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Thermal Regeneration of CO_2 Spent Palm Shell-Polyetheretherketone Activated Carbon Sorbents

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***Abstract*—**Activated carbons (M4P0, M4P2, and M5P2) used in this research were produced from palm shell and polyetherether ketone (PEEK) via carbonization, impregnation and microwave activation. The adsorption/desorption process was carried out using static volumetric adsorption. Regeneration is important in the overall economy of the process and waste minimization. This work focuses on the thermal regeneration of the CO_2 exhausted microwave activated carbons. The regeneration strategy adopted was thermal with nitrogen purge desorption with N_2 feed flow rate of 20 ml/min for 1 h at atmospheric pressure followed by drying at 150^0C.Seven successive adsorption/regeneration processes were carried out on the material. It was found that after seven adsorption regeneration cycles; the regeneration efficiency (RE) for CO_2 activated carbon from palm shell only (M4P0) was more than 90% while that of hybrid palm shell-PEEK (M4P2, M5P2) was above 95%. The cyclic adsorption and regeneration shows the stability of the adsorbent materials.

***Keywords*—**Activated carbon,Palm shell-PEEK, Regeneration, thermal.

I. Introduction

ADSORPTIONof contaminants with activated carbon is one of reliable method used water treatment and air purification.Activated carbon has been used in CO_2 capture and separation [1], [2]. The cost of CO_2 capture step takes about 2/3 of the overall carbon capture and subsequent storage process [3]. Once the activated carbon(AC) is exhausted, the material becomes a residue that has to be discarded and substituted by a fresh activated carbon sorbent. For economic and environmental reasons, the spent GAC is not disposed of, but must undergo several cycles of regeneration [4]. Therefore of equal importance to adsorption capacity is the ease of regeneration and the lifetime of the adsorbents. For large-scale industrial applications of ACs, the costs of AC production and ease of sorbent regeneration is considered [5]. Due the significance of regeneration, a lot of research effort was devoted to various regeneration techniques such as thermal, microwave, solvent extraction [5], chemical, biological, wet oxidative, ultrasound and photo catalytic methods [6]. Of all the methods, thermal regeneration is the most cost-effective method [5]. During regeneration of sorbent, steam or heated nitrogen is used to desorb contaminants and then recycle the carbon material.After series of repetitive heating and cooling the carbon material is damaged [7]. In order to improve on these, improvement in thermal stability of carbon porous carbon material is needed.

PEEK is one of the commonly used engineering thermoplastic materials combining ketone and aromatic moieties [8]. The excellent thermal properties of the polymer are attributed to the stability of the aromatic backbone, which makes up the bulk of the monomer unit [9]. It's on this note that this work improving the thermal properties and regeneration capability of the activated carbon by blending palm-char and PEEK char. The main purpose of the current study was to investigate the regeneration and desorption capability of CO_2 spent ACs by carrying out successive adsorption–regeneration cycles.

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II. Experimental

A. Material and Sorbent Preparation

The raw palm shell was washed several times with distilled water. The palm shells were then dried at 105^0C for 24 hrs in an oven and later sieved to size 0.85- 1.7mm. The dried materials were loaded into a stainless steel tubular reactor and then heated in furnace. Heating rate of 10^0C/min was selected to achieve carbonization temperature of 700^0C under nitrogen flow of 100 cm^3/min for 2hrs. The resultant palm char was allowed to cool to room temperature while maintaining the inert environment throughout the period.

The PEEK Char (PEKC) was obtained by pyrolysis of granulated Victrex PEEK (Polyether ether ketone) at 800^0C in a furnace.Palm kernel char (PKC) was blended with PEEK char at different percentage by weight (0, 20, 20%). For the impregnation process, the char was mixed with K_2CO_3 solution in the ratio 1:1. The impregnation ratio defined as the dry weight of activation agent per weight of the char. The mixture of precursor and chemical solution was stirred at 85°C and 6 r.p.m for 2 h. It was then placed in an oven for 24 hours at 105^0C. The activation involves changing 10 g of impregnated sample into a high temperature quartz reactor. It was then pre-heated in microwave oven (Samsung ME0113M model) in flowing stream of nitrogen (200 cm^3/min). The flow was then switch over to CO_2 at flow rate of 200 cm^3/min. Power level of 400W and 500 W was chosen from the power controller with irradiation time of 6 min. The resultant microwave palm shell-PEEK activated carbon was washed thoroughly with 0.1 M hydrochloric acid and deionized water

until pH 6.5-7 is reach.The blended palm-PEEK char AC was denoted as M4P0, M4P2, M5P2, which stands for palm-PEEK char containing 0, 20, 20 of PEEK char activated for six minutes under microwave power of 400, 400, and 500W respectively.

B. Regeneration and Adsorption/Desorption Cycles

Desorption and Regeneration of sorbent is important so that the sorbent can be used in repeated CO_2 adsorption [10]. Adsorption-Desorption cycles were carried out to determine the regeneration performance of the porous carbons. In addition, it will highlight the reproducibility of the system [11] and reversibility of CO_2 adsorption on the porous carbons [12]. The method adopted for the regeneration was thermal with nitrogen purge desorption. A feed flow rate of 20 ml/min was supplied to the sample column for 1 hr at atmospheric pressure. The sorbent was dried at 150^0C, 1 atm for 1 hr under nitrogen flow. The sorbent was subjected to seven adsorption–desorption's cycles and its maximum CO_2 adsorption capacity at different pressures and temperatures were assessed.

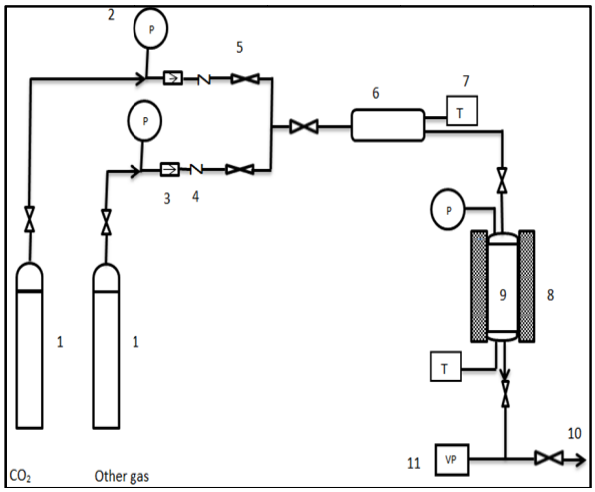

Fig. 1 Schematic diagram of the volumetric adsorption set-up: 1. Feed gas 2. Pressure gauge 3. Flow controller/reader 4. Check valve 5. Valve 6.Loading cell 7.Thermocouple 8.Electric furnace 9. Adsorption cell 10. Vent11. Vacuum pump

The sorbent CO_2 adsorption/desorption capacity was carried in a fabricated packed-bed adsorption system (Fig. 1). For each adsorption measurement, CO_2 was passed into the loading cell to reach the required initial pressure. The valve between the loading cell and the adsorption cell was open to allow the gas contact the adsorbent in the cell. It was allowed to reach equilibrium state i.e. condition at the temperature and pressure constant. For the desorption experiment, Vacuum pump was used to evacuate the loading cell. The valves were then closed; the pressure and temperature in the loading and adsorption cell were taken. The gas was then fed in reverse order i.e. from the adsorption cell to the loading cell. The pressure and temperature in the loading cell and the adsorption cell were recorded until the two remained constant. The CO_2 adsorption/desorption capacity was obtained based on mass balance across the loading and adsorption cell.

III. Results and Discussions

A. Regeneration and Adsorption/Desorption Cycles

Ease of regeneration is a critical property that must be considered when designing CO_2 sorbents [13]. From Fig. 2 the CO_2 adsorption capacity (q) of M4P0 activated carbon is reported over 7 consecutives adsorption–desorption cycles. The results clearly indicate that, there is little change in the adsorption capacity upon the number of cycles (Fig. 2). After the first cycle, the regeneration efficiency (RE) for CO_2 reaches up to nearly 99%. The sorbent demonstrated over 90% of regeneration efficiency over seven cycles (Fig. 3).

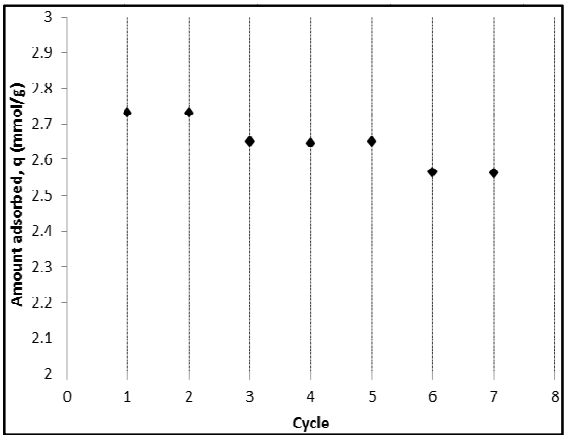

Fig. 2Equilibrium adsorption capacity of M4P0 over 7 adsorption/desorption cycles at 30^0C, 1 bar

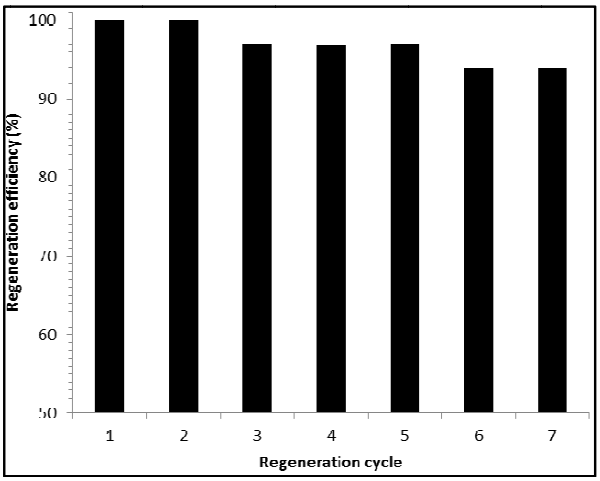

Fig. 3 Variations in regeneration efficiency of M4P0 after 7 successive CO_2 adsorption cycles

The repetitive of successive cycles affects less significantly the single step stripping efficiency (SSE) (Fig. 4). This implies that the adsorption process is reversible and can be easily regenerated. It also shows that the adsorption process is physisorption due to the fact that only week interaction forces hold the CO_2sorbate to the surface of the M4P0

sorbent.Moreover, this feature is highly desirable for potential industrial scale applications [14].

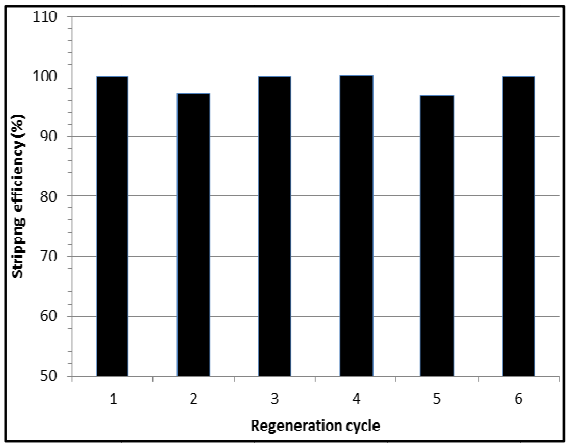

Fig. 4 Variations in single step stripping efficiency of M4P0 after 7 successive adsorption cycles

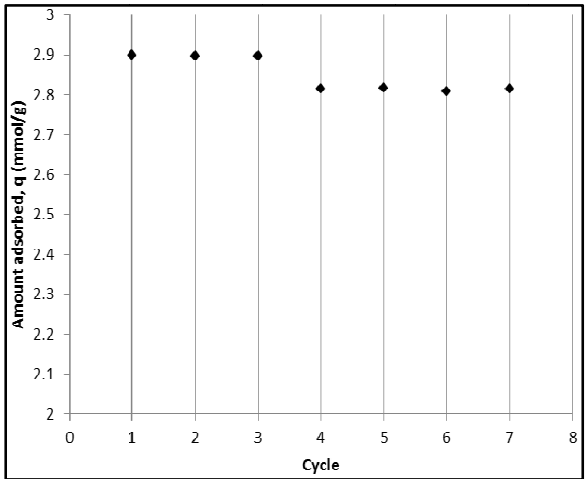

Fig.5Equilibrium adsorption capacity of M4P2 over 7 adsorption/desorption cycles at 30^0C, 1 bar

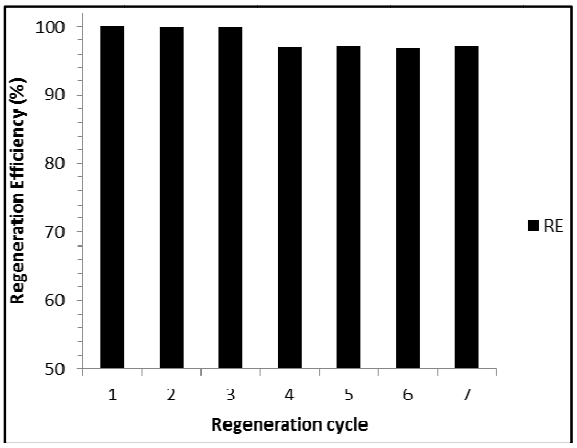

Fig. 6 Variations in regeneration efficiency of M4P2 after 7 successive CO_2 adsorption cycles

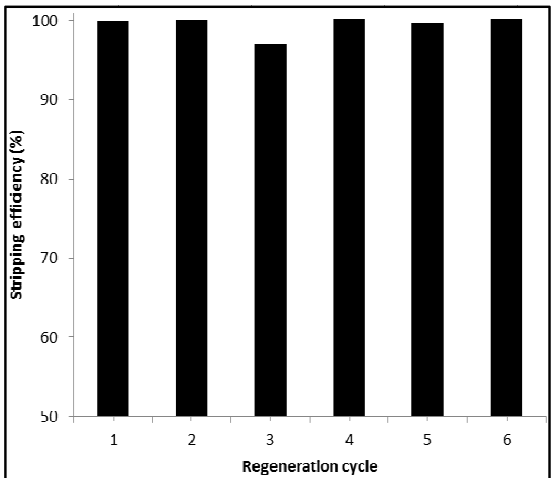

Fig. 7Variations in single step stripping efficiency of M4P2 after 7 successive adsorption cycles

The CO_2 adsorption capacity (q) of M4P2 activated carbon after 7 series of adsorption-desorption cycles is shown in Fig. 5. Results clearly indicate that, there is little change in the adsorption capacity upon the number of cycles. After the seven cycles the regeneration efficiency (RE) for CO_2 reaches is above 95% (Fig. 6). The adsorption desorption cycles affects less significantly the single step stripping efficiency (SSE) (Fig. 7). The SSE increase and then slightly decrease. This implies that the sorbent can be regenerated easily and then reuse, which is a very important property for any adsorbent intended to be used for industrial application.

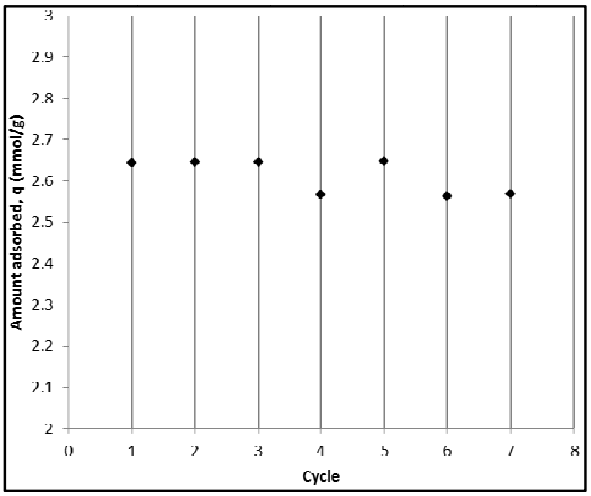

Fig. 8 Equilibrium adsorption capacity of M5P2 over 7 adsorption/desorption cycles at 30^0C, 1 bar

The CO2 adsorption capacity (q) of M5P2 after 7 consecutive adsorption–desorption cycles is also shown in Fig. 8. Results clearly indicate that, there is little change in the adsorption capacity upon the number of cycles. After seven adsorption cycles the regeneration efficiency (RE) for CO2 is above 95% (Fig. 9). The adsorption desorption cycles affects

less significantly the single step stripping efficiency (SSE) (Fig. 10). The SSE increase and then slightly decrease. This shows that the sorbent can be regenerated easily. M5P2 and M4P2 demonstrated higher adsorption capacity after the seven adsorption cycles than M4P0. This could be due to the presence of PEEK in the samples.

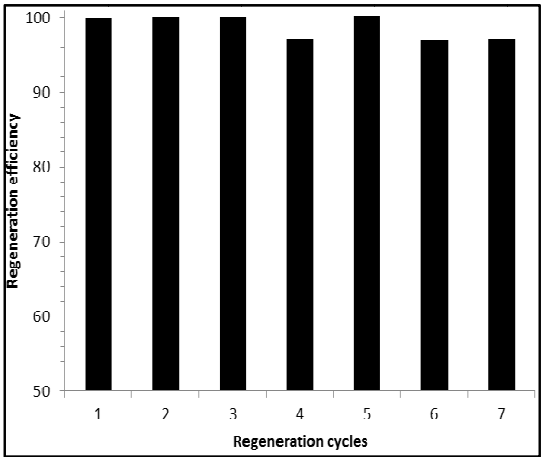

Fig. 9Variations in regeneration efficiency of M5P2 after 7 successive CO_2 adsorption cycles

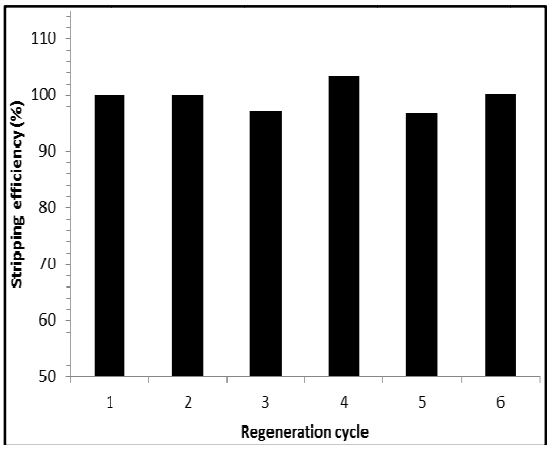

Fig. 10Variations in single step stripping efficiency of M5P2 after 7 successive adsorption cycles

The porous carbons presented were easily and quickly regenerated over multiple cycles with only little loss in CO_2 adsorption capacity. Therefore these sorbents demonstrated good regeneration efficiency which is very important property for any adsorbent intended to be used for industrial application.

B. Desorption Rate

The CO_2 desorption capacity (q_d) for the activated carbon at 303.15K and pressure of 4 bars is shown in Fig. 11. The amount desorbed was -4.62, -5.04, -5.71 mmol/g for M4P0, M4P2 and M5P2 respectively at 4 bar. The amount desorbed for all the samples increases with time, but about 70% of desorption happened within the first 2 to 4mins.

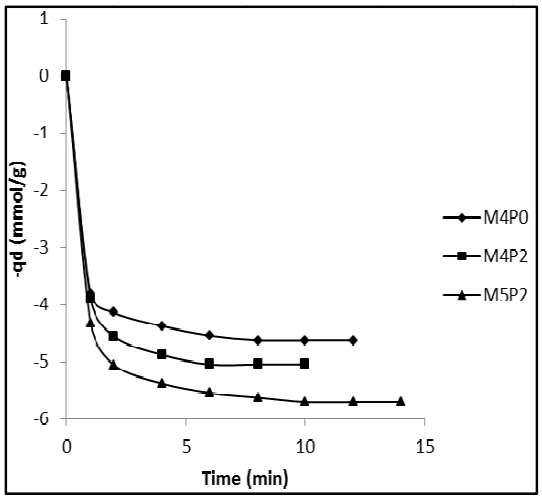

Fig. 11 CO_2 desorption rate from PCs at 4 bar

Most of the adsorbed CO_2 is quickly removed from the AC, due to a favourable porous structure, which allows fast transportation of CO_2 [14] out of the sorbent. The fast desorption rate could also be related to the fact that the process is physisorption where the adsorbate and adsorbent are held by only weak vanderwaal forces.

C. Comparison of Regeneration Capacity of Spent CO_2 Sorbents

Regeneration efficiency of different spent CO_2 sorbents was given in Table I. The methods of regeneration employed for the sorbents are: thermal, thermal with N_2 purge and depressurization. The least regeneration efficiency among all the sorbents was 63.94 (Table I) after 10 cycles for coconut shell AC. This could be related to change in textural properties after series of adsorption and desorption processes. Regeneration of over 97% was reported after 20 cycles of regeneration on KACI15 (15 wt% potassium carbonate activated carbon) sorbent which shows that the sorbent retains stable CO_2 sorption performance. The palm shell-PEEK activated carbon (M5P2) also demonstrated high regeneration efficiency of 97.2 which could be related to the presence of PEEK.

TABLE I
COMPARISON OF REGENERATION CAPACITY OF SPENT CO_2 SORBENTS

Sorbent	Method	No. Cycles	Regeneration Efficiency	Ref.
2ACSH, coconut shell AC modified with 32% NaOH.	Thermal Nitrogen purge	10	63.94	[15]
HTC, hydrothermally carbonized waste	Depressurization	9	97.00	[16]
Amine-Grafted activated carbon	Thermal.	4	91.11	[17]
KACI15		20	97.42	[18]
SBA-15	Thermal	6	91.4	[18]
HSC, solid amine sorbent	Thermal	2	68.00	[18]
M4P0, Microwave palm shell sorbent	Thermal with N_2 purge	7	93.80	This study
M5P2, Microwave palm-PEEK sorbent	Thermal with N_2 purge	7	97.20	This study

IV. Conclusions

Thermal regeneration of CO_2 spent adsorbents was carried out; sorbent stability was accessed by the number of regeneration cycles. High regeneration efficiency was achieved for all the CO_2 spent activated carbon. Palm-PEEK activated carbons perform better with regeneration efficiency above 95% than the one from palm-shells only. Seven cycles of adsorption–desorption were carried out, activated carbon sorbent were found to be stable after these seven cycles. There is only slight decrease in adsorption capacity after successive adsorption–desorption cycles. The sorbents demonstrated good regeneration efficiency which is very important property for any adsorbent intended to be used for industrial application.

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