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Investigation on H_2S Removal Factors of Activated Carbons Derived from Waste Palm Trunk

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Critical factors for H_2S removal of activated carbons prepared from a waste palm trunk were investigated. Two kinds of activated carbons were prepared by different methods, steam and KOH activations. Regardless of high specific surface area and oxygen content of the KOH-activated carbon, the steam-activated carbon showed more than 11 times higher H_2S removal performance, which was even higher than a commercial activated carbon fiber. It was suggested that minerals contained in the steam-activated carbon acted effectively to remove H_2S. The results suggest a potential utilization of waste palm trunks as an available cheap precursor for the H_2S removal adsorbent.

1. Introduction

In Malaysia, as oil palm cultivations are actively carrying on and trees about 25–30 years old are usually replanted, huge amounts of biowastes, such as tree branches, fruit shells, fronds, and trunks, are regularly generated[1)]. Various attempts for recycling the biowastes have been examined[1–4)]. Among them, preparations of activated carbons via pyrolysis of solid biowastes are one of hopeful ways to solve a part of environmental problems and to produce useful material at the same time[1–3,5)]. The trunks take up the largest weight among the palm tree wastes, and thus it is the most important task to find out its effective utilization for environmental protection.

Malaysia is also one of principal natural gas-producing countries. However, Malaysian crude natural gas is sour because maximum 1% of hydrogen sulfide, H_2S, is involved in typical Malaysian crude natural gases[6)]. Therefore, it is strongly required to refine the crude natural gas prior to the shipping.

Recently, we have been studying the production of activated carbons which can be specialized to use for the H_2S removal in the natural gas using waste palm tree trunk, a typical biowaste in Malaysia, as a raw material. In this study, the factors to govern the adsorption amount of H_2S of activated carbons prepared from waste palm trunk were investigated to develop an optimum method to prepare cheap and effective H_2S removal adsorbent for the refinement of the Malaysian crude natural gas.

2. Experimental

2.1 Sample preparation

A dried waste palm trunk (WPT, less than 2 wt.% of moisture content) was supplied from the Malaysian Palm Oil Board (MPOB), Malaysia. The dried WPT was first pulverized and sieved to 100–250 μm, and then carbonized at 500 °C for 1 h in N_2. The carbonized WPT was then activated by steam or KOH activation method. For the steam activation, 90% steam with N_2 carrier at 150 °C was supplied to the horizontal furnace, in which the carbonized WPT was set at the center, at isothermal temperature of 650 °C for 1 h. The obtained steam-activated biochar was designated as SAC. The KOH activation was carried out as follows; firstly, a mixture of KOH and the carbonized WPT at mixing ratio of 2:1 was heated to 600 °C at a ramping rate of 10 °C/min, and then held at 600 °C for 1 h. After cooling down to room temperature, the specimen was washed with distilled water once, with conc. HCl solution for three times, and then with distilled water once again to be pH ~ 7 to remove catalyst residues, followed by drying in an air oven at 80–100 °C for 3 h and in a vacuum oven at 150 °C for more than 3 h. Thus obtained KOH-activated biochar was referred to as KAC.

2.2 Sample characterization

Porosities were evaluated by the α_S analysis of nitrogen adsorption isotherms measured at 77 K by a volumetric equipment (NOVA 4200e, Quantachrome Instruments). Carbon, hydrogen, nitrogen, and ash contents were measured using an elemental analyzer (MT2 CHN Corder, Yanako). The assay of O (Odiff) was defined by subtracting a sum of the contents of C, H, and N from 100%. Elemental compositions of ashes were analyzed by X-ray fluorescence analysis (XRF, EDX-800, Shimadzu Co.). Microscopic structural features and elemental compositions were analyzed using a scanning electron microscopy (SEM, JSM-6320F, JEOL) equipped with an energy dispersive X-ray spectroscopy (EDX, LINK ISIS, Oxford Instruments plc) at operation voltage of 15 keV. The crystal structure of ashes was studied using an X-ray diffractometer (XRD, Ultima III, Rigaku Co.) with a mono-

chromic CuKα radiation at 40 kV and 30 mA at room temperature. X-ray photoelectron spectroscopy (XPS, JPS-9000MC, JEOL) measurements were carried out with a monochromatic MgKα radiation (1253 eV) under 7×10^{-7} Pa. The acceleration tension and emission current of the X-ray source were 10 kV and 10 mA. The C1s peak of graphitic carbon (284.6 eV) was used as a reference to calibrate the binding energy scale.

2.3 H_2S removal test

Assessments of the H_2S removal performance of the WPT-derived activated carbons, SAC and KAC, were carried out by using a home-made fixed-bed reactor. As a reference, a commercially available activated carbon fiber, OG7A, was also tested. A 200 mg of each sample was loaded in a glass tube (9 mm in inner diameter, 12 mm in outer diameter, and 440 mm in length) and kept at 30 °C. The length of the packed samples was set to be 26–30 mm. A standard gas of H_2S (100 ppmv) balanced by pure N_2 was purchased from Asahi Sanso Company, Japan. The H_2S/N_2 mixed gas was diluted with pure N_2 to be 50 ppmv of the inlet H_2S concentration, and introduced through the sample at total flow rate of 50 mL/min. The outlet gases were periodically collected in gasbags, and the H_2S concentrations were measured using a gas chromatography with a flame photometric detector (GC-FPD, GC2800FPD, Yanaco Co. Ltd.). The breakthrough time was defined as the time, at which H_2S was first detected in the outlet gas.

3. Results and discussion

3.1 Sample characterization

Carbonization yield of the dried WPT was 36.2%, which was comparable with the reported values[2]. During the carbonization, large amounts of volatiles were removed, giving rise to remarkable increases of C and ash contents and decreases of H and O contents (Table 1). Yields of the carbonized WPT after steam and KOH activations were 75.9 and 60.7%, respectively, suggesting higher developments of porosity for KAC than for SAC. Both activation processes induced a decrease of the C content and an increase of the O content (Table 1). In terms of the ash content, however, there was a remarkable difference; the ash content of SAC increased from 11% to 18% by the steam activation, but that of KAC became zero (Table 1). It was likely that the ashes in KAC were removed away by the washing with conc. HCl after the KOH activation. N_2 adsorption isotherms at 77 K and the analyzed data of porosity of KAC and SAC are shown in Fig. 1 and Table 1. As expected from the activation yield, KAC possessed well-developed porous structures, though both KAC and SAC were microporous and their average pore widths, w, calculated by the α_S analysis were almost same.

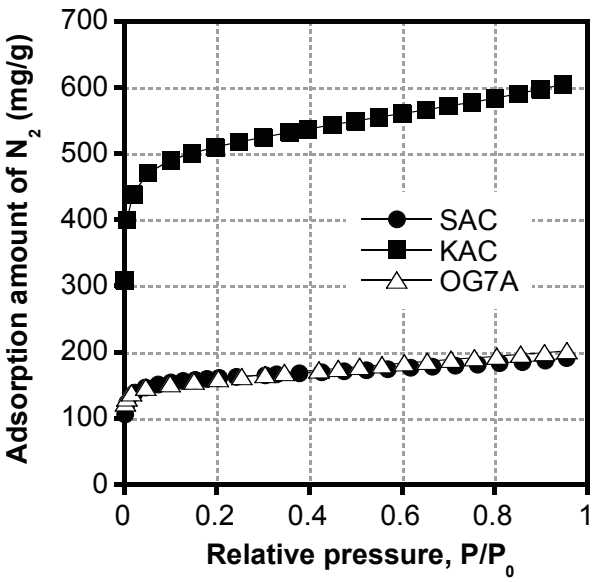

Fig. 1 N_2 adsorption isotherms of steam- and KOH-activated WPT samples (SAC and KAC) and a commercial activated carbon fiber (OG7A) at 77 K.

3.2 H_2S removal test

Fig. 2 shows H_2S breakthrough curves for SAC and KAC. Results of OG7A, a commercial activated carbon fiber, are also shown in Fig. 2 as a benchmark. For all cases, no H_2S was detected in the outlet gas just after the introduction of the 50 ppmv H_2S mixed gas to the samples, and then the outlet H_2S concentration started to increase after the certain period passed. From these results, breakthrough times were calculated, which are

Table 1 Elemental composition from CHN analysis and porosity of dried and treated WPT samples and a commercial activated carbon fiber (OG7A)

Samples	Elemental composition					Porosity		
	C (wt.%)	H (wt.%)	N (wt.%)	O(diff)[a] (wt.%)	Ash (wt.%)	a_s[b] (m^2/g)	V_T[c] (cm^3/g)	w[d] (nm)
Dried WPT	45.72	5.84	0.37	48.06	3.09	-	-	-
Carbonized WPT	80.79	2.55	0.57	16.09	11.07	-	-	-
SAC	74.19	2.08	0.17	23.55	18.40	577	0.23	0.79
KAC	55.74	3.73	0.10	40.43	0.00	1852	0.72	0.78
OG7A	88.96	1.19	0.69	9.16	0.00	595	0.24	0.81

[a] Oxygen content calculated as O(diff) = 100 – (C + H + N), [b] specific surface area, [c] total pore volume, [d] average pore width

tabulated in Table 2. Regardless of the much higher specific surface area of KAC (Table 1), SAC showed the remarkably long breakthrough time of 390 min; as compared with the commercial activated carbon fiber having similar porosity, the breakthrough time of SAC was more than 8 times longer. On the other hand, although KAC and OG7A showed steep uptakes of the outlet H_2S concentration after the breakthrough times passed, the breakthrough curve of SAC relatively gradually increased with time. Therefore, total removed amount of H_2S by SAC was much larger than that by KAC or OG7A, more than 11 or 15 times, respectively (Table 2). Here, the total removed amount of H_2S was estimated by subtracting total amount of H_2S detected in the outlet gases from total introduced amount of H_2S from time 0 to the time when the outlet H_2S concentration became same with the inlet one, 50 ppmv. The results suggest that porosity is not necessarily the predominant factor for the H_2S removal. Also, the large oxygen content of KAC seemed not to contribute to increase the H_2S removal capability. It should be noted that, moreover, the activated carbon derived from WPT has a great potential as the H_2S adsorbent, even compared to the commercial adsorbent.

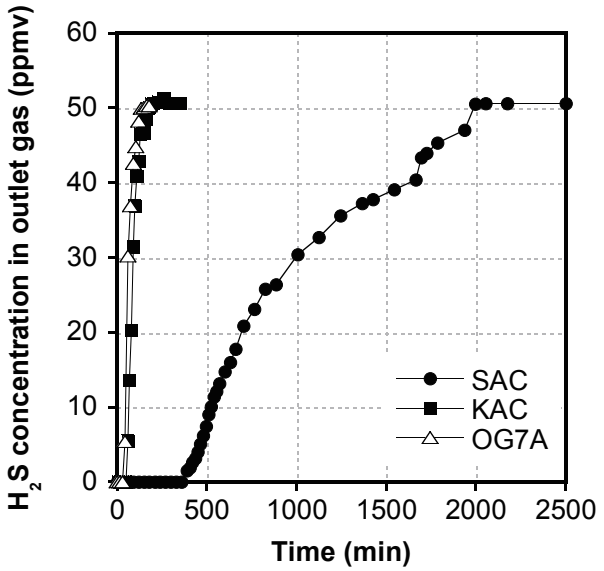

Fig. 2 H_2S breakthrough curves of steam- and KOH-activated WPT samples (SAC and KAC) and a commercial activated carbon fiber (OG7A) at 303 K. Inlet H_2S concentration = 50 ppmv.

Table 2 H_2S removal performance of WPT-derived activated carbons and a commercial activated carbon fiber (OG7A)

Samples	Breakthrough time (min)	Total removed amount of H_2S (mL/g)
SAC	390	12.4
KAC	60	1.1
OG7A	45	0.8

3.3 Analysis of minerals in SAC

Besides the specific surface area and oxygen content, there was a critical difference between SAC and KAC, which was the ash content (Table 1). It has been reported that potassium acts as a catalyst and/or reactant to fix H_2S on carbon adsorbent as sulfur in a presence of oxygen[7–9]. Although the H_2S removal tests in this report were performed in oxygen-free atmosphere, we hypothesized that some elements in SAC worked to fix H_2S effectively. Therefore, detailed analyses of minerals in SAC were performed.

In Table 3, elemental compositions determined from the XRF analyses of SAC before and after the H_2S removal test are shown. It was found that K was the primal inorganic element of the pristine SAC, followed by Cl and Si. After the H_2S removal test, the S content remarkably increased from 1.5 to 16%; this increase should be due to the fixed H_2S on SAC. An increase of the S content resulted in decreases of other elements after H_2S adsorption experiments, relatively, although non-uniform distributions of elements in biomass-derived materials could give rise to some errors in quantitative analysis results.

The fixation of H_2S was also confirmed by SEM-EDX results. As shown in Fig. 3(a), SAC before the H_2S removal test showed only peaks of K, Cl, and Si except for O and C. After the H_2S removal test, however, an intense S peak was indeed observed (Fig. 3(b)). On the other hand, in the case of KAC, only very weak peaks of S and Cl were found before the H_2S removal test; even after the H_2S removal test, an increment of the S peak intensity was slight, which agreed with the H_2S removal test results.

Fig. 4 shows XRD patterns of SAC before and after the H_2S removal test. Besides broad peaks originated from (002) and (10) diffractions of graphitic structures, some sharp peaks were observed. The characteristic peaks were assigned to KCl[10]. Not remarkable changes were found after the H_2S removal test.

XPS results supported a presence of KCl in SAC (Fig. 5). Binding energies of $K2p_{3/2}$ of SAC before the H_2S removal test was found to be about 293.2 eV, which was in agreement with the literature data of 293.6 eV, when we considered a difference of the reference value for the binding energy scale calibration (0.4 eV)[11]. A peak at 295.7 eV would be due to a satellite peak of $K2p_{1/2}$; although it has not been clearly mentioned, such satellite peak can be seen in the literature[11]. Furthermore, the binding energy of Cl2p peak of SAC before the H_2S removal test, 198.8 eV, almost agreed with the reported value, 199.2 eV[11], taking into account the aforementioned difference of the reference value. In the K2p XPS spectrum of SAC before the H_2S removal test, another peak was certainly observed, whilst the intensity was not so strong. At present, we were not able to assign the peak at high binding energy of 298.2 eV, but it might be attributed to complex oxides, such as KFeOx. For example, although it has not been clearly

Table 3 Elemental composition from XRF analysis of SAC samples before and after H_2S removal test (wt.%)

Samples	K	Cl	Si	S	Fe	P	Cr	Cu	Rb	Ni	Br
Before H_2S test	70.36	19.48	7.05	1.47	0.97	0.24	0.23	0.15	0.06	n.d.[a]	n.d.[a]
After H_2S test	56.45	19.34	5.90	16.21	0.82	0.77	0.22	0.13	0.05	0.06	0.06

[a] Not detected.

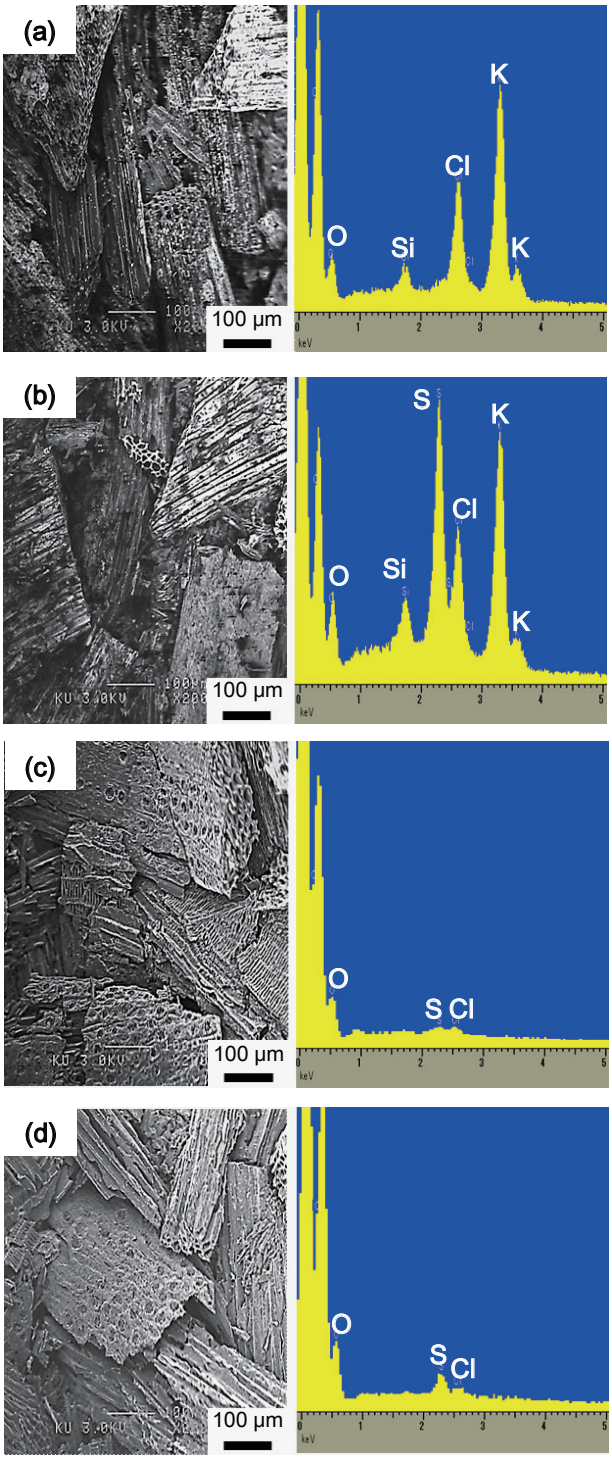

Fig. 3 SEM-EDX results of (a) SAC before H_2S removal test, (b) SAC after H_2S removal test, (c) KAC before H_2S removal test, and (d) KAC after H_2S removal test. (left) SEM images; (right) EDX spectra.

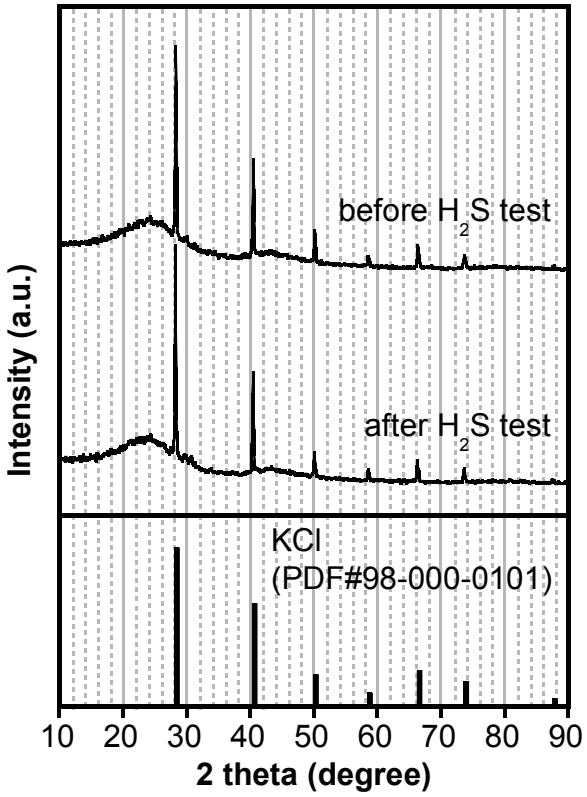

Fig. 4 XRD profiles of steam-activated WPT (SAC) before and after H_2S removal test.

assigned, shoulder peaks at 298.0 and 299.0 eV have been observed in K2p XPS spectra of Fe-K-O catalysts[12]. This not-assigned peak at 298.2 eV decreased its intensity after the H_2S removal test (Fig. 5(c)). These results suggest that a certain kind of potassium compounds involved in SAC might work as the effective H_2S removal agent even at a small quantity.

4. Conclusions

Activated carbon prepared by the simple steam activation technique from a type of biowastes, Malaysian waste palm trunk (WPT), was demonstrated to exhibit the excellent H_2S removal performance; the H_2S removal capacity was more than 11 or 15 times of the KOH-activated WPT or the commercial activated carbon fiber. It was found that high specific surface area is not necessarily indispensable, but minerals involved in the WPT-derived activated carbon were suggested to be effective for the H_2S removal.

Given the great abundance of biowastes, such as WPT,

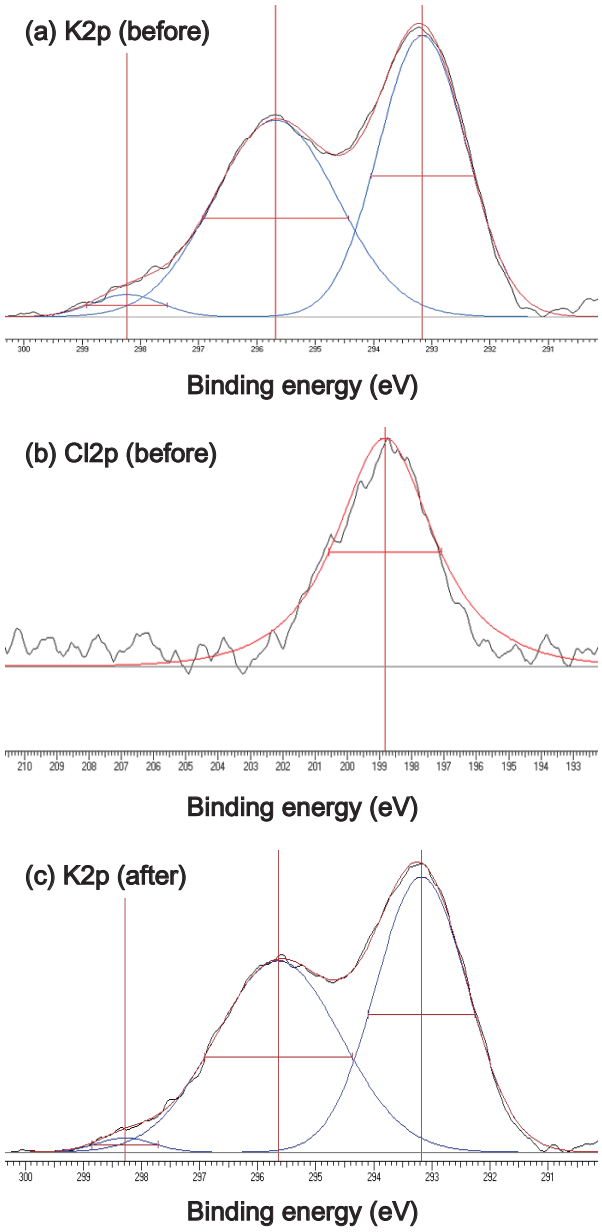

Fig. 5 XPS spectra of (a) K 2p and (b) Cl 2p for SAC before H_2S removal test and (c) K 2p for SAC after H_2S removal test. (Black lines) observed spectra; (blue lines) deconvoluted peaks; (red lines) reproduced spectra by a sum of deconvoluted peaks.

in Malaysia, and the requisite to remove H_2S contained in the Malaysian natural gas, the present study was considered to suggest a feasibility of on-site regeneration and utilization of biowastes at low cost.

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