Original Research Article

Performance Evaluation of Modified Periwinkle Shell–Derived Adsorbent for CO_2 Post-Combustion Capture

ABSTRACT

Seashells and other waste shells are gaining attention as a cost—effective, sustainable, renewable alternative source of $CaCO_3$ formed after CO_2 adsorption. Consequently, this study evaluated the performance of periwinkle shell as a potential~~n~~ adsorbent for CO_2 capture. The periwinkle shells were washed, dried, then calcined at 800^{0}C for 2 hrs, crushed, and sieved with 0.25 -1.44 mm sieves. Some portion of the calcined sample were~~wa~~s activated with KOH in a 2:1 ratio of KOH to the periwinkle shell. A portion of the activated periwinkle shell was modified with deep eutectic solvent (DES) prepared with 15 ml of choline chloride and 30 ml of glycerol, stirred for 60 min at 80 ^{0}C until it formed a completely homogenous mixture. 20 ml of the deep eutectic solvent was added to 10g of KOH-activated periwinkle shell and later dried in a furnace at 800 ^{o}C for 2 hrs to form a DES-modified activated periwinkle shell. Likewise, 60 ml of polyethylene glycol (PEG) was added to 30 g of another portion of the KOH-activated periwinkle shell and dried at 800 oC for 2 hrs to form the modified PEG-activated periwinkle shell sample. Furthermore, the developed samples were characterized using SEM imaging and FTIR spectra for surface morphology and functional group analysis. CO_2 adsorption was performed on all adsorbents to ascertain their suitability for CO_2 capture after 1 and 3 hours. The results showed that the unmodified calcined periwinkle shell sample outperformed the other modified samples by capturing 0.1565 mmol/g of CO_2 after 1hr and increased to 0.4168 mmol/g after 3 hrs. The Langmuir adsorption model best described the adsorption process. The relatively low adsorption capacity of the developed adsorbents suggested that they were unsuitable for CO_2 capture. Recommendations for future studies were also highlighted.

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Comment [TC2]: I suggest that the authors re-write the abstract. Please note that the abstract represents a summary of the most striking features and the results in this study.

***Keywords**: Periwinkle shells, bio-adsorbents, CO_2 capture, Deep Eutectic Solvent, post-combustion.*

1. INTRODUCTION

The continuous emissions of greenhouse gases (GHGs), which are the by—products of many industrial and anthropogenic processes, have been identified as the major causes of many environmental problems like an increase in mean global temperature, excessive flooding, wildfires, melting of polar ice caps, droughts, etc. [1], [2]. For a sustainable planet, GHG emissions must be reduced to meet the COP21 Paris Agreement of less than 2 ^{o}C [3]. Consequently, various governments around the globe have developed timelines and mitigation measures guided by strict GHG emission policies and regulations to curb the further degradation of the environment. The central focus areas have been increasing the contribution of renewable energy sources like solar, wind, hydro, geothermal, etc., in the total energy mix and the scaling up of carbon capture utilization and storage (CCUS) technologies. These two focus areas are intended to mitigate the adverse effect of GHG emissions on the environment and contribute to our planet's sustainability [4], [5].

Developing and scaling up CCUS has become necessary due to the role fossil fuels are expected to play in providing energy needs for an ever-increasing global population. According to the United Nations report on global population growth, the global population is expected to grow from ~~its current~~ 8 ~~billion~~ to 9.7 billion people by 2050 [6], and the energy demand is expected to double. ~~rise to about twice today's value~~. Fossil fuel will continue to play a significant role in meeting the global energy demand. For instance, while crude oil demand is expected to grow at 7%, driven mainly by demand in petrochemical feedstock, the demand for natural gas is expected to increase by~~grow at~~ 29%~~,~~ mainly due to the need for lesser GHG emitting fuel (compared to other fossil fuels). Thus oil and gas alone (excluding coal) are expected to account for more than half of the total energy mix going into 2040 [7]. The continuous use of these fossil fuels will, in no doubt, result in the emissions of GHG that are inimical to a sustainable environment. ~~Interestingly~~ On the other hand, the mining and processing of the essential metals (cobalt, nickel, copper, lithium, manganese, zinc, etc.) required for developing clean energy technologies like lithium batteries, solar PVs, and wind turbines also contribute to GHG emissions. According to the IEA report [7], the mining and processing of l~~L~~ithium carbonate, class 1 n~~N~~ickel, a~~A~~luminium, and c~~C~~obalt sulfate emit about 5, 10, 12, and 17 tons of CO_2-equivalent per ton of metal, respectively. Although the CO_2 emissions from clean-tech components and equipment manufacturing are small compared to emissions from fossil fuel sources, it still requires to be sequestered to enable a holistic approach to a sustainable environment.

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Carbon capture and storage (CCS) technologies are the established means by which CO_2 from carbon-intensive processes is captured [8], [9]. Incorporating or retrofitting CCS technologies into high carbon footprint processes can help make fossil fuel utilization competitive and safe in the coming decades. The CCS technologies use techniques like oxyfuel combustion, the pre-and post-combustion methods for carbon capture. Details of these processes can be found ~~elsewhere~~ from the work conducted by Blomen et al. [10], and Osman et al ~~[10],~~ [11]. The prominent technologies used in these CO_2 capture processes are mostly solvents like amines and solid adsorbents like zeolite. Although amines are the most used and mature technologies, their drawbacks, like high regeneration energy requirement, solvent losses, and corrosivity [12], limit their use. These drawbacks have allowed for using relatively efficient and cost-effective solid adsorbents. eg, activated carbons, metal-organic frameworks, and zeolites. However, typical solid adsorbents are still relatively expensive and thermally unstable. To reduce the associated costs of solid adsorbents and improve their thermal stability, attention has shifted to exploring bio-based adsorbents from waste shells for CO_2 capture. Consequently, egg shells and seashells have been investigated and found effective for CO_2 capture [13], [14]. These bio-based shells provide a sustainable source of $CaCO_3$, comprising about 90 – 96% of the shells [15], the principal component responsible for CO_2 adsorption. During the CO_2 adsorption process, calcined $CaCO_3$, comprising mainly CaO, reacts with CO_2 to form $CaCO_3$. The $CaCO_3$ is then heated to regenerate CaO to continue the adsorption cycle.

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Like other waste seashells, Periwinkle (tympanotonus fuscatus) shells contain large amounts of sustainable $CaCO_3$. The use of this waste shell in many applications has been discussed extensively in the open literature [16]. However, studies on their use as adsorbents for CO_2 capture are limited in the available literature. Furthermore, using potentially effective modification agents like deep eutectic solvents (DES) and polyethylene glycol (PEG) for modifying periwinkle shell-based adsorbents are rare. This study, therefore, aims to investigate the performance of adsorbents developed from calcined periwinkle shells, activated with KOH, and modified with DES and PEG for CO_2 capture.

1.1. The Deep Eutectic Solvent (DES) and Polyethylene Glycol (PEG).

DES has numerous bonding hydrogen donors and pairs acceptors for the CO_2 capturing system [17]. These deep eutectic solvents can be formed from the mixtures of choline chloride and glycerols, often called deep eutectic solvent glycerine, usually in their molar ratio using 1mol of choline chloride with 2 mol of glycerol. The DES consists of hydrochloride-ethylenediamine, which possesses a good quality of gravimetric uptake and exhibits suitable performance in the presence of H_2O, with unique tolerance against temperature rise and relative low heat absorption process, which favors regeneration. Those properties aid the DES in CO_2 capture [18]. In the presence of PEG, CO_2 adsorption capacity is expected to increase since PEG acts as a hydrogen ion acceptor for their strong affinity for H^+. Moreover, the Hydroxyl groups in polyethylene glycol positively influence CO_2 capture [19].

2. MATERIALS AND METHODS

2.1. Calcination of Periwinkle Shell.

Samples of periwinkle shells were collected and washed to remove the dust and other water-soluble materials. The washing process continued until the water was colorless, then dried. Then 500 grams of the periwinkle shell was weighed in a precision electronic balance of model WT 6002A and heated using a muffle furnace with model SXL without air at 800 ^{o}C for 2 hrs before crushing to finer particles and sieved with (0.25 mm – 1.4 mm) sieve. The calcined and sieved periwinkle shell was stored in an amber bottle, herein referred to as calcined periwinkle shell (CPS). Figure 1a shows the calcined periwinkle shell sample.

2.2. Activation of Periwinkle Shell.

Chemical activation was done by thoroughly mixing 100 grams of calcined periwinkle shell CPS in 1000 ml of 1M KOH solution until it formed a slurry. It was left for 72 hrs, then washed with de-ionized water and dried in an oven at 110 ^{o}C for 2 hrs. Two portions of the calcined sample were activated in the ratios of 2:1 with the KOH solution. The final activated calcined samples were depicted as APS1 and APS 2, respectively. Figure 1b shows the activated periwinkle shell sample.

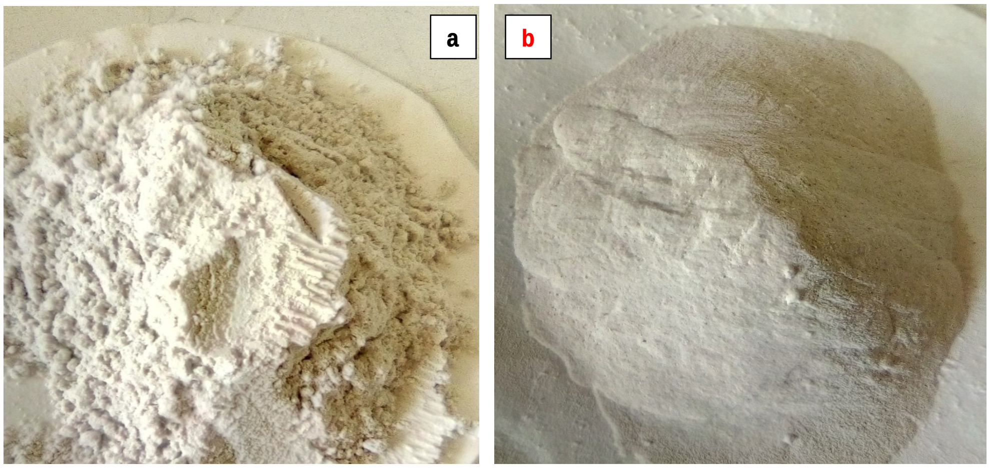

Fig. 1. (a) Calcined and (b) activated periwinkle shell

2.3. Modification of Activated Periwinkle Shell.

The activated periwinkle shell was functionalized with two reagents: the deep eutectic solvent (DES) and polyethylene glycol (PEG). Deep Eutectic solvent (DES) was prepared by adding choline chloride with Glycerol. 15 ml of choline chloride was added to 30 ml of glycerol in a sealed vacuum flask and stirred on a magnetic stirrer for 60 mins at 80 ^{o}C until a homogenous and transparent sample was formed. 20 ml of the prepared deep eutectic solvent was then added to 10 ml of APS1 in the ratio of 1:2 for APS1: DES, both introduced into a vacuum flask and placed on a magnetic stirrer for 360 mins at 150 ^{o}C, until it formed a slurry. The sample was left in the vacuum flask for 72 hrs, then dried in a furnace for 2 hrs at 800 ^{o}C. This modified sample was designated as APS-DES. Also, 30 g of APS 2 was introduced into a flat bottom flask, and 60 ml of polyethylene glycol was added and placed on a magnetic stirrer for 6 hrs at 150 ^{o}C. The sample was dried in a furnace for 2 hrs at 800 ^{o}C and designated as APS-PEG.

2.4. Characterization of Adsorbents

The formulated APS-DES and APS-PEG adsorbents were characterized using the Infrared spectrometer (Varian 660 MidIR Dual MCT/DTGS Bundle with ATR) for the Fourier transform infrared spectroscopy (FTIR) analysis and the Hitachi SU 3500 scanning electron microscope for the SEM analysis. These analyses were performed to have an in-depth understanding of the surface morphology of the modified periwinkle shell adsorbents and to know the functional groups responsible for the adsorption process.

2.5. CO_2 Adsorption Experiment

The CO_2 adsorption apparatus used for the CO_2 adsorption experiments works on the principles of Sievert's law, as presented by Sadie [20]. Measured amounts of the APS-DES and APS-PEG adsorbents were placed in the reactor, immersed in a water bath for temperature control, and dosed with CO_2 gas. Initial and final (equilibrium) pressures and corresponding temperatures were recorded. Initial pressure ranges were 2 and 15 psia at 26 ^{o}C. Adsorption experiments were performed at retention times of 1 and 3 hours. These time frames were chosen to understand the relationship between the adsorption capacity and time. The corresponding adsorption capacity at each condition was also measured. Details of the apparatus and experimental procedures can be found elsewhere [21].

3. RESULTS AND DISCUSSIONS

3.1 Characterization of the Calcined and Modified Periwinkles Samples

The SEM and FTIR images of the calcined, DES and PEG-modified periwinkle shell reveal the surface morphologies and active functional groups of the different periwinkle samples(~~. See f~~Figures 2 and 3). The SEM images in figure 2 show that the calcined periwinkle shell possesses a rigid structure with relatively distributed void spaces, unlike the DES and PEG-modified structures. The modified structures' surface area is relatively clogged with little or no void spaces.

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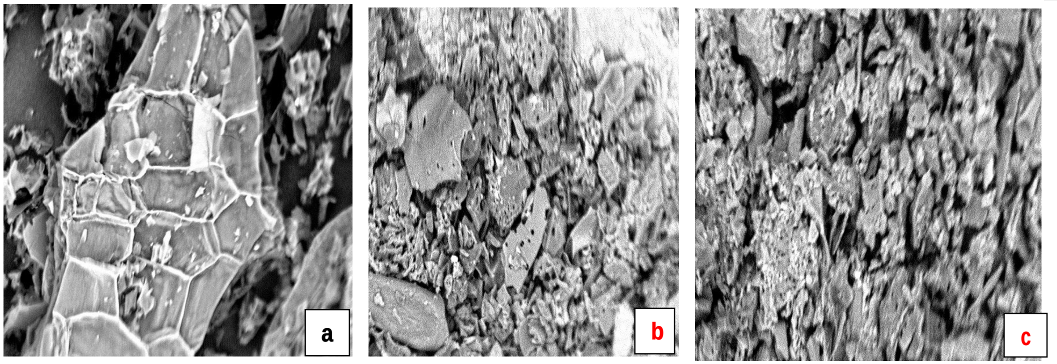

Fig. 2. SEM images of (a) calcined (b) DES modified (c) PEG-modified periwinkle shell

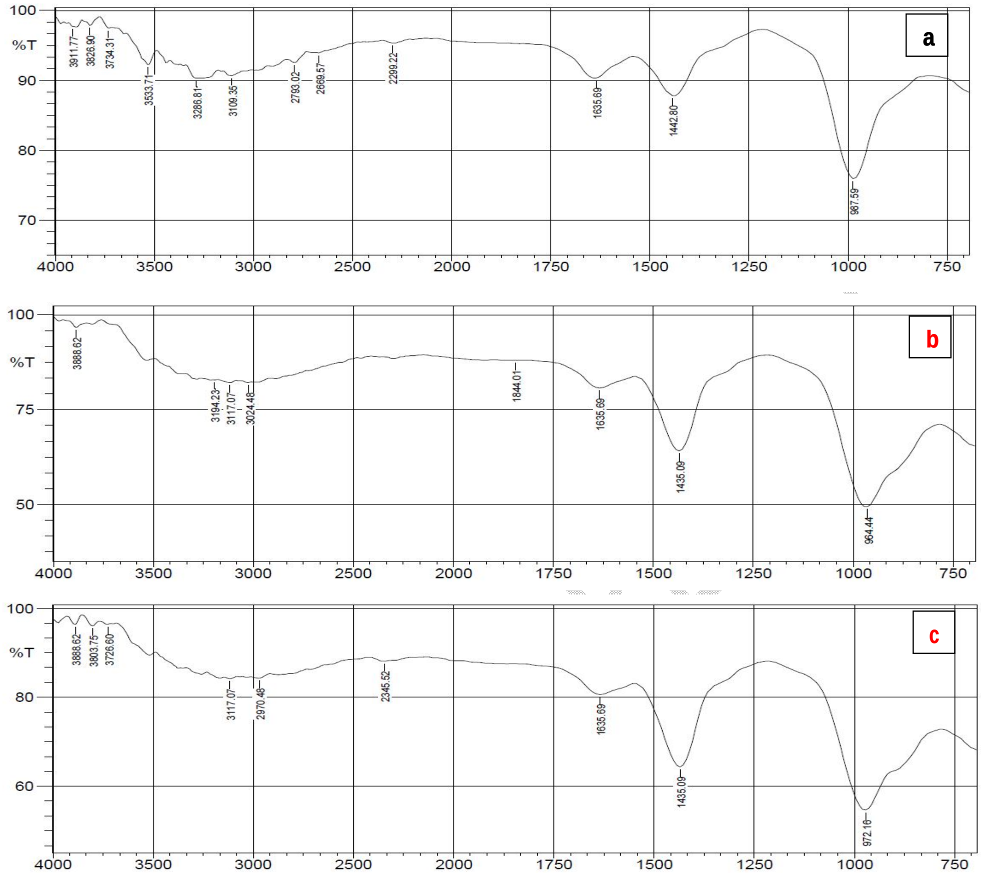

Fig. 3. FTIR spectra of (a) calcined (b) DES modified (c) PEG-modified periwinkle shell

The clogging of the pore spaces might be due to the viscous nature of DES and PEG, which may block the available pore spaces. The lack of void spaces may affect the samples' adsorption capacities. Furthermore, the FTIR spectra show that the samples are pretty simple structures, with the calcined sample having more functional group bands (12) than the PEG (9) and DES (8) modified samples. All three samples had the double bond C-H stretching of the alkenes group, C-C stretching of the aromatic groups, N-H bends of primary amines, and the –OH stretching corresponding to carboxylic acids. However, the unmodified calcined sample had, in addition to the other stated functional groups in the modified samples, the H-C=O stretching of the aldehyde group and the –OH stretching of the alcohol and hydroxyl group.

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3.2 CO_2 Adsorption Capacity of the Samples

Figure 4 shows the results of the CO_2 adsorption experiments after 1 and 3 hours measured at an ambient temperature of 26 ^{o}C. All four samples had increasing adsorption capacity with increasing pressure. This can be attributed to the fact that the high impact forces with which CO_2 molecules penetrate the porous structure of the adsorbents cause the molecules to have access to the pore spaces hence, an increase in adsorption capacity [22], [23]. The calcined periwinkle shell, CPS, had a better adsorption capacity than the modified samples. After 1 hour, the CPS sample had an adsorption capacity of about 0.16 mmol/g, while the APS, APS-DES, and APS-PEG samples had adsorption capacities of 0.09 mmol/g, 0.07 mmol/g, and 0.05 mmol/g, respectively. Likewise, the adsorption capacities of the samples CPS, APS, APS-DES, and APS-PEG had adsorption capacities of 0.42 mmol/g, 0.15 mmol/g, 0.11 mmol/g, and 0.21 mmol/g~~,~~ respectively~~,~~ after 3 hours.

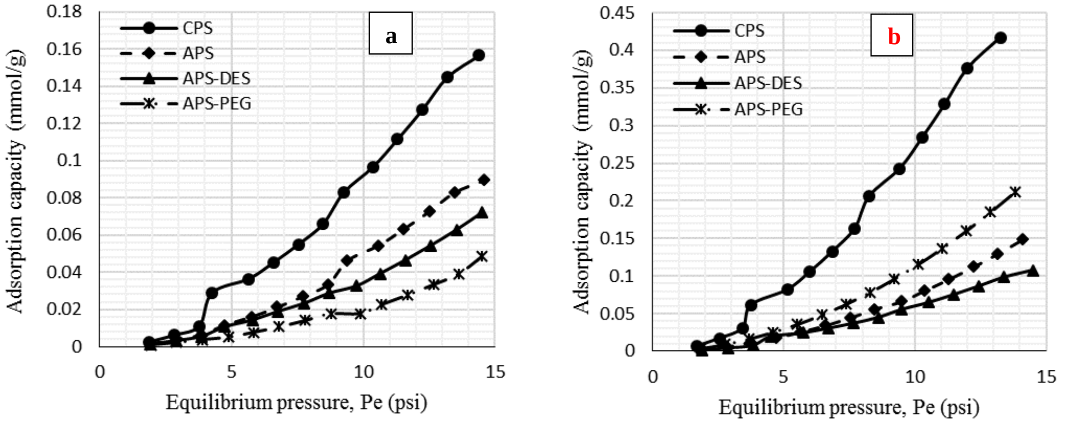

Fig. 4. CO_2 adsorption after (a) 1 hour and (b) 3 hours.

The increase in the retention time from 1 ~~hour~~ to 3 hours increases the contact time between adsorbent and adsorbate. Hence adsorption capacities of all the samples increased with time [24]. The adsorption capacity of the CPS sample outperformed all the modified samples. This relatively high adsorption compared to the modified samples may be due to the presence of more void spaces as well as n~~N~~itrogen and o~~O~~xygen sites of the additional H-C=O stretching of the aldehyde group as well as the –OH stretching of the alcohol and hydroxyl group, in the sample. The presence of more nitrogen and oxygen sites in an adsorbent enhances the CO_2 adsorption process [25], [26]. Furthermore, the adsorption capacities of the modified samples, APS, APS-DES, and APS-PEG, reduced significantly compared to the CPS sample. The reduced adsorption capacity is evident in the relative lack of void spaces, increased logging, and fewer CO_2 reactive functional groups identified in the modified samples, as seen in figures 2 and 3. Also, the increasing viscosity of the modifying agents could be responsible for clogging the available pore spaces required for the adsorption process. The modification of an adsorbent with certain CO_2 reactive agents can reduce their specific surface area available for adsorption and their pore spaces [23], resulting in adsorbent clogging. This clogging due to reduced surface area and pore spaces could be responsible for a decreased adsorption capacity. Figure 5 shows the adsorption isotherms for the various samples. The Langmuir and Freundlich models were used in this study to model the CO_2 adsorption of the samples.

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Table 1 shows the isotherm parameters. The table shows that the Langmuir and Freundlich isotherm models can reliably describe the CO_2 adsorption of the CPS sample since both models gave a coefficient of determination of more than 0.95. However, the Langmuir model had the highest R^2 of 0.98 and thus can best describe the CPS sample CO_2 adsorption process, implying that adsorption is mostly a monolayer phenomenon. Also, the Freundlich isotherm exponent of the CPS sample is greater than 1, indicating a favorable adsorption process. The Langmuir maximum adsorption capacity, Q_m, is observed to decrease from 1.39 mmol/g for CPS to 0.28, 0.21, and 0.03 mmol/g for APS, APS-DES, and APS-PEG samples, respectively. The Langmuir R^2 value of the adsorbents also showed a decrease in value from 0.98 for the CPS sample to 0.95, 0.94, and 0.79 for APS, APS-DES, and APS-PEG samples, respectively. Similarly, the Freundlich adsorption constant decreased from 0.22 for the CPS sample to 0.005, 0.00098, and 0.00045 for APS, APS-DES, and APS-PEG samples, respectively. This reduction in the Langmuir maximum adsorption capacity and R^2 and the Freundlich adsorption constant validate the modified adsorbents' poor adsorption performance.

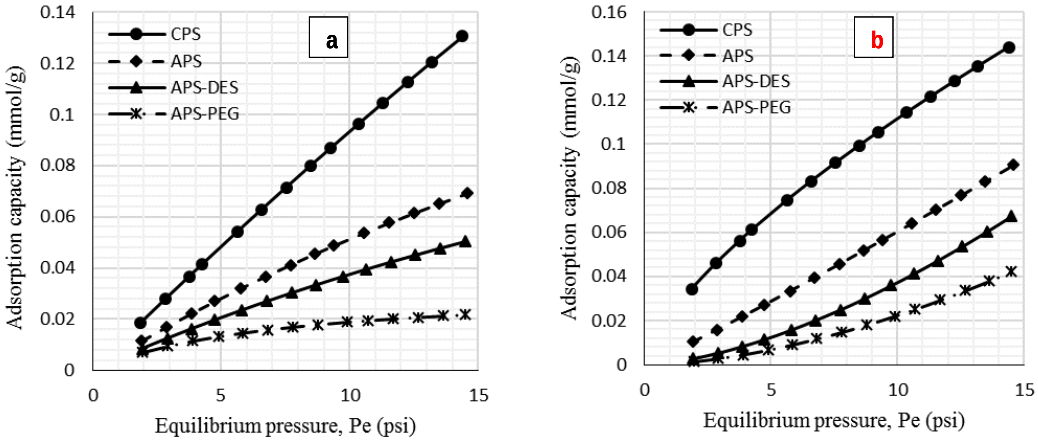

Fig. 5. (a) Langmuir and (b) Freundlich adsorption isotherms

Table 1. Adsorption isotherm parameters for the samples.

Samples	Isotherm Parameters					
	Langmuir			**Freundlich**		
	Q_m	K_L	R^2	K_f	n	R^2
CPS	1.39	0.007	0.98	0.02200	1.42	0.96
APS	0.28	0.022	0.95	0.00500	0.93	0.98
APS-DES	0.21	0.022	0.94	0.00098	0.63	0.99
APS-PEG	0.03	0.140	0.79	0.000452	0.59	0.98

However, the relatively low adsorption capacities of the investigated samples indicate that periwinkle shells modified with DES and PEG are unsuitable for CO_2 adsorption. This poor adsorption performance could be due to inadequate pre-treatment of the periwinkle shells before calcination. Iyer et al. [13], Sacia et al. [14], and Vonder-Haar [27] showed that the pre-treatment of seashells and other $CaCO_3$-rich shells like eggshells with an optimized concentration of acetic acid increased the pore structures and surface areas of the shells, which ultimately led to a better adsorption capacity. This improvement in their surface morphology and hence adsorption capacity was attributed to the formation of calcium acetate, which has a greater molar volume than $CaCO_3$. Thus an improved pore development and surface area. Furthermore, the poor adsorption performance could result from the fact that DES and PEG are unsuitable for modifying periwinkle shells for use as adsorbents. Consequently, the modification suitability of these chemical agents on waste shells should be further investigated. The periwinkle sizes of 0.25 -1.44 mm could also be a factor. Hence particle size optimization of the shells for maximum adsorption is required. Also, further research should be performed on the suitability of periwinkle shells as adsorbents for CO_2 capture.

4. CONCLUSION

This study evaluated the CO_2 adsorption performance of calcined periwinkle shells (CPS), KOH-activated CPS (APS), DES-modified APS, and PEG-modified APS. The results showed that the unmodified calcined periwinkle shells performed better than the KOH-activated and the DES and PEG-modified APS samples, with a CO_2 adsorption capacity of 0.16 and 0.42 mmol/g after 1 and 3 hours, respectively. The adsorption process of the CPS sample followed the Langmuir monolayer model of adsorption. Further studies on the effect of acetic acid pre-treatment of the periwinkle shells, particle sizes optimization, and the modification suitability of the chemical agents (DES and PEG), were advocated.

Comment [TC9]: This conclusion is a better summary which can be included in the abstract.

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