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Synthesis, Adsorption and Catalytic Properties of Eggshell-Coconut Pith for Transesterification of Waste Cooking Oil

HARENDRA KUMAR*, and ANNAM RENITA

Department of Chemical Engineering, Sathyabama Institute of Science and Technology, Chennai-600119, India

*Corresponding author: E-mail: hkumar11@rediffmail.com

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This study aims to develop a sustainable heterogeneous biocatalyst prepared from calcined eggshell waste impregnated with waste coconut piths for producing biodiesel from used cooking oil. Waste eggshells were subjected to thermogravimetric analysis for calcinations at suitable temperature under inert atmosphere. It was subjected to impregnation of coconut pith by physical and chemical adsorption. The prepared eggshell-coconut pith catalyst was optimized at different parameters like temperature, mass ratio of coconut pith, eggshell and variant concentration of the solvent used for socking of coconut pith and eggshell. The adsorption of coconut pith on the eggshell surface were characterized by BET analysis and SEM analysis, the size of atom of eggshell was increased after impregnation of coconut pith by 100 μm. The adsorption of coconut pith on eggshell was validated by Langmuir and Freundlich adsorption models and order of impregnation reaction was verified by pseudo-first and pseudo-second order models. The effect of process parameters like amount of catalyst loading, oil: alcohol ratio, time, speed of iteration, pH of the solvent and temperature, which enhanced the yield of biodiesel to ~ 87%.

Keywords: Adsorption, Activated coconut pith, Biodiesel, Calcined eggshell, Transesterification.

INTRODUCTION

The entire world anticipates the production of energy through a variety of means to fulfill the requirements of all its population [1]. In order to meet the requirements of the population as a whole, a renewable impregnated calcined eggshell and activated coconut (ESCP) pith heterogeneous catalyst was synthesized to increase the yield of sustainable biodiesel energy from waste cooking oil. The impregnation of activated coconut pith and calcined eggshell formed a heterogeneous catalyst, which was used for the production of biodiesel from the waste cooking oil, its yield of biodiesel was increased from 20% to 87% by ESCP catalyst [2].

The eggshell consists of 95-98% of $CaCO_3$ [3], which calcined to CaO at a different temperature range of 400 to 800 ºC and the calcined temperature was optimized by TGA analysis, the optimum temperature for maximum conversion of $CaCO_3$ to CaO was 700 ºC [2]. The coconut pith has a microporous structure [4] and consists of lignin and cellulose [5], and lignin being more hydrophilic than cellulose [6]. Due to the porous structure of the coconut-pith.

The calcined eggshell-coconut pith catalyst was prepared by the impregnation of different mass ratio (1:1, 1:2, 1:3, 2:1, 3:1) of calcined eggshell (CES) and activated coconut pith (ACP), soaked in KOH solution and impregnated in different normality of HNO_3 acid for the duration of 1, 2 and 3 h, which was continuously stirred to get the mixed solution. The solution was centrifuged to separate the centrifuged semi-solid, which was then calcined at 400-800 ºC to produce the required eggshell-coconut pith (ESCP) catalyst. The product was then analyzed to find the adsorption efficiency of the coconut pith on the eggshell by FTIR, BET and SEM analysis.

EXPERIMENTAL

Synthesis: The process flow sheet for the impregnation of coconut pith on calcined eggshell is depicted in Fig. 1.

Eggshell: The chicken eggshells waste was collected from the local cafeteria and washed thoroughly with deionized water to remove the unwanted deposited substances from the surface of waste eggshells. It was dried in an oven at 100 ºC and crushed. The crushed eggshell was sieved through a standard 100 μ size to achieve a uniform particle size prior to calcination.

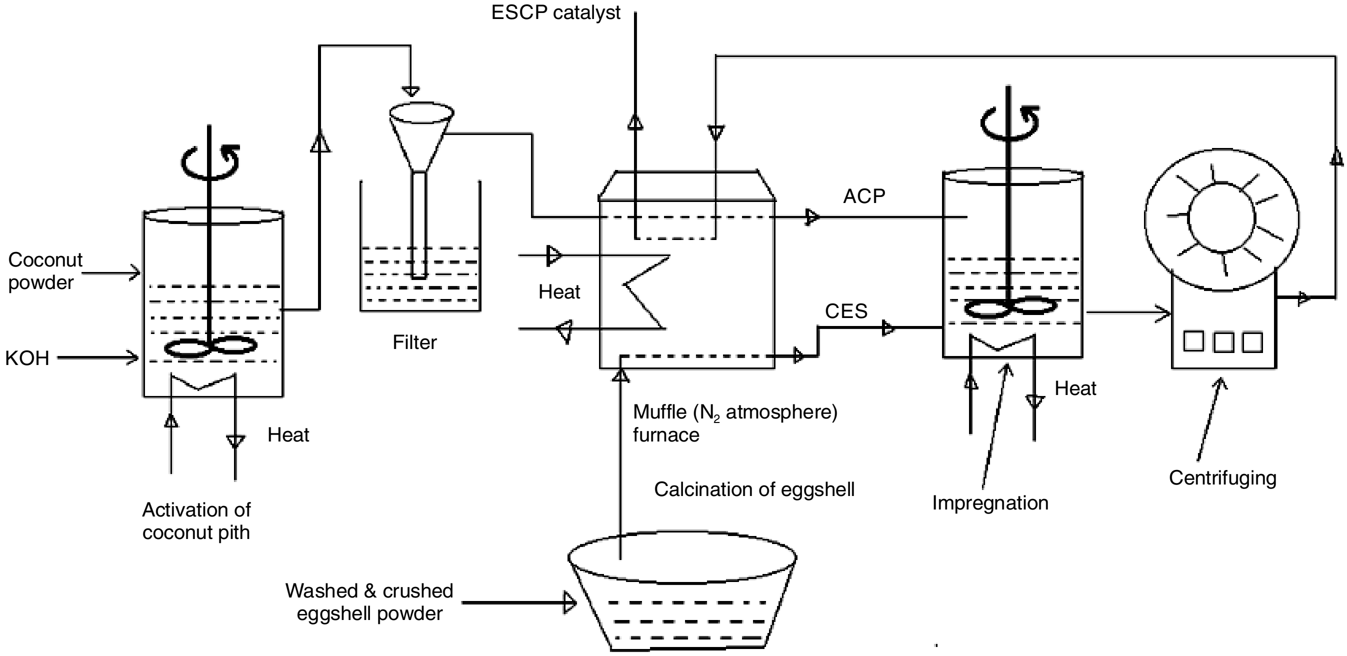

Fig. 1. Process flow sheet for impregnation of ACP and CES

Coconut-pith: The waste coconut pith was also collected from the local cafeteria and the outer layer was removed. The waste coconut was utilised to remove the brown-colored fibres (coconut pith), which were then manually crushed and powdered. The powdered coconut pith was sieved to 100 μ size [7].

Method of impregnation of calcined eggshell and activated coconut pith

Calcination of eggshell: The waste chicken eggshells were collected and washed two-three times by deionized water to remove unwanted substances from the surface of the eggshell. It was dried in an oven at 100 ºC and ensured to be free from moisture and then crushed to get a uniform particle size of 100 μ, which was ensured by sieving of a 100 μ particle size sieve. The crushed eggshell powders were weighed for five batches, each of 10 g and calcined these batches of egg-shells were in muffle Furness at a temperature from 400-800 ºC in N_2 inert gas atmosphere for a duration of 1 to 4 h at the time interval of 1.0 h, it was placed in a desiccator for further use. The calcined eggshells were subjected to TGA analysis to determine the optimum temperature of calcination for the maximum conversion in CaO [8].

Activation of coconut pith: The waste coconut piths were collected from the outside of the cafeteria of IGCAR (Indira Gandhi Centre for Atomic Research) and grinded to make a uniform size of 100 μ size, which was ensured by sieving of a 100 μ size sieve. The coconut piths were soaked in 7 M of KOH solution for a duration of 1 to 4 h, then further calcined at 400 ºC optimum temperature [9]. The duration of soaking of coconut pith was determined for maximum adsorption of coconut pith on eggshell, the activated coconut pith was abbreviated as (ACP).

Impregnation of calcined and activated eggshells: The activated coconut pith (1 to 10 g) was dissolved individually in 100 mL each of 0.1 N of HNO_3 as a ten batch and stirred to get a uniform mixture [10] and subsequently different combinations of calcined eggshells (CES) (1 to 10 g) were added to activated eggshells (ACP) solution and further stirred for different duration of 1 to 5 h to determine the optimum ratio of ACP/CES and time for the maximum adsorption. The mixed solution was centrifuged at different times ranging from 1 to 5 h for calcined eggshell at different temperature range from 200 to 700 ºC. There was a two-phase formation after centrifuging, the bottom phase was semi-solid and the top phase was the mother solution. The concentration of the mother solution was determined, which was the least concentration compared to the initial concentration, the difference in concertation of ACP and CES in the initial and mother solution was the adsorbed concentration of ACP and CES. This procedure was repeated for all the combinations of ACP and CES at different times and temperatures. The speed of agitation of impregnation was kept at the constant optimum speed of 700 rpm for all the combinations. The semi-solid phase after centrifuging was undergone further calcination at the optimum temperature of 600 ºC for the optimum duration of time. The calcined mixture of ACP and CES was require an impregnated catalyst, it was abbreviated as ESCP.

Method of adsorption

Variation of eggshell/coconut-pith ratio: The calcined eggshell and activated coconut pith were taken in different mass ratios like 1:5, 1:4, 1: 3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, respectively and stirred at the optimum temperature, time, speed in 100 mL of 0.1 N HNO_3 and obtained adsorption of coconut pith after centrifugation [11]. The mass ratio of calcined eggshell and activated coconut pith at maximum adsorption was determined as the optimum mass ratio of calcined eggshell and activated coconut pith.

Effect of nitric acid: The calcined eggshell and activated coconut pith of 1:1 mass ratio was stirred at the different concentrations of nitric acid *viz.* 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10 and 0.11 N at the optimum parameters and centrifuged for 10 min at 2400 rpm. The amount of eggshell and coconut pith composition was determined in the mother liquid. The difference in the amount of eggshell-coconut pith from feed and mother liquid will be loaded amount of eggshell and coconut pith.

Effect of concentration of calcined eggshell and activated coconut pith: The calcined eggshell and activated coconut pith of 1:1 mass ratio were stirred with different concentrations *viz.* 20, 40, 60, 80, 100, 120 and 140 mg/mL of mixed solution at an optimum parameter of time, speed and temperature. It was centrifuged and then the maximum adsorption was determined. The corresponding concentration of feed solution at maximum adsorption was considered the optimum concentration of the feed solution.

Effect of time: The calcined and activated coconut pith solutions were stirred for different periods of 1.0, 2.0, 3.0, 4.0, 5.0 and 7.0 h at the optimum temperature, speed and mass ratio. It was centrifuged at 2400 rpm and adsorption was determined by a change in the concentration of mother solution and feed solution individually for all batches. The optimum time was determined for the maximum adsorption of activated coconut pith.

Loading of ACP on CES with the variation of feed concentration: The calcined eggshell and activated coconut pith solution were prepared for different concentrations (20-140 mg/mL) and stirred at optimum parameters for each batch separately, it was centrifuged separately and determined the amount of ACP loaded per unit mass of CES (mg/mg) by the following eqn. 1:

$$\text{Amount of ACP loaded} = \frac{C_o - C_e}{C_o} \quad (1)$$

where C_o = initial concentration of ACP in feed, C_e = final concentration of ACP at equilibrium.

Adsorption of ACP with a variation of temperature: The calcined eggshell and activated coconut pith were stirred at varying temperatures from 30 to 90 ºC at constant other parameters like speed, time, the mass ratio (1:1) and concentration of feed solution. It was centrifuged and determine the adsorption after every 10 ºC interval of temperature.

Effect of contact time: The calcined eggshell and activated coconut pith were stirred at optimum parameters and kept for a time duration of 1, 2, 3, 4, 5, 6 and 7 h, it was centrifuged individually for all batches and placed in a desiccator for 1 to 7 h to contact the subtract and determined the percentage adsorption of ACP for each batch separately by eqn. 2.

$$\text{Adsorption (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o = initial liquid phase concentration of ACP, C_e = equilibrium liquid concentration of ACP.

Effect of pH: The calcined eggshell and activated coconut pith solution were prepared in nitric acid of optimum strength. The pH of the solution was adjusted to 2 to 8 by adding HCl and NaOH and stirring the solution of every batch at optimum parameters and percentage adsorption was determined.

Effect of speed of stirring: The calcined eggshell and activated coconut pith were stirred at a different speed from 200 to 800 rpm keeping the other optimum parameters constant. It was centrifuged for every batch of process operation and the percentage adsorption was also determined by eqn. 2.

Equilibrium studies: The calcined egg-shell and activated coconut pith different initial concentrations were prepared from 20-140 mg/mL at 30 ºC. The equilibrium adsorption of ACP was determined (eqn. 3), and the validity of the Langmuir and Freundlich adsorption isotherms was verified.

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

where C_o = initial concentration of ACP, C_e = equilibrium concentration of ACP (mg/mL), V = volume of solution (mL), W = mass of dry adsorbent (mg).

RESULTS AND DISCUSSION

Calcination of eggshell: The eggshell was calcined at different temperatures ranging from 100-800 ºC in a muffle furnace in inert gas atmosphere for a duration of the time period from 1.0 h to 4.0 h and optimized the temperature of calcination at 600 ºC, the weight loss of eggshell for each batch of process operation was determined, the percentage loss of eggshell was calculated from following chemical equation followed by mole concept method [12,13]:

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2 \uparrow \quad (4)$$

After 1 h of heating, the eggshell's colour changed partially from white to black and then from black to light brown, indicating that some CO_2 was released. After 3 h of heating at 600 ºC, the eggshell's colour changed again and this time partially from brown to white [14]. The calcinated eggshell became 100% white at 700 ºC upon 4.0 h heating, it means that almost CO_2 has released and only CaO remains [14].

The mass deviation of the calcinated eggshell was determined as -1.96% based on the TGA plot, whereas the minimal mass deviation of -23.37% was obtained from the DTG (derivative thermogravimetry) analysis and the residual mass at 797.9 ºC was found to be 76.63%. The optimum operating temperature for calcination of eggshell was 797.9 ºC for 4 h.

Effect of concentration of KOH for maximum loading of coconut pith: The pulverized coconut pith was filtered using a screen with a mesh size of 100 μ. Subsequently, it was immersed in different concentrations of KOH solution, maintaining a consistent ratio of 5 g of pith per 100 mL of KOH [15]. TThe maximum loading capacity of coconut pith was tested at various concentrations ranging from 1 to 8 M of KOH. It was found that the loading of coconut pith began to decrease at 8 M KOH. However, as the concentration of KOH increases, the pith degraded and lost some of its qualities [16,17]. The reason for this behaviour is that when the material is exposed to KOH solution, the double covalent link is weakened, leading to the formation of a hydroxyl (-OH) functional group with the lignin. A higher concentration of KOH makes this group more stable, but it damages the lignin's benzene structure, so no -OH functional group forms after 7 M [17]. The properties of coconut pith and its composition is given in Table-1. Hence 7 M concentration of KOH would be the maximum and optimum loading of coconut pith as 65.25 mg/mL as shown in Fig. 2.

TABLE-1
PROPERTIES AND COMPOSITION OF COCONUT PITH [Ref. 17]

Properties	Value	Composition	Value (%)
Length of cell of coconut pith	0.8-1.06 mm	Carbon	62.55
		Hydrogen	6.1
Width of the cell of coconut pith	1.4-1.6 mm	Oxygen	27.4
		Nitrogen	2.0
Area of cross-section for cell of coconut pith	1.6×10^{-4} mm^2	Silicon	1.1
		Calcium	0.5
Density	1.45-1.52 g/cm^3	Lignin	0.35

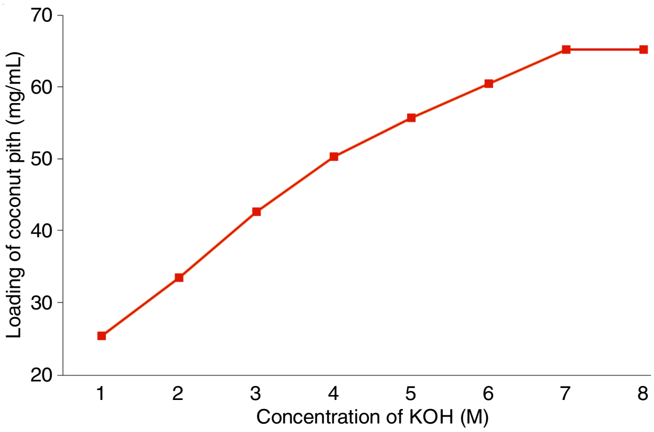

Fig. 2. Effect of KOH concentration for the loading of coconut pith

Effect of calcined eggshell and activated coconut pith mass ratio to adsorption in nitric acid: Before calcination, the eggshell consisted approximately 95-98% $CaCO_3$ whereas after calcination, all of the $CaCO_3$ is transformed into CaO. The adsorption was evaluated by testing multiple ratios of CES and ACP, including 1:1, 1:2, 1:3, 1:4, 1:5, 5:1, 4:1, 3:1, and 2:1, to find the optimal combination of eggshell and coconut pith for maximal adsorption. It was found that the adsorption subsequently increases for CES/ACP ratio from 5:1 to 1:1 and subsequently decreases from 1:1 to 1:5, the CES/ACP mass ratio of 1:1 was giving maximum adsorption in the nitric acid medium as shown in Fig. 3.

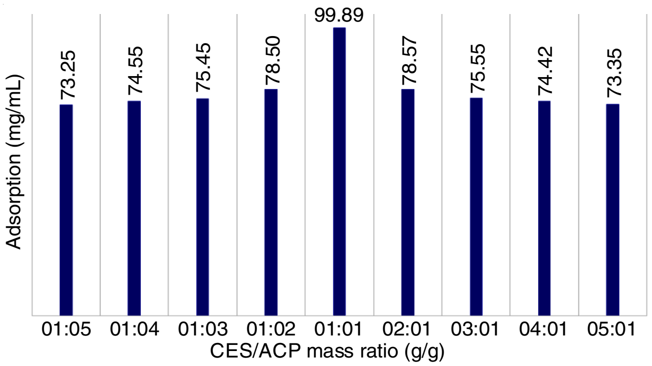

Fig. 3. Effect of ratio of eggshell/coconut pith to adsorption of CES and ACP (mg/mL)

The coconut pith consists of cellulose, which has 62.5% carbon, 6.1% hydrogen, 27.4% oxygen, 2.05% nitrogen, 0.5% calcium and 0.35% lignin [17]. This composition forms the functional group of -O-, CH=O and this -CH=O functional group was linked with KOH and formed -OH functional group during ACP formation, these -OH functional group was verified by peak at 3431 cm^{-1} from the FTIR spectrum. The eggshell, composed of $CaCO_3$, underwent calcination to produce CaO [18], which was confirmed by the presence of a peak at 709.96 cm^{-1} in the FTIR analysis. Thus, CaO was reacted with HNO_3 and formed $Ca(NO_3)_2$ in eqn. 6 during the CES formation [18].

$$CaO + HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O \qquad (5)$$

Calcined eggshell nitrate form of eggshell: During the formation of ACP, cellulose contained potassium (K) with a functional group of -OH. The K combined with $-NO_3$ in a nitric acid solution, resulting in the formation of KNO. This compound was separated and confirmed to be present in the liquid through FTIR analysis. The cellulose still retained the -OH and -O- functional groups, which were free to form bonds. This was confirmed by the presence of a peak at 3431 cm^{-1}, indicating the -OH functional group, while the peak at 2516 cm^{-1} indicate the presence of $Ca(OH)_2$. The majority of $-NO_3$ functional group was released as KNO_3 during the final stage of ESCP catalyst formation, with only a small amount potentially linking with -O-, calcium and lignin. Consequently, the presence of CaO, -OH, and $-O-Ca-NO_3$ was confirmed together with the composition of cellulose and lignin in the final step of ESCP catalyst synthesis. A chemical composite compound of eggshell and coconut pith was formed by combining one mole of cellulose with one mole of CaO (CES). The maximum adsorption occurred at a 1:1 ratio of CES and ACP, resulting in an increase in the surface area of the eggshell-coconut pith (ESCP) by 4.19 m^2/g as confirmed by BET analysis. This increase in surface area confirms the adsorption of ACP on calcined eggshell [19].

Effect of concentration of nitric acid on the loading of CES and ACP: The CES and ACP of 1:1 mass ratio was mixed and dissolved in different strengths of nitric acid (0.02 -0.11 N) at the interval of 0.01 N [19] of each batch and stirred at optimum parameters. It was observed that the loading of ACP and CES gradually increases up to 0.1 N HNO_3 and after that loading of CES and ACP becomes constant. The loading of ACP followed the same pattern as CES in the loading plot, indicating that CES served as a carrier for ACP. However, after treating with 0.1 N HNO_3, the adsorption declined, suggesting that both CES and ACP were completely loaded [19] (Fig. 4). The highest loading of CES and ACP was achieved while using a 0.1 N nitric acid solution.

Effect of change of feed concentration to the final product concentration: An equimolar mixture of CES and ACP was dissolved in nitric acid at different concentrations ranging from 20 to 140 mg/mL. Each batch of the process was conducted under optimal conditions and the resulting product was centrifuged for 10 min. The data indicates that the concentration increased in direct proportion to the availability of free bonds in the eggshell and cellulose. At a initial concentration of 100 mg/mL,

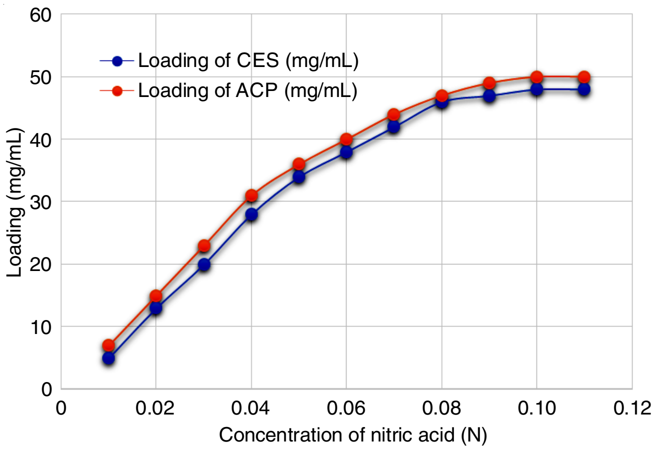

Fig. 4. Effect of concentration of nitric acid for loading of CES and ACP

the maximum adsorption of CES and ACP occurred when all the free bonds of cellulose were occupied with radicals. Beyond this concentration, the adsorption remained nearly constant as there were no more available free bonds in the adsorbent. Fig. 5 shows that a concentration of 100 mg/mL was the most effective for achieving maximal adsorption of CES and ACP.

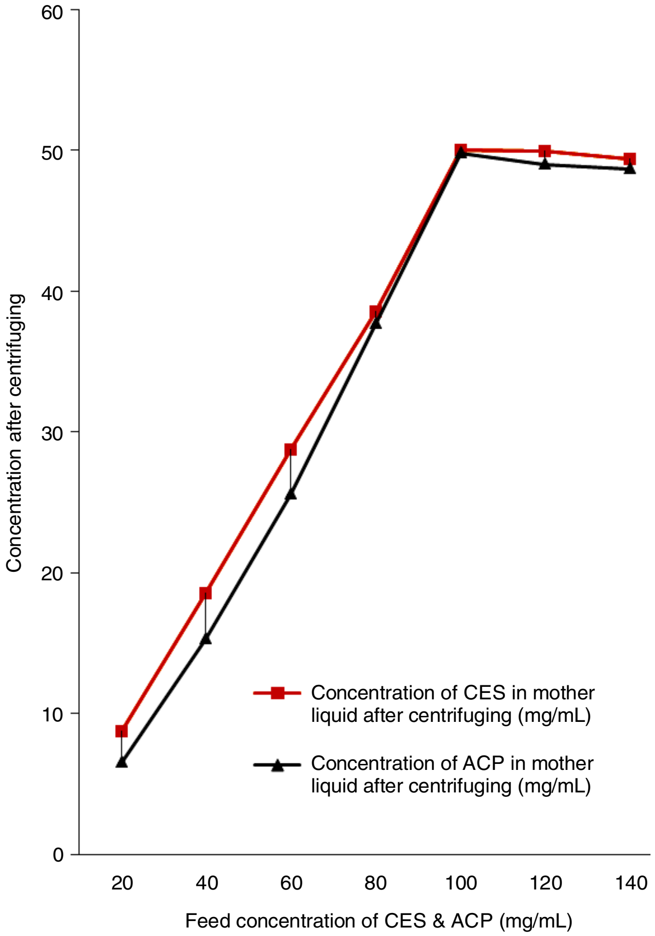

Fig. 5. Effect of change of feed concentration to concentration of final product (mg/mL)

Effect of feed concentration to loading of ACP to CES: At a mass ratio of 1:1, the feed concentration of CES and ACP was varied between 20 and 140 mg/mL, with 20 mg/mL intervals between batches, while other optimal parameters remained fixed. At a concentration of 20 mg/mL, the amount of ACP was 0.74 mg/mg. As the feed concentration increased, the amount of ACP gradually increased, reaching a maximum of 0.99 mg/mg at 100 mg/mL. From there, it remained relatively constant as the feed concentration increased, which is due to the fact that the free bond in ACP's cellulose is not readily available. Therefore, at a feed dosage of 100 mg/mL for both CES and ACP, the maximum loading of ACP to CES was 0.99 mg/mg (Fig. 6).

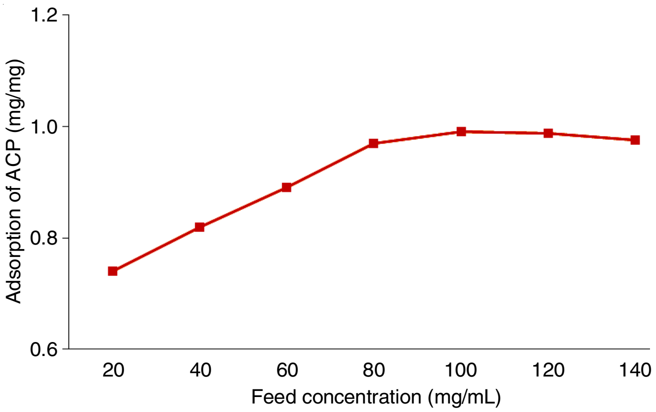

Fig. 6. Effect of concentration of feed to adsorption of ACP (mg/mL)

Effect of change in feed concentration to percentage adsorption of ACP on CES: The feed concentration of ACP and CES with 1:1 mass ratio solution was varied from 20 mg/mL to 140 mg/mL in HNO_3 medium with the interval of 20 mg/mL and stirred at constant optimum parameters like stirring speed, time and temperature. When the feed concentration was 20 mg/mL, the adsorption percentages of ACP and CES were approximately 35% and 70%, respectively. As the feed concentration increased to 100 mg/mL, the adsorption percentages of CES and ACP began to reverse, with the former showing an increase and the latter a decrease (Fig. 7). Adsorption occurred up to a concentration of 100 mg/mL, followed by subsequent desorption. The concentration of the feed solution at 100 mg/mL represents the state of equilibrium. The adsorption of ACP was around 49% whereas the CES accounted approximately 51%.

Effect of time on the adsorption of ACP on CES: The feed concentration for 1:1 mass ratio of CES and ACP solution was stirred with varying times from 1 to 7 h while keeping the other optimum parameters constant. The adsorption of ACP was observed from the first to third hour of the experiment, which increased steadily from 25 mg/mL to 40 mg/mL and then reached a saturation indicating that adsorption became saturated by the third hour (Fig. 8). The free radical in the ACP was fully bonded, leaving no remaining unbound sites for subsequent bonding with CES. Therefore, the minimal desorption occurred between 4 to 7 h.

Effect of temperature on adsorption of ACP: The calcined eggshell and activated coconut pith were taken in equal amounts, dissolved in 0.1 N HNO_3 and stirred at a different temperature varying from 30 to 90 ºC with the interval of 10 ºC, keeping

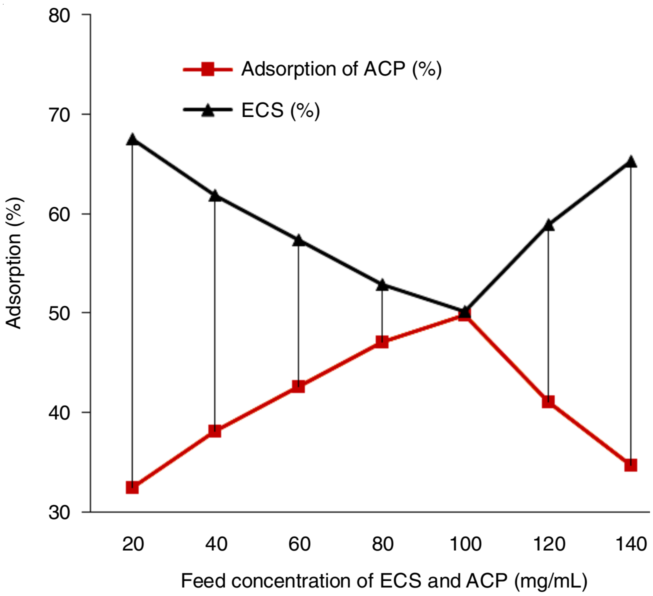

Fig. 7. Effect of feed concentration on percentage adsorption of ACP on CES

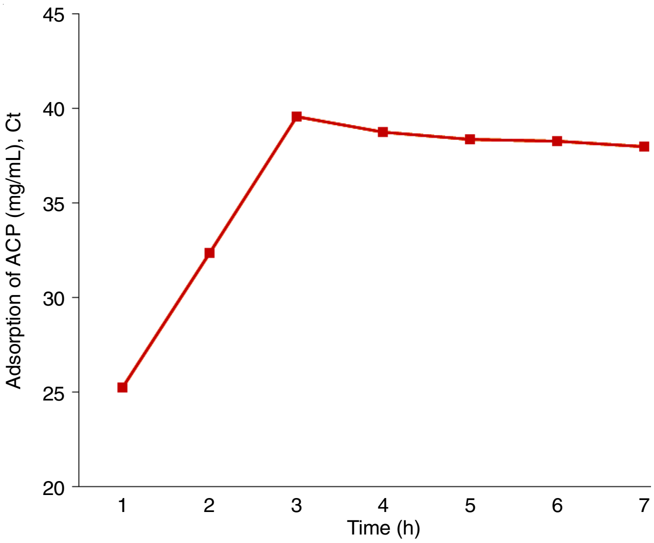

Fig. 8. Effect of time to the adsorption of ACP (mg/mL)

other parameters constant and observed the adsorption of ACP as depicted in Fig. 9, when the temperature was increased from 30 to 40 °C. Intially, the adsorption increases but not proportionally until 70 °C because at high temperature, the electrons were freely available for adsorption [20]. At high temperature more will be free electrons for the formation of bound but it will continue when all electrons of the outermost orbit were getting exhausted and hence no new bond formation will take place and it was continued to maintain same adsorption after 70 °C because there were no free electrons to form the bond between CES and ACP [21].

Effect of contact time on the adsorption of ACP on eggshell: Calcined eggshell and activated coconut pith were impregnated at optimized parameters, and after stirring, the solution was left to settle for a different time interval. The initial adsorption of ACP was 62% after 1 h of contact time. The adsorption steadily increased until 5 h of contact time and then it

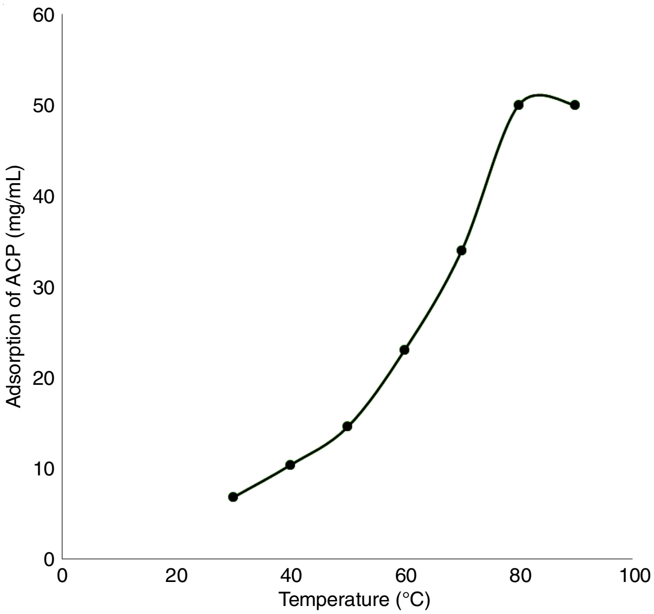

Fig. 9. Effect of temperature on adsorption of ACP

become saturated (Fig. 10). This was happened due to the absence of a chemical interaction between CES and ACP at shorter contact times. As duration of contact increases, the quantity of bonds and their length also increase [22]. Additionally, the number of adsorbate molecules will reach a maximum value with more time, leading to an increase in the percentage of adsorption. The adsorption remained constant between 5 and 7 h of contact time, as all the adsorbate had formed bonds with the adsorbent and the adsorption reached saturation at 5 h of contact time.

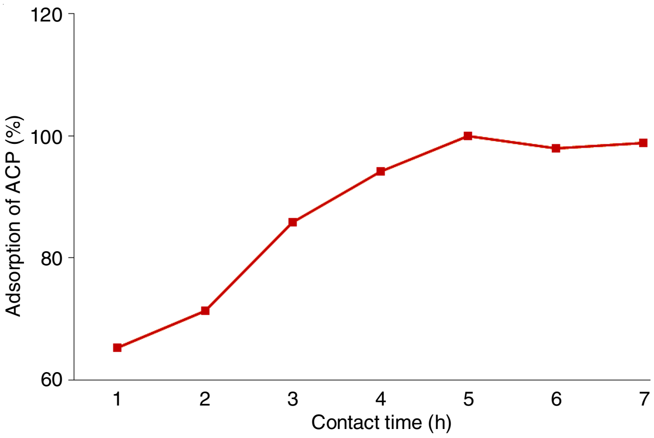

Fig. 10. Effect of contact time on the adsorption of ACP

Effect of pH on the adsorption of ACP by calcined eggshell: The solution consisting of calcined eggshell and activated coconut pith was combined in 0.1 N HNO_3 and agitated. The pH value and the % adsorption of ACP were observed under optimal conditions for other parameters. The pH levels were modified by introducing either HCl or KOH, depending on the specific correction needed. Fig. 11 shows that the adsorption increased from 62% at pH 2 to 99% at pH 6, and then decreased to 65% at pH 8, which was happened due to the acidity levels

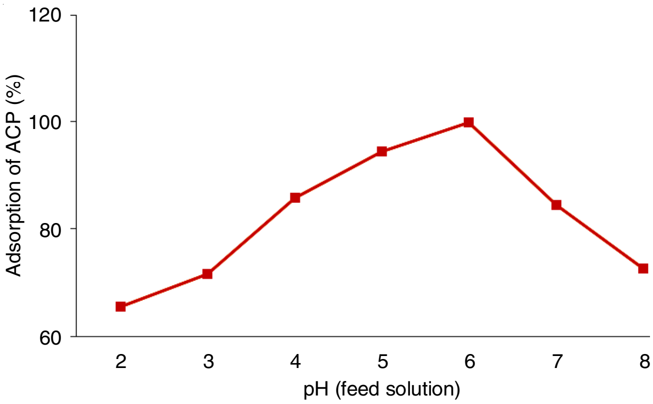

Fig. 11. Effect of pH on the adsorption of ACP

of feed solution as it exceed the saturation levels [23]. There was an increase in the desorption of ACP, leading to a decrease in the percentage of ACP adsorbed, in the more basic feed solution. This is because the -OH functional group in eggshells facilitates the formation of hydroxide of calcium as $Ca(OH)_2$ [24], which in turn separates the OH functional groups of lignin and cellulose in coconut pith [25,26].

Effect of stirring rate on the adsorption of ACP by CES: The calcined eggshell and activated coconut pith of 1:1 ratio was stirred with different speed ranging from 200 to 800 rpm while keeping the other parameters optimum and monitored the adsorption of ACP as shown in Fig. 12. Adsorption was 62% at 200 rpm and 99.1% at 600 rpm; however, adsorption decreased after 600 rpm for the following reasons: (1) the adsorbate and adsorbent were not thoroughly mixed at lower iteration speeds, so new bond formation did not occur; (2) free radicals were ionized at 600 rpm, leading to increased new bond formation and, consequently, more adsorption. For higher iteration speeds, the adsorbate started to disintegrate from the adsorbent surface and thus, the adsorption of ACP decreased with increasing iteration speeds.

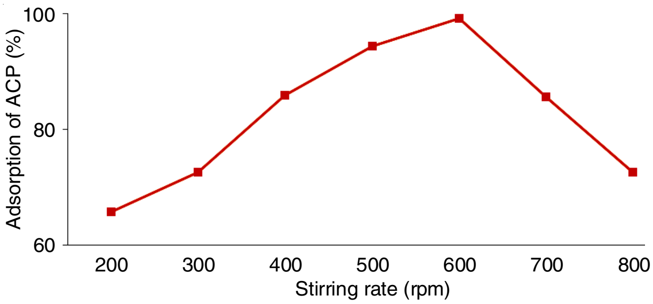

Fig. 12. Effect of stirring rate on the adsorption of ACP by CES

Isotherms and kinetic studies: Applying the Langmuir and Freundlich isotherm equations to the ACP adsorption synthesis data, we were able to derive an adsorption isotherm that exhibited a state of equilibrium between the adsorbate concentration, the amount of adsorbent accumulation, and the concentration of dissolved adsorbate.

Langmuir adsorption plot for adsorption of ACP by CES: The Langmuir adsorption isotherm can be presented as follows [26]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (9)$$

where C_e = adsorbent concentration at equilibrium (mg/mL), q_e = adsorption capacity at equilibrium (mg/g), b = adsorption equilibrium constant (mL/mg), q_m = maximum adsorption capacity of adsorbent (mg/mg).

The equilibrium constant for adsorption of ACP (b) and maximum adsorption capacity were found to be -5.198 mL/mg and 0.184 mg/mg respectively, while the correlation coefficient (R^2) was found to be as 0.9896. The value of R^2 represents the good fitness of the experimental data for linear Langmuir adsorption isotherm for the adsorption of ACP on CES.

Linear Freundlich Isotherm plot for adsorption of ACP by CES: The Freundlich adsorption isotherm can be presented as follows [26]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (10)$$

where C_e = adsorbent concentration at equilibrium (mg/mL), q_e = adsorption capacity at equilibrium (mg/g), n = bond energy between ACP and CES, K_f = bond strength.

The Freundlich equilibrium constant (K_f) and bond energy constant (n) were calculated at equilibrium and found to be as 0.625 mL/mg and 3.31, respectively. The value of 1/n was -0.3018, this shows the heterogeneous selectivity of ACP by CES. Since the value of n was greater than 1.0 indicate that the ACP has adsorbed on the whole surface of CES. The correlation coefficient (R^2) value for the Freundlich and Langmuir adsorption isotherm models was 0.9926 and 0.9896, respectively which indicates that the Freundlich isotherm model is more good fit than the Langmuir adsorption isotherm. The parameters of Langmuir and Freundlich adsorption isotherms for adsorption of ACP on CES is depicted in Table-2.

TABLE-2
PARAMETERS FOR LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM MODEL FOR ADSORPTION OF ACP BY CES

Langmuir isotherm			Freundlich isotherm		
R^2	q_m (mg/mg)	B (mL/mg)	R^2	1/n	K_f (mg/mL)
0.9896	0.184	-5.198	0.9926	-0.3018	0.625

Determination of activation energy for adsorption process from Arrhenius equation: The data measured for adsorption of ACP with varying temperatures were graphically represented for log Y_t *vs.* 1/T (eqn. 11) and Arrhenius activation energy was calculated from Arrhenius equation (eqn. 12) [27]:

$$Y_t = \ln A - \frac{E_a}{RT} \quad (11)$$

$$K = A.e^{-\frac{E_a}{RT}} \quad (12)$$

where A = Arrhenius constant (frequency factor), E_a = activation energy for adsorption of ACP, R = universal gas constant, T = temperature in kelvin, K = kinetics rate constant, Y_t = the amount of ACP adsorbed in temperature ºC. Fig. 13 represents the Arrhenius plot for the adsorption of ACP by CES, the linear

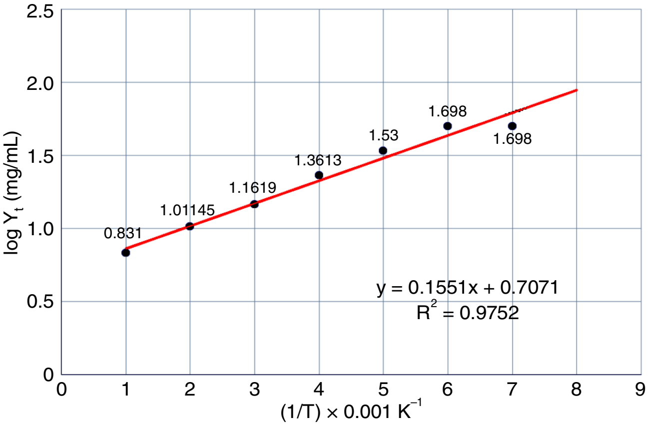

Fig. 13. Arrhenius equation for the adsorption of ACP by CES

plot was obtained and the value of A and E_a. for the adsorption process of ACP by CES from intercept and slop respectively are 2.028 M^{-1} S^{-1} and 1.28867 KJ/mol, this indicates that ACP has better adsorption at a higher temperature compared to lower temperature [28].

Kinetics studies: Initially, the kinetics of adsorption process was evaluated by measuring the rate of change of adsorption per unit time. The results showed that 71% of adsorption completed within 2 h and nearly 99.96% was finished within 5 h. To study the kinetics model of adsorption of ACP by CES, the two most popular models, pseudo-first and pseudo-second order, were adopted [29-31]. The equation of pseudo-first-order and second-order are depicted in eqns. 13 and 14, respectively.

Pseudo first order:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (13)$$

Pseudo second order:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_t} t \qquad (14)$$

where K_1 (mL/h) and K_2 are the equilibrium rate constant for pseudo first-order and pseudo second-order, respectively; q_e (mg/g), q_t(mg/g) and t are the adsorption capacity at equilibrium, adsorption capacity at the time and contact time in h.

The parameter values of pseudo first order and second order kinetics of adsorption of ACP by CES are shown in Table-3. According to Table-3, the R^2 value for the pseudo second-order model for ACP adsorption by CES is higher than that of the pseudo first-order model. This suggests that the pseudo second-order model provides a better correlation for ACP adsorption by CES and that the pseudo second-order model is a better fitted for ACP adsorption by CES than the pseudo first-order model. Additionally, these results showed that the chemisorption process is the rate limiting step for the ACP adsorption process on CES.

TABLE-3
PARAMETERS FOR THE MODEL OF KINETICS
FOR THE ADSORPTION OF ACP BY CES

Pseudo first order		Pseudo second order	
K_1 (mL/h)	R^2	K_2 (g/mg h)	R^2
1.4695	0.9461	99.49	0.9827

Characterization of ESCP catalyst: The calcined eggshell and impregnated eggshell coconut pith catalyst were characterized by TGA, SEM, FTIR and BET analysis. The optimum temperature for calcination of eggshell was 600 ºC. The surface of the calcined eggshell was studied before and after adsorption of activated coconut pith by SEM analysis.

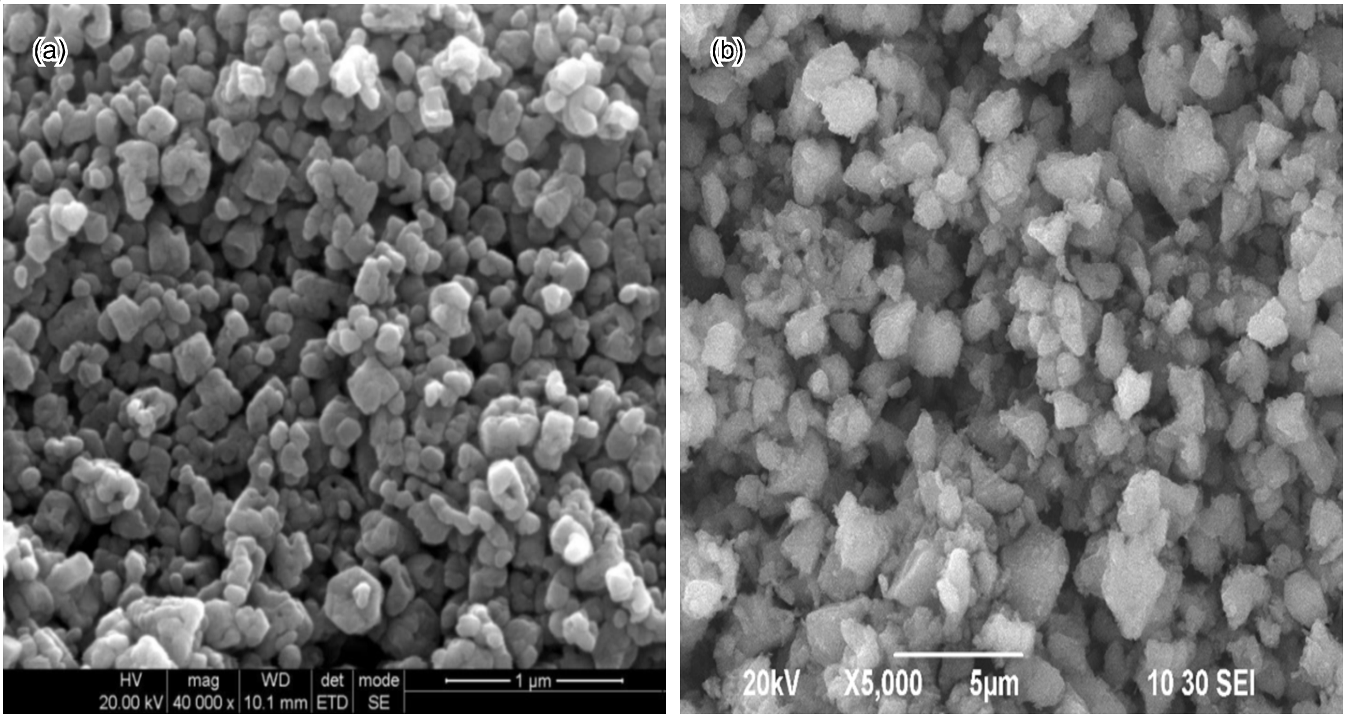

Fig. 14. SEM image (a) before adsorption and (b) after adsorption

The size of the particles of calcined eggshell was increased after the adsorption of activated coconut pith as shown in the SEM image (Fig. 14b), the size of the particle calcined eggshell before adsorption was 1.0 μm where the size of particle of calcined eggshell after the adsorption becomes 1.66 μm, thereby confirmed the adsorption of ACP on CES.

The surface area of the BET was measured by plotting the graph between relative pressure (P/P_0) *vs*. P/V_t ($P_0 - P$) of N_2 to the sample at 200 ºC [32] and the BET surface area was found to be as 4.19 m^2/g. After calcination, 99.9% of $CaCO_3$ in the egg-shell was transformed to CaO [33] and the BET surface area changed depending on the calcination temperature. Based on the results of all the studies comparing the surface areas of various materials, including boiled raw eggshell, commercial CaO and calcined eggshell impregned coconut pith catalyst (ESCP), it was found that the ESCP BET surface area was larger than the other BET surface area of raw eggshell and boiled eggshell [22,28,34]. This finding supports the idea that ACP can be adsorbed on CES. Additionally, the measured value of R^2 (coefficient of regression) was 0.9989, indicating that the data is well-fitting for ACP adsorption.

Transesterification reaction: The prepared eggshell and activated coconut (ESCP) as catalyst was applied for the production of biodiesel by utilizing waste cooking oil with methanol. The waste cooking oil was heated at 60 ºCto remove the moisture content present. The transesterification reaction was carried out first with calcined eggshell as catalyst at a 1:6 molar ratio of waste cooking oil and methanol at 60 ºC for 4 h. A biodiesel yield of 42% was achieved as the maximum, while the maximum production of biodiesel with ESCP catalyst under the same optimal conditions was 87%, resulting in a 45% increase in biodiesel yield by the impregnation of ACP on CES.

Conclusion

The optimized conditions for the impregnation process with calcined eggshell that maximizes the adsorption of activated coconut pith (ACP): 65 mg/mL KOH, 1:1 CES/ACP, 100 mg/mL nitric acid, 80 ºC feed concentration, 5 h contact time, 5.6 pH feed solution, and 600 rpm iteration rate. The adsorption of activated coconut pith (ACP) on calcined eggshell (CES) is most suited to the Freundlich adsorption isotherm model with $R^2 = 0.9926$, which indicates the process parameters are a good fit with the model. The activation energy for adsorption of ACP on CES is determined from the Arrhenius equation as 128862 KJ/mol, which indicates better adsorption of ACP on CES. The kinetics model for adsorption of ACP on CES was also investigated and the pseudo-second-order model is found the most suitable model for adsorption process with equilibrium rate constant (K_2) = 99.49 and coefficient of regression (R^2) = 0.9827. Finally, the prepared eggshell and activated coconut (ESCP) as catalyst was successfully applied for the biodiesel by utilizing waste cooking oil with methanol using transesterification reaction.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C.R.J. Kumar and M.A. Majid, *Energ. Sustain. Soc.*, **10**, 2 (2020); https://doi.org/10.1186/s13705-019-0232-1
2. L. Chen, K. Liu, P. Han, B.Yang and L. Feng, *J. Chem.*, **2021**, 6674453 (2021); http://doi.org/10.1155/2021/6674453
3. P.R. Ross, J. Paramanandham, P. Thenmozhi, K.S. Abbiramy and M. Muthulingam, *Int. J. Res. Environ. Sci. Technol.*, **2**, 2249 (2012).
4. H. Kumar, A.A. Renita and S.A. Jabasingh, *Environ. Progr. Sustain. Energy*, **40**, e13632 (2021); https://doi.org/10.1002/ep.13632
5. H. Kumar, A.A. Renita and A. Anderson, *Mater. Today Proc.*, **47(Part 4)**, 1054 (2021); https://doi.org/10.1016/j.matpr.2021.06.244
6. M.P. Gundypalli, H. Kajiura, T. Ishimizu and D.Bhattacharyya, *Biomass Conver. Biorefin.*, **12**, 2349 (2020); https://doi.org/10.1007/s13399-020-00890-z
7. Y.C. Wong and R.X. Ang, *Open Chem.*, **16**, 1166 (2018); https://doi.org/10.1515/chem-2018-0127
8. M.A. Chowdhury and K.J. Fatima, *Int. J. Textile Sci*., **5**,132 (2016); https://doi:10.5923/j.textile.20160506.02
9. A. Shwetha, Dhananjaya, S.M. Shravana Kumara and Ananda, *Int. J. Zool. Stud.*, **3**, 31 (2018).
10. N.Sh. El-Gendy, S.F. Deriase, A. Hamdy and R.I. Abdallah. *Egypt. J. Petrol*. **24**, 37 (2015); https://doi.org/10.1016/j.ejpe.2015.02.004
11. O. Awogbemi, F. Inambao and E. I. Onuh, *Heliyon*, **6**, e05283 (2020); https://doi.org/10.1016/j.heliyon.2020.e05283
12. Coir Board, Ministry of MS & ME, Government of India, Coir Pith Wealth from Waste a Reference, India International Coir Pith (2016); www.coirbard.com
13. U.J. Etim , S.A. Umoren and U.M. Eduok, *J. Saudi Chem. Soc.*, **20**, 567 (2016); https://doi.org/10.1016/j.jscs.2012.09.014.
14. R. Mustapha, M.H.Ch. Harun, A.M.A Ali and S. Hamzah, *Biointerf. Res. Appl. Chem.*, **11**, 10006, (2021); https://doi.org/10.33263/BRIAC113.1000610015.
15. A. Jamshaid, A. Hamid, N. Mohammad, A. Naseer, M. Ghauri, J. Iqbal, S. Rafiq and N.S. Shah, *ChemBioEng*, **4**, 240 (2017); https://doi.org/10.1002/cben.201700002
16. B. S. Zadeh, H. Esmacili and R. Foroutan, *Indones. J. Chem*., **18**, 2460, (2018); https://doi.org/10.22146/ijc.28789
17. M. Panchal, G. Raghvendra, S. Ojha, M. Omprakash and S.K Acharya, *Mater. Res. Express*, **6**, 115613 (2019); https://doi.org/10.1088/2053-1591/ab4cb3
18. E. del Angel-Meraz, M.A. Pantoja-Castro and A.E. Cruz-Perez. *IOSR J. Appl. Chem.*, **12**, 83 (2019); https://doi.org/10.9790/5736-1203018387
19. O. Awogbemi, F. Inambao and E.I. Onuh, *Heliyon*, **6**, e05283 (2020); https://doi.org/10.1016/j.heliyon.2020.e05283
20. A. Adriano-Mendes, R.C. Giordano, R. de L.C Giordano and H.F. de Castro, *J. Mol. Catal. B: Enzym*., **68**, 109 (2011); https://doi.org/10.1016/j.molcatb.2010.10.002
21. O.S. Tyagi, N. Atray, B. Kumar and A. Datta, *MAPAN J. Metrol.*, **25**, 197 (2010); https://doi.org/10.1007/s12647-010-0018-6
22. A. Mittal, L. Korup and J. Mittal, *J. Hazard. Mater.*, **146**, 243 (2007); https://doi.org/10.1016/j.jhazmat.2006.12.012
23. M. Peleg, M.D. Normand and M.G. Corradini, *Food Sci. Nutr*., **52**, 830 (2012); https://doi.org/10.1080/10408398.2012.667460
24. N. Puagsang, I. Chanakeawsomboon, S. Chantrapromma and A. Palamanit, *Environ. Asia*, **14**, 23 (2021); https://doi.org/10.14456/ea.2021.3
25. X. Liu, K. Li and S. Sun, *Biomass Conver. Bioref*., **13**, 3187 (2021); https://doi.org/10.1007/s13399-021-01440-x

26. E. Quayson, J. Amoah, S. Hama, A. Kondo and C. Ogino, *Renew. Sustain. Energy Rev*., **134**, 110355 (2020); https://doi.org/10.1016/j.rser.2020.110355
27. A.M.M. Eid, N.A. Elmorzugi and H.A. El-Enshaw, *Int. J. Pharm. Pharm. Sci*., **5**, 434 (2013).
28. H. Kumar and A.A. Renita, *Asian J. Chem*., **34**, 2451 (2022); https://doi.org/10.14233/ajchem.2022.23887
29. R. Ezzati, *Chem. Eng. J*., **392**, 123705 (2020); https://doi.org/10.1016/j.cej.2019.123705
30. H. Kumar, AA. Renita and A. Anderson, *Int. J. Geo-Marine Sci*., **51**, 445 (2022); https://doi.org/10.56042/ijms.v51i05.65561
31. F.V. Silva-Medeiros, N. Consalin-Fibho, M. X. de Lime and F. P. Bazzo, *Environ. Technol.*, **37**, 3087 (2016); https://doi.org/10.1080/09593330.2016.1176076
32. O. Abatan, P.A. Alaba, B.A. Oni, K. Alcpojevwe, V. Efeovbokhan and F. Abnisa, *SN Appl. Sci*., **2**, 1996 (2020); https://doi.org/10.1007/s42452-020-03866-w
33. T.E. Kose and B. Kivanc, *Chem. Eng. J*., **178**, 34 (2011); https://doi.org/10.1016/j.cej.2011.09.129
34. F. Boukhlifi, S. Chraibi and M. Alami, *J. Environ. Earth Sci*., **3**, 181 (2013).