treatment effects when significance was observed. The effects were considered not statistically significant when the p-value was higher than 0.05 at the 95% confidence level.

3. Results and discussion

3.1. Adsorption properties of bioadsorbent

The adsorption properties of bioadsorbent derived from H₃PO₄ pretreated CS and PKS were compiled in Table 1. For all the models, the ANOVA analysis showed p-value was less than 0.01 for the parameters, physical activation, activation temperature and gas carrier × activation temperature, signifying that the models were stiffly significant at the 99% confidence level for CS and PKS bioadsorbent. We may observe that there is an increase in the adsorption properties of the pretreated bioadsorbent as compared to the non-treated bioadsorbent. This could potentially be due to the removal of some components, e.g. tar-like matter, and phosphoric acid deposited in pores, which occurred better at higher activation temperature, leading to the development of micropores and mesopores [30]. Table 1 illustrates the effect of physical activation and activation temperature on adsorption of methylene blue using PKS and CS bioadsorbent. Activation temperature influenced the adsorption properties in two competitive ways. First and foremost, it was able to promote the diffusion rate of adsorbate molecules across the external boundary layer and internal pores of the adsorbent will enhance the adsorption rate. Furthermore, it can attenuate the force between adsorbent and adsorbate, improving the desorption rate [31]. The adsorption of methylene blue on both the bioadsorbents decreased significantly when the activation temperature went up to 900°C. The decrease of adsorption rate might be due to the limited quantities of available active sites on the surface of the bioadsorbent [32]. The quantity of active sites accessible for methylene blue adsorption rises once the porosity of the adsorbent increases [33]. Hence the result showed that high activation temperature will cause the decreased of porosity in bioadsorbent. Table 1 demonstrates that the air activated bioadsorbent obtained the highest methylene blue adsorption. This result verifies that the air activation promotes mesopore in bioadsorbent. Comparatively, bioadsorbents undergoing two-stage continuous physical activation achieved higher methylene blue adsorption than one-stage physical activation. Oxygen from air acted as a catalyst to enlarge or create mesopores in carbonaceous materials. The highest methylene blue adsorption (208.40 mg g⁻¹) for CS adsorbent was obtained when the CS was activated at 800°C in Air > N₂ activation. On the other hand, PKS sample activated at 700°C under Air > N₂ activation achieved the highest methylene blue adsorption (253.26 mg g⁻¹). Eventually, Air > N₂ physical activation delivered bioadsorbent with a highly mesoporous surface.

Iodine adsorption is the most fundamental parameter used to define and characterize the performance of adsorbent. Iodine adsorption was used as an approximation of the surface area of an adsorbent as well as a measure of micropores [34]. Besides, adsorbents with a high iodine adsorption number perform better in eliminating small sized contaminants in the field [35]. Table 1 reveals that both bioadsorbents obtained the lowest iodine adsorption via air activation, which may be caused by the high reactivity during air activation. The finding of Kyritsis [36] illustrated that oxygen will react at the entrances of the pores but does not penetrate into the narrow pores. Some researchers had reported that oxidation will partially destruct the micropore walls and, thus, generate low surface area on the adsorbent [37]. Moreover, the process of dehydrogenation occurred under N₂ activation but not under air activation due to the instability of the residue in the air [38]. The dehydrogenation properties will restrict the formation of tar and diminish the production of other volatile products, resulting in changeable aromatization of the carbon skeleton by the creation of a porous structure and surface area [39]. Under the circumstances, bioadsorbent prepared via N₂ activation achieved higher iodine adsorption when compared with air activation. Table 1 shows that the iodine adsorption for both bioadsorbents under two-stage continuous physical activation is higher than one-stage physical
activation. After performing an ANOVA analysis on two-stage continuous physical activation, the result defined that the highest iodine adsorption was achieved when the lignocellulosic biomass was propelled by the $\text{N}_2 > \text{Air}$ activation. The highest iodine number (525.57 and 501.37 mg g$^{-1}$) was recorded in the

Table 1. ANOVA for methylene blue and iodine adsorption of CS and PKS bioadsorbent (control—bioadsorbent without $\text{H}_3\text{PO}_4$ pretreatment). Note: means followed by the same letter in the same column are not significantly different at $p \leq 0.05$ according to Tukey multiple comparison test.

| physical activation | adsorption properties | iodine adsorption (mg g$^{-1}$) |
|---------------------|-----------------------|---------------------------------|
|                     | CS                    | PKS                            |
|                     | CS                    | PKS                            |
| control (non-treated bioadsorbent) | | |
| raw material        | 1.79                  | 0.77                           |
| 75 700 Air          | 104.58                | 86.13                          |
| 75 700 $\text{N}_2$ | 81.51                 | 75.36                          |
| 105 700 Air         | 64.60                 | 66.90                          |
| 105 700 $\text{N}_2$| 61.52                 | 63.06                          |
| one-stage physical activation | | |
| 75 600 Air          | 71.00$^a$             | 78.69$^a$                      |
| 75 700 Air          | 149.96$^a$            | 91.25$^a$                      |
| 75 800 Air          | 103.30$^a$            | 82.28$^d$                      |
| 75 900 Air          | 81.26$^a$             | 70.75$^f$                      |
| 75 600 $\text{N}_2$| 74.59$^a$             | 64.08$^p$                      |
| 75 700 $\text{N}_2$| 107.66$^a$            | 88.18$^b$                      |
| 75 800 $\text{N}_2$| 101.25$^a$            | 85.36$^c$                      |
| 75 900 $\text{N}_2$| 61.52$^a$             | 83.05$^d$                      |
| p-value             | <0.001                | <0.001                         |
| 105 600 Air         | 81.51$^a$             | 87.92$^b$                      |
| 105 700 Air         | 101.76$^a$            | 93.05$^a$                      |
| 105 800 Air         | 94.59$^a$             | 79.21$^e$                      |
| 105 900 Air         | 77.67$^a$             | 67.93$^h$                      |
| 105 600 $\text{N}_2$| 76.13$^a$             | 70.75$^g$                      |
| 105 700 $\text{N}_2$| 95.36$^a$             | 84.85$^d$                      |
| 105 800 $\text{N}_2$| 87.67$^a$             | 82.28$^d$                      |
| 105 900 $\text{N}_2$| 58.19$^a$             | 72.29$^f$                      |
| p-value             | <0.001                | <0.001                         |
| two-stage continuous physical activation | | |
| 105 600 $\text{N}_2$>| 102.79$^a$             | 245.31$^b$                     |
| 105 700 $\text{N}_2$>| 140.98$^a$            | 253.26$^a$                     |
| 105 800 $\text{N}_2$>| 208.40$^a$            | 158.16$^a$                     |
| 105 900 $\text{N}_2$>| 105.35$^a$            | 85.36$^h$                      |
| 105 600 $\text{N}_2$>| 133.29$^a$            | 132.27$^e$                     |
| 105 700 $\text{N}_2$>| 164.57$^a$            | 203.53$^c$                     |
| 105 800 $\text{N}_2$>| 139.45$^a$            | 95.36$^f$                      |
| 105 900 $\text{N}_2$>| 136.37$^d$            | 92.28$^g$                      |
| p-value             | <0.001                | <0.001                         |

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CS and PKS bioadsorbent produced at 600°C under N₂ > Air activation. Small pores are adept at adsorbing iodine molecules, and, thus, the quantity of iodine molecules adsorbed is often considered an indicator of the number of micropores in adsorbent [40–43]. The enhancement of iodine adsorption for both bioadsorbents via N₂ > Air activation indicated the increase of micropores on the bioadsorbent in this study.

Besides, it is proposed that H₃PO₄ impregnation not only promotes the pyrolytic decomposition of raw material but also leads to the formation of cross-linked structure [44]. Aside from affecting the development of the pores, particularly the size, H₃PO₄ pretreatment also affects the resulting adsorption properties. Experimental results show that the amount of adsorption capability increased dramatically with the H₃PO₄ pretreatment. Furthermore, the reaction time of the physical activation has a significant effect on the development of the carbon’s porous networks. The reaction time should just be enough to eliminate all the moisture and most of the volatile components in the precursor to cause pores to develop [26]. Ironically, bioadsorbent treated for a shorter time reached a higher adsorptive capacity than bioadsorbent activated for a longer time. This may be partly due to the prolonged reaction time resulting in structural deformation, hence less surface area for adsorption [45]. For this reason, the bioadsorbent physically activated at 105 min achieved a lower adsorption than bioadsorbent prepared in 75 min.

| physical activation | pore structure and surface area characteristics of bioadsorbent |
|---------------------|---------------------------------------------------------------|
|                     | BET surface area (m² g⁻¹) | pore size (nm) | micropore volume (cm³ g⁻¹) |
|                     | CS   | PKS | CS   | PKS | CS   | PKS |
| control (non-treated bioadsorbent) |       |      |      |     |      |     |
| raw material        | 0.84 | 0.79 | 6.30 | 7.21 | 0.0013 | 0.0014 |
| 75 N₂ 700           | 91.39 | 69.42 | 45.82 | 82.06 | 0.03 | 0.01 |
| one-stage physical activation |       |      |      |     |      |     |
| 75 Air 700          | 124.32 | 99.19 | 47.13 | 36.88 | 0.01 | 0.0004 |
| 75 N₂ 700           | 147.91 | 114.55 | 6.58 | 6.27 | 0.06 | 0.06 |
| 105 Air 700         | 87.75 | 82.27 | 73.87 | 78.43 | 0.04 | 0.03 |
| 105 N₂ 700          | 114.55 | 98.09 | 7.13 | 7.55 | 0.04 | 0.04 |
| two-stage continuous physical activation |       |      |      |     |      |     |
| 105 Air > N₂ 700    | — | 169.76 | — | 6.07 | — | 0.06 |
| 105 Air > N₂ 800    | 179.61 | — | 7.99 | — | 0.05 | — |
| 105 N₂ > Air 600    | 479.17 | 456.47 | 0.62 | 0.63 | 0.15 | 0.13 |

Table 2. The surface area and pore size characterization of the prepared bioadsorbent (control—bioadsorbent without H₃PO₄ pretreatment).

CS and PKS bioadsorbent produced at 600°C under N₂ > Air activation. Small pores are adept at adsorbing iodine molecules, and, thus, the quantity of iodine molecules adsorbed is often considered an indicator of the number of micropores in adsorbent [40–43]. The enhancement of iodine adsorption for both bioadsorbents via N₂ > Air activation indicated the increase of micropores on the bioadsorbent in this study.

3.2. Pore structure and surface area characteristics (BET surface area)

Evaluation of the surface characteristics and pore structures in this study was performed only on the non-treated and pretreated bioadsorbent that obtained the highest adsorption properties from one-stage physical activation and two-stage continuous physical activation.

The properties of the surface and porosity of adsorbent rely on the raw material, parameters of the thermal reaction (temperature and time) and physical activation (surrounding gas composition) [11]. Porosity in carbon materials primitively develops during physical activation due to irregular spacing between aromatic sheets. In spite of that, the pores are consequently clogged up as a result of the deposition of tarry materials [46]. With reference to table 2, the pretreated bioadsorbent achieved a higher surface area than the non-treated bioadsorbent. The high value of BET surface area in pretreated bioadsorbent is indicative of highly developed pore network within the carbon. The pretreated bioadsorbent also has smaller pore size than the non-treated bioadsorbent. The enlargement
of surface area for both pretreated bioadsorbents may be accomplished via the creation of new micropores as propounded by the growth in the micropores surface area and pore volume. H₃PO₄ is the dehydrating agent that penetrates deep into the structure of the carbon causing tiny pores to develop [47]. Simultaneously, the bioadsorbents derived from the CS and PKS by H₃PO₄ pretreatment under appropriate process conditions have higher proportions of microporous and mesoporous with a high surface area. Apart from that, a longer physical activation promoted reduction in both surface area and total pore volume, presumably due to the collapse of smaller pores, as inferred from the decrease in micropore volume [23]. As shown in table 2, the BET surface area of the bioadsorbent prepared by H₃PO₄ for 105 min is lower compared to the bioadsorbent prepared under 75 min. It is also lower in terms of percentage of micropore to the BET surface area of the sample. Generally, further increase in the reaction time resulted in the decrease of the micropore distribution, similar to that of BET surface area.

In this study, two-stage continuous physical activation is attempted for the purpose of clearing off disorganized carbon and opening up clogged pores, and simultaneously creating new pores by selectively burning off the carbon atoms. In conformity with table 2, figures 1 and 2, two-stage continuous physical activation leads to a considerable increase in both the BET surface area and porosity including micropore surface area and micropore volume as compared to single activation. Figures 1 and 2 also depict the porosity ratio distribution of the produced bioadsorbent. The micropore porosity ratio for bioadsorbents prepared under two-stage continuous physical activation was higher than one-stage physical activation. The porosity ratio results declared that bioadsorbent prepared via
Air > N2 activation produced the higher mesoporous structure. This result directly related to the methylene blue adsorption results, as bioadsorbent prepared via Air > N2 activation obtained the highest methylene blue adsorption (table 1). Meanwhile, a significant decrease in pore size for samples prepared under N2 > Air activation implied that this activation method promotes the formation of narrower porosity (eight times smaller than the sample prepared by Air > N2 activation). Table 2 also shows the highest micropore volume (0.15 and 0.13 cm3 g−1 for CS and PKS bioadsorbent, respectively) resulted when both bioadsorbents were activated under N2 > Air activation. The results denoted that N2 > Air activation elicits an increase in pore volume and reduction of pore size, resulting in high surface area for both bioadsorbents. The highest BET surface area was obtained from bioadsorbent prepared under N2 > Air activation with 482.24 and 456.47 mg g−1 for CS and PKS, respectively. This may be explained by the oxygen groups probably being fixed at the most active sites at the entrance of the micropores during the pre-oxidation stage for Air > N2 activation. Therefore, the access of nitrogen to these micropores becomes difficult [48], and as consequence, adding N2 activation after Air activation was not able to induce many pores, thus, the specific surface area was not greatly increased. On the contrary, N2 > Air activation promotes the bioadsorbent with higher microporous structure. CS and PKS bioadsorbent contained 76.55% and 75.22%, respectively, of micropore distribution when prepared under N2 > Air activation. The observed increases in micropore distribution were primarily ascribed to the thermal decomposition of surface functional groups from the inside of pores upon pre-heat treatment with nitrogen [49–51]. This preferentially leads to micropore formation instead of pore enlargement which explains why the pore size of the sample via N2 > Air activation was approximately 10 times smaller than the other samples. This is well visualized by SEM image. The SEM image of bioadsorbent prepared via N2 > Air activation (figure 5o, 5p) shows that the microscopic shape of bioadsorbent is an agglomeration of sub-micrometre particles. The enhancement of the formation of micropore surface area by N2 > Air activation is favourable to promote higher adsorption for the bioadsorbent. The high micropore distribution translates the suitability of the activation method used in this study. Thus, N2 > Air activation acquire a high potential in activated carbon application with its comparable high surface area.

Table 3 shows the characteristics of bioadsorbents produced in this work and also from other recent studies by other researchers. It shows the results of the surface area characteristic of the bioadsorbent made from different precursors and condition of activation. Among them, the bioadsorbent produced in this study apparently possesses the best quality in terms of its porosity characteristics. CS and PKS bioadsorbents prepared under N2 > Air activation acquire a high potential in activated carbon application with its comparable high surface area.

3.3. N2 adsorption

Evaluation of the surface characteristics and pore structures in this study was performed only on the non-treated and pretreated bioadsorbent that obtained the highest adsorption properties from one-stage physical activation and two-stage continuous physical activation.
Nitrogen adsorption is the standard channel to evaluate the porosity of carbonaceous adsorbent. The adsorption isotherm provides the information source for the porous structure of the adsorbent, heat of adsorption, physico-chemical characteristics and others. Figures 3 and 4 established the N2-adsorption isotherm acquired from the raw material, non-treated bioadsorbent and bioadsorbent sample prepared from CS and PKS under the optimum conditions (bioadsorbent with highest adsorption properties from one-stage physical activation and two-stage continuous physical activation). Most isotherms have been shown to conform to one of the five types of International Union of Pure and Applied Chemistry (IUPAC) classification. Both precursors and non-treated bioadsorbent conform to type II isotherm, where B points out the zone where the monolayer becomes filled. The inflection point of the isotherm usually occurs near the completion of the first adsorbed monolayer and with increasing relative pressure, second and higher layers are completed until at saturation the number of adsorbed layers becomes infinite. This indicated that both precursors were non-porous or whole externally. While both high-ash agricultural biomass that had undergone one-stage physical activation (only Air and only N2) and Air > N2 two-stage continuous physical activation conform to type IV isotherm. This indicated a significant microporous and mesoporous network system present in both bioadsorbents. From the result obtained, both bioadsorbents prepared using N2 > Air activation conform to type I isotherm, disclosing that the bioadsorbents are given by microporous solids having relatively small external surfaces such as activated carbons, molecular sieve zeolites and certain porous oxides.

Figure 3. N2-Adsorption isotherm for the sample at 77 K for CS bioadsorbent.

Figure 4. N2-Adsorption isotherm for the sample at 77 K for PKS bioadsorbent.
3.4. Scanning electron micrograph

Evaluation of the surface characteristics and pore structures in this study was performed only on the non-treated and pretreated bioadsorbent that obtained the highest adsorption properties from one-stage physical activation and two-stage continuous physical activation.

Figure 5a,b presents the micrographs for CS and PKS employed as the raw material for the preparation of bioadsorbent. The surface of the raw material was dense and planar without any cracks and crevices. This would account for its poor or negligible BET surface area (table 2). As shown in figure 5a,b, we noticed that the surface of raw material CS shows holes that were spaced out on the surface with smooth edges, whereas raw material PKS was smooth without any ridges or pores. Most of the pores of the CS were closed up and the pores for PKS were not visible at the magnification of the SEM. After the N2 physical activation, the surface morphology showed cracks but no visible pore development occurred on both non-treated bioadsorbents (figure 5c,d). Phosphoric acid pretreatment preserved better starting structure of CS and PKS bioadsorbent. This phenomenon is in relation to the pore structure and surface area characteristics surface morphology of the pretreated bioadsorbent (table 2). Despite that, the cellular structure of CS and PKS was noticeable after chemical pretreatment and physical activation. Large amounts of orderly pores are developing on the pretreated CS and PKS bioadsorbent surface with broken edges (figure 5e,f). This was attributed to a small amount of impurities such as tar that may cause the pore to clog up and inhibit good pore structure development [52]. Thus, activation stage (H3PO4 pretreatment) was able to produce an extensive external surface with high surface area on the pretreated bioadsorbent. In general, the choice of the reaction time for the activation depends on the desired porous structure distributions. Except for a lot of ‘nodule-like’ structures which can be clearly seen in the external surface of the pretreated bioadsorbent which was prepared for 105 min (figure 5i–l), no significant change is observed in the exterior surface structure compared to the bioadsorbent prepared for 75 min, thereby indicating that the gasification occurs mainly in the interior of the particles and presumably is channelled out to the ‘nodule-like’ structures.

According to figure 5c,f, when both lignocellulosic biomasses are prepared under air activation, we noticed that the surface becomes coarser/rougher or more plicated, presumably resulted from the loss of char mass under oxygen attack. Some dirt-covered/impurities and unclear pores were present on the surface of the CS bioadsorbent (figure 5e). Such rudimentary porous structure and deposition of tarry substances in the interstices of the sample was caused by the incomplete volatile release [6,57–59]. In contrast, the surface morphology of PKS (figure 5f) with large pores was covered with silica. Oxygen from the high reactivity of air activation reacted at the entrances of the pores and does not penetrate into the narrow pores was stated by Savova et al. [60]. Henceforth, this may clarify that bioadsorbent prepared with air activation produced an oxidized carbon with the low BET surface area and low micropore porosity ratio 9.19 and 5.16% for CS and PKS bioadsorbent. Further, the bioadsorbents induced by air consisted of the surface area with a predominantly macroporous structure with the pore size of 6.58 and 6.27 nm for CS and PKS bioadsorbent, respectively (table 2). Correspondingly, some researchers proved that using nitrogen gas as carrier gas produced a very small surface area [16,23]. Better information may be obtained from figure 5g; carbon skeleton structure appeared on the surface of CS under N2 activation. The smooth surface area with absence of pores urged the low BET surface area for CS bioadsorbent prepared under N2 activation. Besides, the micrographs (figure 5d) manifested that the surface condition of the PKS bioadsorbent was primitively hard and rough, and the pores were clogged by the silica bodies. Based on the study of Razali et al. [61] silica acted to protect the biomass structure and enhance its mechanical strength. Figure 5h demonstrated the silica still present on the bioadsorbent activated with N2 activation. The presence of the silica on the surface of bioadsorbent will produce limited surface area, suggesting an inhibition of the reaction. The limited surface area may be caused by the low micropore volume; as demonstrated in table 3, the micropore volumes for CS and PKS bioadsorbents are only 0.06 and 0.04 cm3 g−1, respectively.

Additional physical activation stage via N2 after air activation (Air > N2) for 75 min had reduced the silica compounds that naturally attached to the surface of CS and PKS (figure 5m,n). The rough appearance was observed at CS adsorbent produced under Air > N2 activation. The formation of longitudinal cells in the transverse section shows the fragility and lightness of the CS bioadsorbent. Likewise, the open pores appearing on the CS bioadsorbent surface can be due to the reduction of volatile species. On the other hand, occasional cracking occurred on the surface area of PKS activated under Air > N2 activation method. The cracking was probably due to the drastic combustion when oxygen was present during the air activation. The clogged-up pore and drastic combustion had
inclined the BET surface value (179.61 and 169.76 mg g\(^{-1}\) for CS and PKS) for bioadsorbents prepared under Air > \(\text{N}_2\) activation. Additional stage of air activation after \(\text{N}_2\) activation (\(\text{N}_2 > \text{Air}\)) increased the development of pores structure on the bioadsorbent (figure 5(o,p)). The well-developed porous structure was due to the significant reduction of the silica compounds attached to the surface of CS

| physical activation       | CS                                | PKS                                |
|---------------------------|-----------------------------------|-----------------------------------|
| control (non-treated bioadsorbent) | ![Image](a) | ![Image](b) |
| raw material              | ![Image](c) | ![Image](d) |
| \(\text{N}_2\)            | ![Image](e) | ![Image](f) |
| sample without            | ![Image](g) | ![Image](h) |
| \(H_3\text{PO}_4\) pretreatment and activated at temperature 700°C for 115 min | ![Image](i) | ![Image](j) |
| one-stage physical activation | ![Image](k) | ![Image](l) |
| Air                       | ![Image](m) | ![Image](n) |
| sample activated at       | ![Image](o) | ![Image](p) |
| temperature 700°C for 75 min | ![Image](q) | ![Image](r) |
| \(\text{N}_2\)            | ![Image](s) | ![Image](t) |
| sample activated at       | ![Image](u) | ![Image](v) |
| temperature 700°C for 75 min | ![Image](w) | ![Image](x) |
| Air                       | ![Image](y) | ![Image](z) |
| sample activated at       | ![Image](aa) | ![Image](ab) |
| temperature 700°C for 115 min | ![Image](ac) | ![Image](ad) |

**Figure 5.** (a–p) Scanning electron micrograph of bioadsorbent activated under different physical activation in low magnification (50 μm).
and PKS, which open up more reactive surfaces for the activation process. When the sample was prepared under $N_2 > Air$ activation, the CS surface structures (figure 5o) have burnt-out pore with tunnel. The unclogged pore contributed high BET surface area with high micropore porosity ratio (76.55%) for CS bioadsorbent stimulated under $N_2 > Air$ activation. At the same time, the morphology of PKS attests substantial changes provoked by $N_2 > Air$ activation. Figure 5p clearly attested the porous nature with a predominant microporous character (pore size for PKS bioadsorbent is 0.63 nm) responsible for the developing of high surface area and high iodine adsorption. In addition, figure 5o,p also proved that $N_2 > Air$ activation managed to unclog the pores deposited with tarry material, silica or silicate derivatives during the process of physical activation. The surface morphology in figure 5o,p shows favourable characteristics for high adsorption capability, elucidating that $N_2 > Air$ two-stage continuous physical activation is effective in creating well-developed pores for CS and PKS bioadsorbents.

Overall, it was observed that bioadsorbent generated under one-stage physical activation failed to create sufficient porosities, caused by the deficient decomposition of organic constituents existing in the carbonaceous precursors. Thus, the pores were significantly clogged by the residues of products, leading to a decreased surface area with less porosity. $N_2 > Air$ activation prompted the bioadsorbent with the surface area consisting of abundant micropores, instigating the high BET surface area for both bioadsorbents. The SEM results have displayed that $N_2 > Air$ activation created new ultra-micropores and enlarged existing pores to generate new supermicropores and mesopores. Besides, $N_2 > Air$ activation would have made previously closed ultra-micropores accessible. Lignocellulosic biomass generated with $N_2 > Air$ activation thereupon was suggested as it was able to reduce the formation of silica, which blocked the pores and constrained the development of pores structures.
3.5. CHNS/O and ash content

Evaluation of the element data in this study was performed only on the non-treated and pretreated bioadsorbent that obtained the highest adsorption properties from one-stage physical activation and two-stage continuous physical activation.

The physico-chemical characteristics and potential uses of adsorbent are greatly influenced by the biomass feedstock, feedstock pretreatments, carbonization method and activating conditions, such as temperature, gas type and reaction time [62]. Table 4 presents the contents of carbon, hydrogen, nitrogen, oxygen and ash content of the bioadsorbent. Compared with the non-treated bioadsorbent, H3PO4 pretreated bioadsorbent displayed a very distinctive chemical composition. The carbon content was much higher, whereas its contents of hydrogen, nitrogen, sulfur and ash, were lower. This distinctive chemical composition suggests that the H3PO4 pretreated bioadsorbent might have its unique structure, which would considerably affect its adsorption behaviour. For instance, the high-ash content could render the bioadsorbent less polar and give rise to its higher affinity to non-polar adsorbates compared with the ordinary activated carbons [30]. Carbon content will be higher after physically activation [63]. Generally, the carbon content should increase with physical activation temperature, because there is an enrichment of elemental carbon, while the other elements, such as nitrogen, are largely removed with the off-gases during the physical activation [64]. Table 4 shows that the carbon content of both bioadsorbents increased as the ash content decreased significantly. This could have been caused by physical activation at high temperature in which most of the organic substances were degraded and discharged as gas and liquid tars, while leaving the material with high carbon purity [65,66]. As shown in table 4, CS and PKS bioadsorbent prepared under N2 activation have a higher carbon content compared with Air activation. Whereas, the ash content for both bioadsorbents produced under air activation was higher than under N2 activation. A greater value of ash content aids the limited combustible components kept in the pretreated biomass [67]. Under the circumstances, it was inadequate to carbonize the CS and PKS using only air as the carrier gas in the whole activation process.

According to table 4, the carbon content of bioadsorbents prepared under one-stage physical activation is lower than two-stage continuous physical activation. The increased carbon content was due to the thermal degradation of volatile components [68]. The highest carbon content for CS and PKS bioadsorbent was 69.12 and 65.11% when both bioadsorbents were activated at 600°C under N2 > Air activation. Owing to the high carbon content, bioadsorbent which was prepared by two-stage continuous physical activation is the preferred adsorbent in comparison to one-stage physical activation. The increase of carbon content also indicates an increase in the polarity upon mild oxidation of N2 > Air activation. This indicates that the PKS and CS bioadsorbent fits into the active carbon. Moreover, the off-gases that develop during N2 > Air activation in an oxygen-poor environment are used for their energy potential. The remaining solid that is rich in elemental carbon may be used in various applications [64]. Table 4 illustrates that the ash content for bioadsorbent prepared under Air > N2 was higher than N2 > Air activation. The higher ash content from Air > N2 activation suggests the presence of higher amount of oxides or inorganic impurities formed at the surface of bioadsorbent. It is known that the presence of ash can affect the chemical characteristics and the adsorptive behaviour of activated carbon [68]. Thus, bioadsorbent with the low level of ash obtained via N2 > Air activation obtained in the present study has a desirable characteristic. The elemental analysis revealed that the sample with the highest carbon content was prepared via N2 > Air activation, which supports the fact that this physical activation is suitable for producing high-grade activated carbon. Nitrogen content and sulfur content of the samples prepared in two-stage continuous physical activation were very low in the analysis. For elemental analysis, oxygen content is also an important aspect, because it can form surface oxygen functional groups, such as carboxylic acid and carbonyls that have an impact on the adsorption process [55,69]. The higher the oxygen content, the lower the amount of surfactant adsorbed [70]. In this present study, N2 > Air activation formed highly porous bioadsorbent with oxygen content that is lower than other carbon materials produced by conventional processes.

3.6. FTIR

Evaluations of the surface chemical characteristics in this study were performed only on the bioadsorbent that obtained the highest adsorption properties and the highest surface area for both bioadsorbent prepared under one-stage physical activation (N2 for at 700°C) and two-stage continuous physical activation (N2 > Air at 600°C).
| physical activation                  | time (min) | gas carrier | temp. (°C) | C   | N   | S   | H   | O   | ash |
|-------------------------------------|------------|-------------|------------|-----|-----|-----|-----|-----|-----|
| control (non-treated bioadsorbent)  | 75         | N₂          | 700        | 46.45| 47.12 | 0.53| 0.48| 0.01| 0.01| 8.32| 4.65| 44.69| 47.74| 34.43| 37.21|
| one-stage physical activation       | 75         | Air         | 700        | 63.03| 59.22 | 0.38| 0.39| 0.01| 0.01| 8.15| 4.56| 28.43| 35.82| 9.95 | 9.65 |
|                                     | 75         | N₂          | 700        | 63.44| 61.88 | 0.39| 0.38| 0.01| 0.01| 8.65| 4.01| 27.51| 33.72| 6.89 | 7.54 |
|                                     | 115        | Air         | 700        | 54.23| 49.76 | 0.42| 0.43| 0.01| 0.01| 9.12| 5.07| 36.22| 44.73| 13.65| 14.11|
|                                     | 115        | N₂          | 700        | 57.85| 52.58 | 0.31| 0.40| 0.01| 0.01| 8.79| 4.93| 33.04| 42.08| 12.08| 12.87|
| two-stage continuous physical activation | 115   | Air > N₂    | 700        | —    | —    | 62.03| —    | —    | 0.35| —    | —    | 1.40| —    | 36.16| 6.13 | 9.28 |
|                                     | 115        | Air > N₂    | 800        | 56.90| —    | —    | 0.07| —    | 0.06| —    | —    | 6.76| —    | 36.21| 8.13 | 14.37|
|                                     | 115        | N₂ > Air    | 600        | 63.91| 65.11 | 0.06| 0.33| 0.06| 0.06| 3.88| 1.50| 26.88| 33.00| 5.42 | 5.56 |
Figure 6 displays the FTIR spectra of bioadsorbents derived from CS and PKS prepared under N2 single physical activation and N2 Air two-stage continuous physical activation. Figure 6 suggests that N-containing groups were introduced to the structure of bioadsorbent that was prepared under N2 activation. Peaks of 1539, 1558 and 1618 cm\(^{-1}\); and 1558 and 3319 cm\(^{-1}\) indicate the presence of N–H stretch on the CS and PKS bioadsorbent, respectively [71]. The higher adsorption rate and capacity toward heavy metal was obtained in the case of nitrogenated carbons. In this aspect, nitrogen-containing porous carbons with high surface area are recently receiving a great deal of attention due to their specific structures and unique properties [72–75]. For example, they show enhanced adsorption capacity of anions, resulting from a positively charged carbon surface, and improved thermal stability by incorporating heteroatoms when they are used as catalytic supports [75].

The new appearance of bands from 650 to 900 cm\(^{-1}\) indicate an increase in aromatic nature for the activated compounds [76] prepared under N2 > Air activation. The peaks of 742, 812 and 899 cm\(^{-1}\) in CS bioadsorbent and 723, 781, 814 and 916 cm\(^{-1}\) might be due to the presence of C–H out of plane bending in benzene derivatives. FTIR reveals the broad peaks at 1213 and 1212 cm\(^{-1}\) on CS and PKS bioadsorbents under two-stage continuous activation, respectively. Peaks detected at 1200–1300 cm\(^{-1}\) attribute to C–O–C group of stretching mode in acids, alcohols, phenols, ethers and esters [77,78]. It can be stated that N2 > Air activation formed ester linkages with the –OH groups helping to cross-link the polymer chains of the bioadsorbent. Additionally, the general increase in band intensities with activation treatment from around 600 to 1300 cm\(^{-1}\) is indicative of phosphorus-containing groups being formed during thermal activation [76]. Two-stage continuous physical activation (N2 > Air) also promoted two sharp peaks at 1368 and 1578 cm\(^{-1}\) for CS bioadsorbent and one sharp peak at 1368 cm\(^{-1}\) for PKS bioadsorbent. These sharp peaks can be ascribed to the asymmetric COO\(^{-}\) vibration and symmetric COO\(^{-}\) vibration, respectively [79,80]. Absorptions at 1578 cm\(^{-1}\) present on CS adsorbent correspond to C–C stretching vibrations and NH2 in the benzene ring. Based on the study, both bioadsorbents expressed a more distinct absorbance by oxygenated groups at 1740 cm\(^{-1}\). This peak absorption reveals that mild oxidation from N2 > Air physical activation increases the concentration of carbonyl functional groups on the surface of the CS and PKS bioadsorbent. Mild air oxidation generates a more uniform spatial distribution of oxygenated functional groups for the adsorbent [81].
bands at 1725–1740 cm\(^{-1}\) are the characteristic stretching vibration of carbonyl group C=O in esters and carboxylic acids [79,80]. Whereas, there are strong peaks located at 2302 and 2384 cm\(^{-1}\) for CS bioadsorbent and 2302 and 2346 cm\(^{-1}\) in PKS bioadsorbent. These peaks assign to the vibration of C=N and C=C, respectively [82]. CS bioadsorbent showed a weak but visible absorption at 2564 cm\(^{-1}\) considered as S–H bond stretching vibration. These clearly demonstrated that –SH group had been successfully grafted onto the surface of CS bioadsorbent prepared under N\(_2\) > Air physical activation. Figure 6 displays the peaks of 2967 cm\(^{-1}\) in CS bioadsorbent and 2869 and 2972 cm\(^{-1}\) in PKS bioadsorbent which represent the characteristic of C–H stretch of imidazole. Anisuzzaman [77] stated that spectra range between 2800 and 3000 cm\(^{-1}\) refers to the C–H stretching in the alkane group. Likewise, figure 6 indicates spectra’s vibrations, implied that it may have the presence of monomeric alcohols or phenols due to the wavenumbers corresponding to 3010, 3439 and 3670 cm\(^{-1}\) for CS bioadsorbent and 3635 cm\(^{-1}\) for PKS bioadsorbent prepared under N\(_2\) > Air activation. Anisuzzaman [77] also reported that the peaks detected in the spectra at bandwidths of 3300–3800 cm\(^{-1}\) represent O–H stretching vibration of surface hydroxylic functional groups in low concentrations. Besides, the band of O–H stretching vibrations reveals the existence of chemisorbed water from the activated bioadsorbent. The asymmetry of this band indicates the presence of strong hydrogen bonds in the adsorbent [83].

The surface chemistry and pore structure of porous carbons determine its application. The surface chemistry could be modified by various methods, such as acid treatment, oxidation, ammonization, plasma, microwave treatment and others. Oxygen-containing functional groups have been devoted as the main groups responsible for heavy metal binding on the activated carbon surface [48]. It was found that the N\(_2\) > Air two-stage continuous physical activation not only greatly increased the specific surface area but also caused the formation of oxygen-containing groups (–OH and C=O) on the CS and PKS bioadsorbent surface. Oxidation is one of the most conventional modification techniques used to induce or enhance oxygen functional groups on the surface of activated carbon such as carboxylic, lactones, phenols, ketones, quinones, hydroxyl and carboxylic anhydride [48,84]; it can also remove the mineral elements and improve the hydrophilic nature of the surface [48,85]. These acidic surface groups are polar and enhance the ion exchange properties of the carbon, thereby increasing the adsorption of cation [48,85]. Thus, the surface oxygen-containing functional group had been adequately introduced to the bioadsorbent via N\(_2\) > Air activation in this study. Owing to the high surface areas and well-developed porous structures, and the presence of different types of functional groups on their surfaces, the porous bioadsorbent prepared via N\(_2\) > Air may be applied in many areas including the protection of natural environment by removing sulfur compounds, nitrogen oxides and carbon dioxide; purification of wastewater by removing heavy metal ions, aromatic compounds and dye molecules; use of catalysis or catalyst supports and others.

3.7. TGA

Evaluations of the thermal behaviour characteristics in this study were performed only on the bioadsorbent that obtained the highest adsorption properties and the highest surface area for both bioadsorbents prepared under N\(_2\) > Air two-stage continuous physical activation at 600°C.

By analysing the TGA results, we found that bioadsorbent prepared under two-stage continuous activation gained a low weight loss. Three zones of the profile are obtained for both cases. Apparently with respect in increasing temperature from 400 to 800°C, the total weight loss for pretreated CS and PKS are 22.29 and 16.36%, respectively. From this result (figure 7), it was found that both physically activated bioadsorbents exhibit high thermal stability. The high thermal stability behaviour may be
due to the new oxygen functional groups introduced on the bioadsorbent via two-stage continuous activation. Some researchers had stated oxygen-containing function groups, such as anhydride, lactones and epoxy groups containing –C=O–C–, exhibited better thermal stability and were only decomposed at a higher temperature [86,87]. Approximately 63.83 and 69.01% of the mass for CS and PKS bioadsorbent, respectively, are still not volatilized at 1000°C. The greater thermal stability of the activated bioadsorbents is also thought to be because they have more stable structures with higher carbon assay [88]. Thus, TGA result displays that both bioadsorbents prepared via N2 > Air activation achieved high amount of residue.

4. Conclusion

Ash leaching method with phosphoric acid prior to physical activation is able to remove a huge fraction of ash-forming elements in biomass; however, it is unable to remove ash components such as silica or silicate from high-ash agricultural biomass such as PKS and CS. Removal of the silica compounds attached to the surface of the agriculture biomass opens up more reactive surfaces for the physical activation process and, thus, creates a bioadsorbent with a higher surface area. From this study, higher reduction of silica was achieved by additional stage of air activation after N2 activation (N2 > Air) which increased the development of pores structure on the bioadsorbent. This novel process was able to expose mesopores and micropores that were previously covered/clogged in nature, and simultaneously create new pores. The optimum condition to achieve the highest BET value for H3PO4 pretreated PKS and CS is via two-stage continuous physical activation of N2 > Air under 600°C activation temperature. Introducing low-temperature activation process as applied in this study modestly increases the feasible expansion potential towards industrial scale. This novel process of two-stage continuous physical activation meets the recent industrial adsorbent requirements of low activation temperature, high fixed carbon content, high yield, high adsorption properties and high surface area, which are the key factors in large-scale production and usage.

Data accessibility. Adsorption properties; BET surface area; N2 adsorption; FTIR and TGA files have been uploaded to the Dryad Digital Repository at: http://dx.doi.org/10.5061/dryad.ch8gf53 [89].

Authors’ contributions. C.L.L.: data collection, analysis and interpretation of data, drafting the article or revising it critically for important intellectual content. P.S.H.: agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. M.T.P.: final approval of the version to be published. K.L.C.: drafting the article or revising it critically for important intellectual content. U.R.: final approval of the version to be published. M.M.: acquisition of data. W.Z.G.: analysis and interpretation of data. R.A.R.N.: data collection. S.N.A.R.: data collection. P.S.K.: data collection.

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