



PREPARATION OF CARBONACEOUS HEAVY METAL ADSORBENT FROM PALM SHELL USING SULFUR IMPREGNATION

Katsuyasu SUGAWARA¹⁾, Takaaki WAJIMA^{1)*}, Takahiro KATO¹⁾,
Takuo SUGAWARA¹⁾

¹⁾ Department of Materials-process Engineering and Applied Chemistry for
Environments, Faculty of Engineering and Resource Science,
Akita University, 1-1, Tegata-Gakuen cho, Akita 010-8502, Japan
e-mail: wajima@gipc.akita-u.ac.jp

ABSTRACT

We attempt to prepare a heavy metal adsorbent from palm shell with a simple-two step process using pyrolysis and sulfur impregnation. Palm shell was pyrolyzed with three different methods; rapid pyrolysis, slow pyrolysis, and KOH pyrolysis, and the prepared char with high specific surface area was sulfurized with H₂S impregnation to obtain the sulfur-impregnated char with the adsorption ability of heavy metals. The pyrolysis char with high specific surface area can be obtained by KOH pyrolysis, which was pre-treated with KOH solution before slow pyrolysis, and can added sulfur into KOH pyrolysis char using H₂S gas. The sulfur content of sulfur-impregnated char increased with increasing the time of H₂S treatment, and increased the adsorption amount of Pb²⁺ from aqueous solution. The sulfur impregnated char was more effective for Pb²⁺ and Zn²⁺ adsorption than commercial charcoal.

Keywords: Palm shell, Heavy metal adsorption, Carbonaceous adsorbent, Pyrolysis, Sulfur impregnation

INTRODUCTION

In recent years, wastewater treatment techniques have shown great progress in various aspects. Most industries are treating polluted water at their plant sites. Regarding the removal of toxic heavy-metal ions from

industrial wastewater, coagulative precipitation, ion exchange and reverse osmosis are generally used [1]. However, it still seems necessary to develop a new method that attains a higher removal level at low cost. As a result, various types of adsorbents or ion exchangers have been tried.

Activated carbon is well known as a porous material, with large specific surface area, which is useful in the adsorption of both gases and solutes from aqueous solution. Therefore, it has been widely used for the separation of gases, recovery of solvents, removal of organic pollutants from drinking water, and as a catalyst support [2]. As environmental pollution is becoming a more serious problem, the need for activated carbon is growing. It is a versatile adsorbent because of its good adsorption properties.

Various materials are used to produce activated carbon and some of the most commonly used are agriculture wastes such as coconut shell [3], pistachio shell [4], saw dust [5], walnut shell [6], tropical wood [7] and almond shell [8]. Palm shell (also known as *endocarp*) is a cheap and abundant agricultural by-product in tropical countries like Malaysia and Indonesia. Palm shell has been successfully converted into well-developed activated carbon by thermal activation (physical activation) and chemical activation using with carbon dioxide (CO₂) and H₂PO₃ [9-11].

However, it is known that activated carbon is relatively less effective in removing metal species from aqueous solution as compared to removing organic compounds [12]. One reason for this can be attributed to the relatively non-polar characteristic of activated carbon which somewhat inhibits attraction between charged metal species and its surface, even though some surface functional groups may exist on the surface. Since adsorption capacity and rates were influenced by the chemical nature of the surface of activated carbon [13], one of the methods for the improvement of the adsorption of heavy metals is the introducing sulfur in the material, because sulfur is a soft base and should interact with heavy metals such as Pb²⁺, Cd²⁺ and Zn²⁺, which are soft acids, rather than with hard bases such as oxygen, according to the Pearson theory [14, 15]. Little information is available, however, on the process of sulfur impregnation and the property of sulfur impregnated char.

In this study, we attempt to prepare the carbonaceous heavy metal adsorbent from palm shell with two-step process using the pyrolysis and sulfur impregnation. We determined the pyrolysis process to obtain the char with high specific surface area for sulfur impregnation, sulfur impregnation with H₂S to the pyrolysis char, and the abilities of the obtained sulfur impregnated char for heavy metal adsorption.

MATERIALS AND METHODS

The experimental procedure is shown in Fig. 1. The raw material, palm shell, was pyrolyzed with three different methods; rapid pyrolysis, slow pyrolysis and KOH pyrolysis, to prepare the char with high specific

surface area, which was preferable for the sulfur impregnation. The prepared char with high specific surface area was sulfurized with H₂S impregnation to obtain the sulfur impregnated char. Finally, the adsorption abilities of the obtained sulfur impregnated char for heavy metals were determined.

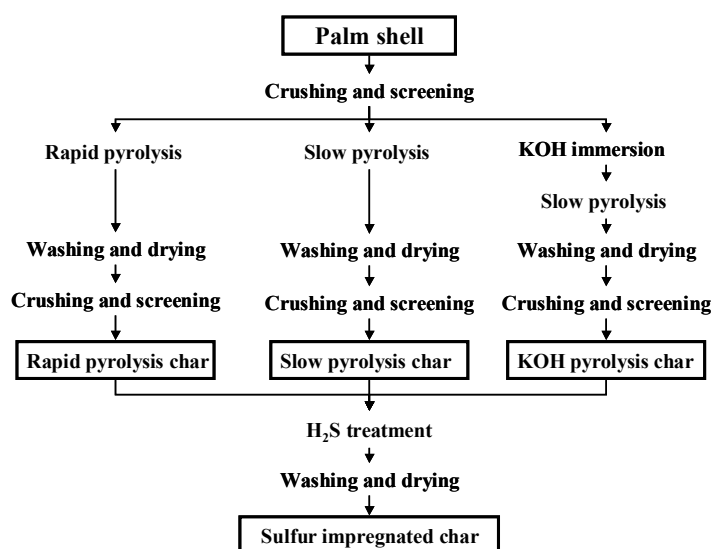


Fig. 1. Preparation of sulfur impregnated char from palm shell.

Raw material

Palm shell obtained from Malaysia oil palm shell were dried, crushed and sieved to a particle sizes ranged from 212 to 355 μm . Table 1 shows proximate and ultimate analyses of palm shell.

Tab. 1. Chemical analyses of palm shell

Ultimate [wt. % d.a.f]					Proximate [wt. %, d.b.]		
C	H	N	S	O	V.M.	Moist.	Ash
55.4	6.4	0.4	<0.05	38.0	68.8	8.4	2.3

Pyrolysis

We used three different types of pyrolysis, as follows. The rapid pyrolysis was carried out using a free-fall reactor, as shown in Fig. 2 (a), which was a fused silica tube (i. d.: 36 mm, length: 2 m), the temperature of which was controlled by an electric furnace composed of 4 sections, each 30 cm long and controlled independently. This apparatus enables palm shell in N₂ gas (at 2 L-NTP/min) to be heated at rates from 10³ to 10⁴ Ks⁻¹. The temperature was 800 °C in the isothermal section of the reactor. Details of the free-fall pyrolyzer have been described elsewhere [16]. Rapid pyrolysis

took place when the palm shell fell down through the hot zone of the reactor, and the pyrolyzed char was collected in a char receiver. After pyrolysis, the pyrolysis char was crushed and sieved again to a particle sizes ranged from 212 to 355 μm to prepare the rapid pyrolysis char.

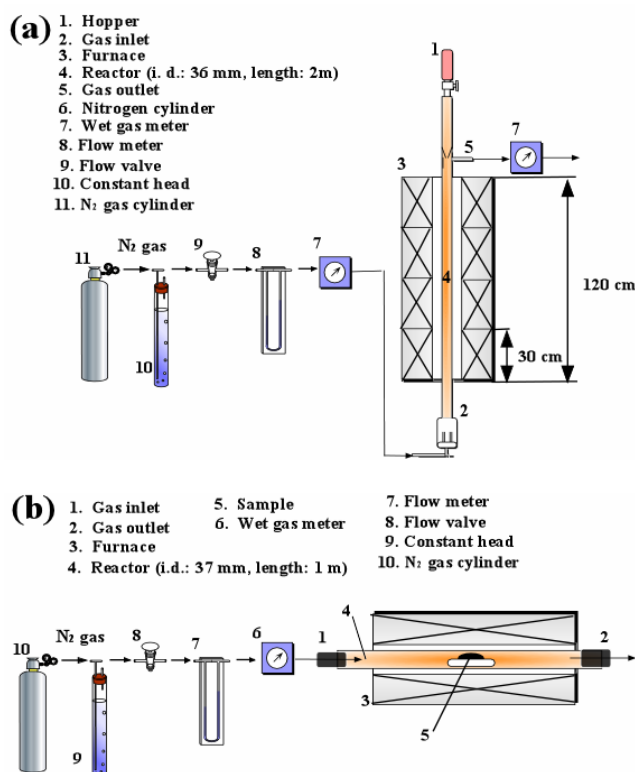


Fig.2. Schematic diagrams of reactors for (a) rapid pyrolysis and (b) slow pyrolysis.

The slow pyrolysis was performed in a horizontal reactor, as shown in Fig. 2 (b), which was a fused silica tube (i. d.: 37 mm, length: 1 m), the temperature of which was controlled by an electric furnace. The palm shell was set in the reactor, and then the N₂ gas went through the reactor at 0.6 L-NTP/min to become N₂ atmosphere in the reactor. The reactor with a N₂ atmosphere (0.6 L-NTP/min) was set in an electric furnace at 800 °C for 30 min to pyrolyze the sample. After pyrolysis, the product was cooled down to room temperature under N₂ atmosphere and was crushed and sieved again to a particle sizes ranged from 212 to 355 μm to prepare the slow pyrolysis char.

The KOH pyrolysis was performed using pre-treated palm shell by the same procedure of the slow pyrolysis, as follows. The palm shell samples were immersed in 5.3 M KOH solution for 2 h at room

temperature. After filtration from KOH solution, the immersed sample was then heated at 750 °C for 30 min in a N₂ atmosphere (at 0.6 L-NTP/min) using a horizontal reactor (Fig. 2 (b)). After heating, the sample was washed repeatedly with distilled water to reduce the pH of the solution to 7, then dried at 110 °C for 12 h, and crushed and sieved again to a particle sizes ranged from 212 to 355 μm to prepare the KOH pyrolysis char.

The palm shell, rapid pyrolysis char, slow pyrolysis char and KOH pyrolysis char were analyzed by equipment for automatic gas adsorption measurement (YUASA IONICS, AUTOSORB-1) to determine the specific surface area.

Preparation of sulfurized carbon

The sulfur impregnation was performed in a vertical reactor, as shown in Fig. 3, which was a fused silica tube (i. d.: 17 mm, length: 1 m), the temperature of which was controlled by an electric furnace. The pyrolyzed sample was set in the reactor, and then the N₂ gas went through the reactor at 0.6 L-NTP/min to become N₂ atmosphere in the reactor. The reactor with a N₂ atmosphere (0.6 L-NTP/min) was set in an electric furnace at 800 °C, and then H₂S gas (0.03 L-NTP/min) was injected to the reactor.

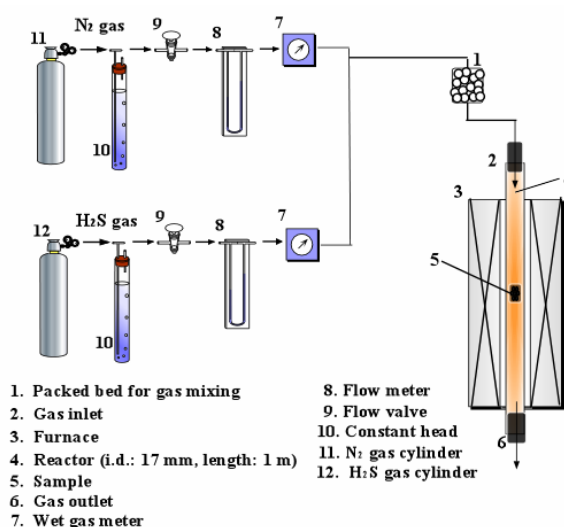


Fig. 3. Schematic diagram of reactor for sulfur impregnation.

After sulfur impregnation for 15, 30 and 60 min, the injection of H₂S gas was stopped, and the product was cooled down to room temperature under N₂ atmosphere and was crushed and sieved again to a particle sizes ranged from 212 to 355 μm to prepare the sulfur impregnated char.

The sulfur contents of the prepared sulfur impregnated chars were analyzed by carbon / sulfur analyzer (HORIBA, EMIA 1200).

The adsorption of heavy metals

The property of heavy metal adsorption for the sulfur impregnated chars was investigated. The comparative study with commercial charcoal (Wako) was performed. We used three types of heavy metals solution with 2.4 mmol/L of Pb^{2+} , Zn^{2+} and Cd^{2+} , which was prepared by $PbCl_2$, $ZnCl_2$ and $CdCl_2$ (WAKO), respectively. 0.5 g of the sample was added into 100 mL of heavy metal solutions, and shaken with shaker (120 oscillation/min) in water bath at 25 °C. One milliliters aliquots of each slurry were removed at varying time intervals, and the concentration of heavy metal ions in the solution was analyzed by atomic absorption spectrometry (AAS) (SHIMADZU, AA-6800) to determine the corresponding adsorption amounts (q_{Metal} [mmol/g]) from the material balance, as follows.

$$q_{Metal} = \frac{(C_{Metal0} - C_{Metal}) \cdot L}{w}$$

where C_{Metal0} is initial concentration of metal ions in the solution [mmol/L], C_{Metal} is concentration of metal ions in the solution during the reaction [mmol/L], L is volume of aqueous solution [L], and w is weight of the sample added to the solution [g].

RESULTS AND DISCUSSION

Pyrolysis char from palm shell

We tried to prepare the pyrolysis char with high specific surface area using three different pyrolysis methods.

Table 2 shows the specific surface area of palm shell, rapid pyrolysis char, slow pyrolysis char and KOH pyrolysis char. The value of specific surface area of palm shell is very minor, 0.4 m²/g. While the rapid pyrolysis char and slow pyrolysis char are 1.3 m²/g and 9.0 m²/g of specific surface areas, respectively, KOH pyrolysis char is 206.9 m²/g, which is 520 times as high as palm shell. It is noted that the yields of rapid pyrolysis and slow pyrolysis char are approximately 30 %, and that of KOH pyrolysis char is approximately 25 %. Almost content of volatile matter, (which is 68.8 wt. % as shown in Table 1), is released from palm shell by all pyrolysis method. In the case of rapid pyrolysis and slow pyrolysis, almost non-volatile matter (about 30 %) is remained because there is a little reaction to create the porous structure in palm shell. However, in the case of KOH pyrolysis, impregnated KOH dehydrates the palm shell, resulting in charring and carbonizing the carbon skeleton with creation of a porous structure [17]. In addition, the activating agent, KOH, influences the pyrolytic decomposition and inhibits the formation of tar, resulting in a decrease in the formation of releasing compounds like acetic acid and ethanol and, thus, prevent the decrease of carbon yield (-5 %). Therefore, the high yield of KOH pyrolysis char with high specific surface area can be obtained.

Tab. 2. Change in specific surface areas of samples with various pyrolysis

	Specific surface area (m ² /g)
Palm shell	0.4
Rapid pyrolysis char	1.3
Slow pyrolysis char	9.0
KOH pyrolysis char	206.9

Sulfur impregnation and heavy metal adsorption

We tried to prepare the sulfur impregnated char from KOH pyrolysis char, which has highest specific surface area in three pyrolysis chars, using H₂S gas.

Table 3 shows the sulfur content of samples during the H₂S impregnation. With increasing the impregnation time, sulfur content of the samples increases rapidly, and after 30-min impregnation increases slowly.

Tab. 3. Sulfur content of samples during the H₂S impregnation

Impregnation time [min]	Sulfur content [wt. %]
0	0.01
15	5.7
30	7.6
60	8.9

Figure 4 shows the adsorption amounts of Pb²⁺ of samples with various sulfur contents. With increasing the sulfur content of the samples to 7.6 wt. %, the adsorption amount of Pb²⁺ increases, and becomes almost same above 7.6 wt. %.

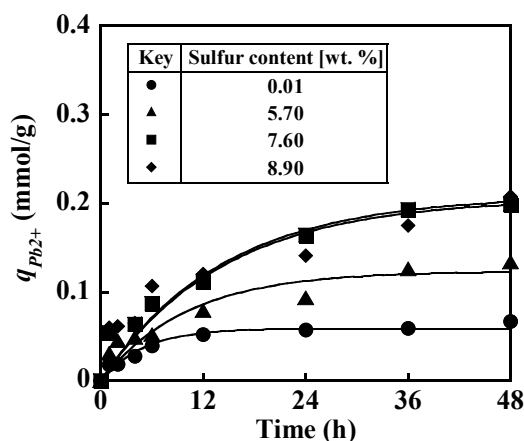
Fig. 4. Adsorption amounts of Pb²⁺ of samples with various sulfur contents.

Figure 5 shows the sulfur content of the sample and the adsorption amount of Pb^{2+} for 48-h reaction as a function of sulfur impregnation time. There is a good correlation between sulfur content and the adsorption amount of Pb^{2+} . It was reported that the activated carbon prepared from palm shell by KOH activation had better adsorption performance for H_2S gas due to the surface chemistry of functional group [18]. It was also reported that, in the treatment of activated carbons with H_2S , thiophenol groups was formed on the surface, and adsorption of Pb^{2+} from aqueous solution increased [19]. It would be considered that the almost surface of KOH pyrolysis char was covered by adsorption of H_2S for 30 min to create thiophenol group, and the adsorption amount of Pb^{2+} increased to 30-min impregnation.

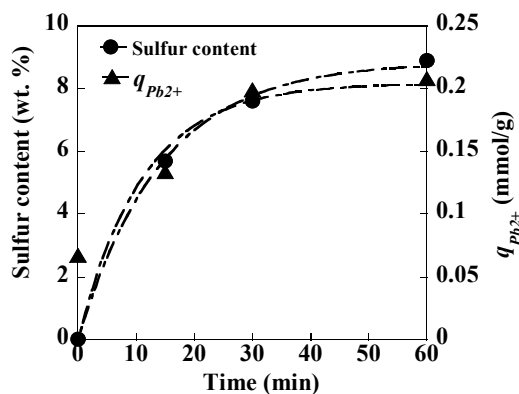


Fig. 5. The sulfur content of the samples and the adsorption amount of Pb^{2+} for 48-h reaction as a function of sulfur impregnation time.

Figure 6 shows the comparison of the adsorption amounts for heavy metals (Pb^{2+} , Zn^{2+} and Cd^{2+}) between sulfur-impregnated char with 7.6 wt.% sulfur content and commercial charcoal. The adsorption amounts of sulfur impregnated char for Pb^{2+} and Zn^{2+} is higher than those of commercial charcoal, while the adsorption amounts of sulfur impregnated char for Cd^{2+} is lower than those of commercial charcoal. According to the Pearson theory [14, 15], Lewis acids were classified into three groups; hard, soft, and borderline. Pb^{2+} and Zn^{2+} belong to borderline, and Cd^{2+} belongs to soft group. It may be considered that borderline group, Pb^{2+} and Zn^{2+} , is favorable for the reaction with thiophenol group on the surface of the char, in comparison with soft group, Cd^{2+} .

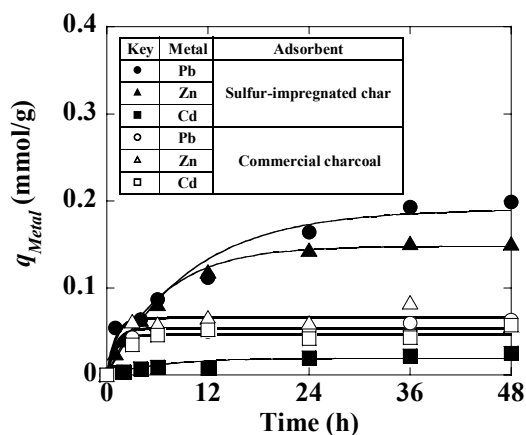


Fig. 6. Comparison of the adsorption amounts for heavy metals (Pb^{2+} , Zn^{2+} and Cd^{2+}) between sulfur impregnated char and commercial charcoal.

CONCLUSION

We tried to prepare carbonaceous heavy metal adsorbent from palm shell using sulfur impregnation, and applied to heavy metal removal. The following results can be concluded:

- (1) The pyrolysis char with high specific surface area can be prepared from palm shell using KOH pyrolysis.
- (2) Sulfur can be added into KOH pyrolysis char using H_2S gas impregnation, and sulfur content of sulfur-impregnated char can be adjusted by sulfur impregnation time.
- (3) Sulfur impregnated char is more effective for Pb^{2+} and Zn^{2+} adsorption than commercial charcoal.

Therefore, the carbonaceous heavy metal adsorbent prepared from palm shell using sulfur impregnation can be achieved, and the adsorbent can be applied to heavy metal removal.

REFERENCES

- [1] *Kagaku Kougaku Binran (5th Ed.)*, Maruzen, Tokyo, 1978, p.1325.
- [2] Y. Sanada, M. Suzuki, K. Fujita, *Kasseitan-Kiso to Ouyou, Koudansha*, Tokyo, 1992.
- [3] C.J. Kirubakaran, K. Krishnaiah, S.K. Seshadri, *Ind. Eng. Chem. Res.*, 1991, 30, 2411-2416.
- [4] I. Abe, H. Tatsumoto, N. Ikuta, I. Kawafune, *Chem. Exp.*, 1990, 5, 177-180.
- [5] Z. Xiongzun, Z. Famnao, L. Lie, L. Qingrong, *J. Nanjing Inst. Forest.*, 1986, 1, 19-30.
- [6] A. Khan, H. Singh, A. K. Bhatia, *Res. Ind.*, 1985, 30, 13-16.
- [7] K. Maniatis, M. Nurmala, *Biomass Energy Ind. Environ.*, 1992, 274, 1034-1308.
- [8] J. Hayashi, A. Kazehaya, K. Muroyama, A.P. Watkinson, *Carbon*, 2000, 32, 1873-1878.
- [9] J. Guo, A. C. Lua, *Mater. Lett.*, 2000, 55, 334-339.
- [10] J. Guo, A. C. Lua, *J. Colloid Interface Sci.*, 2002, 254, 227-233.
- [11] J. Guo, A. C. Lua, *Mater. Chem. Phys.*, 2003, 80, 114-119.
- [12] N. Adhoum, L. Monser, *Chem. Eng. Process.*, 2002, 41, 17-21.

- [13] P.N. Cheremisinoff, F. Ellerbusch, *Carbon Adsorption Handbook*, Ann Arbor Science, Arbor 1980
- [14] R. G. Pearson, *J. Am. Chem.Soc.*, 1963, 85, 3533-3539.
- [15] R. G. Pearson, *J. Chem. Educ.*, 1987, 64, 561-567.
- [16] T. Sugawara, K. Sugawara, Y. Nishiyama, M. A. Sholes *Fuel*, 1991, 70, 1091-1097.
- [17] R.C. Bansal, J.B. Donnet, F. Stoeckli, *Active Carbon*, Marcel Dekker, New York 1992.
- [18] J. Guo, Y. Luo, A.C. Lua, R. Chi, Y. Chen, X. Bao, S. Xiang, *Carbon*, 2007, 45, 330-336.
- [19] A. Macías-Garacía, C. Valenzuela-Calahorro, V. Gómez-Serrano, A. Espínosa-Mansilla, *Carbon*, 1993, 31, 1249-1255.