

Hetero-atom Decoration of Activated Carbon without Post-Treatment

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In this work, we attempt to decorate heteroatoms, including nitrogen and sulphur, into activated carbon without post-treatment. These atoms can be introduced into the carbon framework by the strong acid/base reactions after the carbonisation and activation. Raw materials, which contain the desired heteroatoms, were selected so that the obtained activated carbon would have the heteroatom without the harmful chemical process. Crab and shrimp shells were used as the raw material for nitrogen-doped activated carbon since they both contain chitin, which is the organic compound containing nitrogen atom. Similarly, lignite from Mae Moh (Lampang province, Thailand) which has high sulphur content, is suitable for the preparation of sulphur-doped activated carbon. Two types of activating agents, K_2CO_3 and KOH, were used as the activating agents and the effect from the ratio of raw materials to activating agents were studied. The surface area and the pore structures were determined by nitrogen adsorption analysis and the elemental compositions were characterised by CHNS analysis. It is found that activated carbon prepared from shrimp shells has a higher nitrogen content (1.40 wt%) than that prepared from crab shells (0.47 wt%). The specific area of the obtained activated carbon was as high as 2,100 m^2/g with the optimal condition. Sulphur-doped activated carbon can be easily prepared from lignite with high sulphur contents (14.34 wt%) and commercially comparable specific surface area (650 m^2/g).

1. Introduction

Activated carbons (ACs) are commonly used as a solid adsorbent in the removal of contaminants from gas pollution and wastewater produced by industries. The activation of ACs increases their porosity and specific surface area, which can increase capacity for the adsorption of pollutants. ACs can be produced from the materials containing high carbon content, for example, coal (Lozano-Castelló et al., 2001) coconut shell (Tan et al., 2008), macademia nuts (Tam, 1999), saw dust and wood (Khezami et al., 2005) bamboo woods (Mahanim et al., 2011). To produce ACs, the raw material has to be activated by either physical or chemical activations. For physical activation, carbonisation of the raw material is performed first, and then followed by activation using steam or carbon dioxide. However in chemical activation, an activating agent such as KOH or K_2CO_3 is impregnated into the raw material and the carbonisation/activation will be held simultaneously in an inert atmosphere, such as nitrogen gas.

The introduction of hetero-atoms, such as oxygen (Li et al., 2003), nitrogen for arsenic removal (Han et al., 2016) and CH_4 absorption (Yamashita et al., 2015) and sulphur (Sevilla and Fuertes, 2012, Seema et al., 2014), can improve the adsorption ability of ACs as well as improving the wettability of the ACs (Sethia and Sayari, 2015). The electrochemical capacitance of the carbon electrode can be enhanced by the presence of such heteroatoms (Beguin and Frackowiak, 2010) and in (Itoi et al., 2014) as well as in (Lee et al., 2015). Apart from the typical electrostatic interactions in the electric double-layer, fast redox reactions with electron transfer on the electrode/electrolyte interface resulting from the heteroatoms doping can greatly contribute in enhancing the charge and energy storage capacity, so called pseudocapacitance, as shown in Figure 1. To introduce the heteroatoms into the carbon framework, doping the activated carbon with strong chemicals such

as HNO_3 and H_2SO_4 , are necessary. Additional washing and drying steps are required which lead to the generation of hazardous wastes. To avoid such chemical doping, the use of raw materials with carbon, nitrogen or sulphur already present, are attractive.

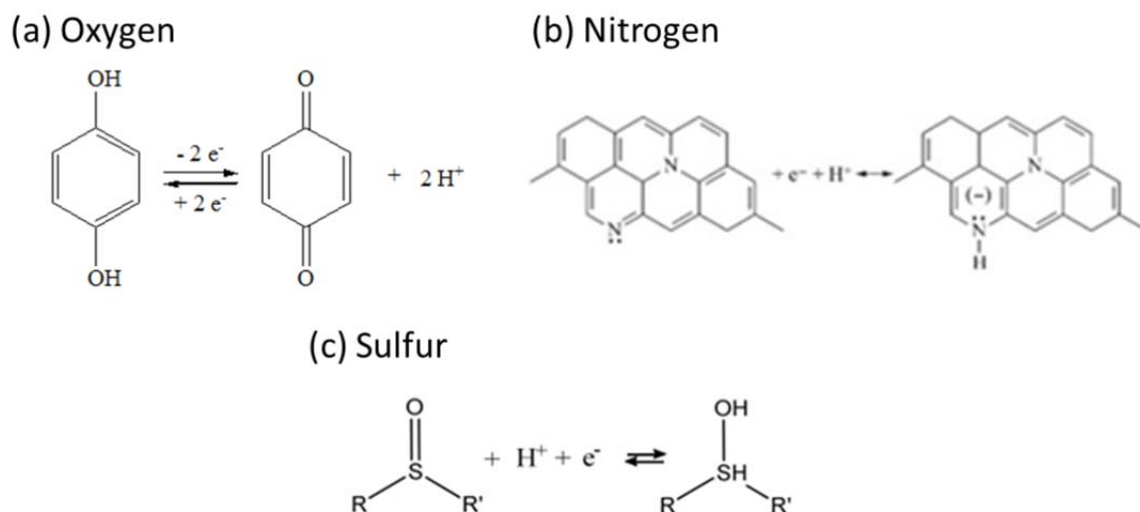


Figure 1: Examples for the redox reactions involved in the pseudocapacitance as a result from the heteroatoms: (a) oxygen, (b) nitrogen, and (c) sulphur

There have been many attempts to produce a cleaner ACs from waste and biomass. Biomass is considered as negative-valued waste that is deposited into the environment. Production of ACs from biomass is an environmentally friendly method and cost-effective, as biomass is inexpensive. Crab and shrimp shells are the waste materials produced by the seafood-processing industry. They both contain chitin, which already has carbon and nitrogen atoms in its composition (Figure 2), allowing nitrogen to be introduced into the carbon framework without post-treatment as previously mentioned (Isa et al., 2012). Lignite from Mae Moh coal fired power plant (Lampang province, Thailand) is notorious for having high sulphur contents, making it undesirable for the use as coal fuel. Burning this lignite would release SO_2 into the atmosphere, which can cause the acid rain. Preparing ACs from this lignite, sulphur could be easily introduced into the ACs. Using these materials allows heteroatoms to be introduced into the activated carbon and avoid harmful chemical processes without the post-treatment.

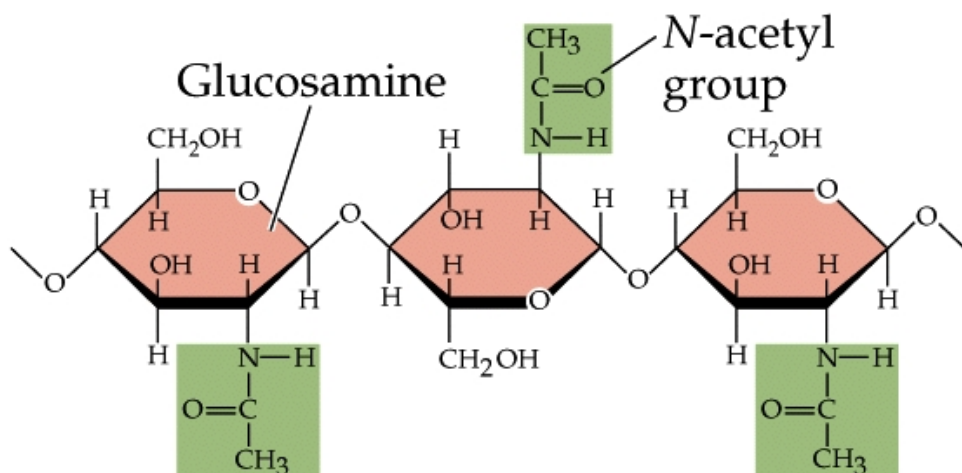


Figure 2: Molecular structure of chitin (N-Acetylglucosamine)

In this paper, ACs were prepared from crab and shrimp shells impregnated with K_2CO_3 as the activating agent. For lignite, KOH is used as the activating agent instead and the effect from the ratio of raw materials to activating agent on the specific surface area and heteroatom content were studied and discussed.

2. Experimental

2.1 Materials and Chemicals

Blue crab shells and giant Malaysian prawns were provided by the seafood industry at Mahachai city, Thailand. The shells were dried and crushed into a powder form. Lignite was acquired directly from MAE MOH coal fired power plant (Lampang province, Thailand). Lignin (99 % laboratory grade) was used as the carbon source for the ACs preparation from crab and shrimp shells. K_2CO_3 and KOH (laboratory grade) were purchased in powder form from KN Science Innovation Co. Ltd. (Thailand).

2.2 Preparation of sample

Crab and shrimp shells were impregnated with lignin and K_2CO_3 . Lignin is used to increase the carbon content in both of crab and shrimp shells, as raw crab and shrimp shells do not contain enough carbon for activation. The ratio by weight was lignin: crab (or shrimp): K_2CO_3 of 1 : 1 : 2, 1 : 2 : 2, and 1 : 3 : 2. The materials were mixed and kneaded in water, then dried at 100 °C overnight. The product was finally grinded into a powder form.

Lignite was impregnated with KOH, with the weight ratio of lignite: KOH of 1 : 1, 1 : 2, and 1 : 4, using the same method described above.

2.3 Activation of AC

A tubular carbonisation furnace was used to carbonise and activate the samples. The sample was heated to 900 °C at a heating rate of 5 °C min⁻¹ in a nitrogen gas flow with a flow rate of 150 mL/min. The temperature was held at 900 °C for 1 h for the carbonisation/activation before cooling down to room temperature in nitrogen atmosphere.

After the carbonisation/activation, the thus obtained samples were washed with 1 M HCl and then filtered to recover the solid portion. They were washed with RO water and filtered until the pH of the samples were neutral. The ACs products were obtained after drying the samples at 100 °C overnight.

2.4 Characterisation

The surface texture of the ACs products was characterised by nitrogen-sorption analysis at 77 K. Specific surface area of all samples were calculated from the isotherms using Brunauer-Emmett-Teller (BET) method. The elemental composition of the raw materials and the as-prepared ACs were done by CHNS analysis.

Table 1: Elemental analysis of crab shell, shrimp shell and AC prepared by crab and shrimp shells

Materials	Ratio	Carbon (weight %)	Hydrogen (weight %)	Nitrogen (weight %)
Shrimp shell	-	42.07	5.74	24.81
Crab shell	-	10.23	2.82	3.94
Crab: K_2CO_3	1 : 1	2.07	1.89	0.36
Shrimp: K_2CO_3	1 : 1	1.56	2.20	1.00
Lignin: Shrimp: K_2CO_3	1 : 1 : 2	15.71	1.17	0.44
	1 : 2 : 2	12.86	1.42	1.40
	1 : 3 : 2	12.47	1.32	1.38
Lignin: Crab: K_2CO_3	1 : 1 : 2	18.17	1.35	0.36
	1 : 2 : 2	10.93	1.67	0.47
	1 : 3 : 2	4.98	2.55	0.70

3. Results and Discussion

3.1 Nitrogen-Doped ACs

3.1.1 Elemental Analysis

Table 1 shows the elemental composition of crab shell, shrimp shell and the AC products. Crab and shrimp shells activated with K_2CO_3 only showed very low carbon contents (1 - 2 wt%) as a result from relatively low carbon content of the raw materials themselves (42 wt% for shrimp and 10 wt% for crab). Another carbon source is required and lignin was selected. Lignin is a carbonaceous substance and is one of the most abundant plant-derived polymer, which can be found in black liquor as a waste discharged from paper pulping industries.

Shrimp shell has considerably higher nitrogen content (24.8 wt%) than crab shells (3.9 wt%). As a result, ACs prepared from shrimp shell have higher amount of nitrogen (0.4 – 1.4 wt%) than those prepared from crab shell (0.4 – 0.7 wt%). The results suggest that shrimp shell is more preferable to produce N-doped ACs rather than crab shell. Increasing the amount of shrimp shell increases the nitrogen content and reasonably reduces the portion for carbon. Based on these results, the optimal ratio of lignin: shrimp shell: K_2CO_3 is 1 : 2 : 2, which lead to the highest nitrogen content (1.4 %) and a sufficient amount of carbon (12.9 %).

3.1.2 Nitrogen-Sorption Analysis

Specific surface area (SSA) of the AC products calculated from the nitrogen adsorption isotherms by BET method are listed in Table 2. It can be clearly seen that crab and shrimp shells activated without lignin showed very low surface areas. As previously mentioned that these raw materials contain relatively low carbon amount, It cannot be simply used as the precursors without the addition of other carbon source, such as lignin, in this case. With the addition of lignin, SSA increases obviously up to ca. 120 m²/g, further confirm the role of lignin as the carbon source. SSA of these ACs are still very low.

Table 2: Specific surface area of ACs prepared by crab, shrimp shells and lignin

Materials	Ratio	Specific surface area (m ² /g)
Crab: K_2CO_3	1 : 1	0.83
Shrimp: K_2CO_3	1 : 1	1.06
Lignin: Shrimp: K_2CO_3	1 : 1 : 2	120
	1 : 2 : 2	75
	1 : 3 : 2	127
Lignin: Shrimp: K_2CO_3 (HCl treated)	1 : 1 : 2	1,430
	1 : 2 : 2	2,100
	1 : 3 : 2	2,030
Lignin: Crab: K_2CO_3 (HCl treated)	1 : 1 : 2	1,800
	1 : 2 : 2	1,690
	1 : 3 : 2	900

The study found that the SSA of the sample is significantly increased with the HCl treatment. As can be seen in Table 2, the AC sample treated with HCl has much higher SSA than those untreated. Generally, calcium carbonate ($CaCO_3$) present in the shells is decomposed to calcium oxide (CaO) and carbon dioxide (CO_2) at above 700 °C during the activation/carbonisation. CaO left in the framework can block the pores, which results in the low SSA. CaO can react with HCl to form calcium chloride ($CaCl_2$) and water. Washing CaO from the ACs with HCl can result in more porous structure and hence higher SSA.

ACs prepared from shrimp shells possess higher SSA than those prepared by crab shells. Increasing the amount of shrimp shell increases the SSA of ACs due to the development of surface functionalities. Too many nitrogen makes the framework collapsed, leading to the decreasing of SSA. The ratio of 1 : 2 : 2 for lignin: shrimp: K_2CO_3 shows the highest SSA of 2,100 m²/g together with a moderate nitrogen content of 1.4 wt%.

3.2 Sulphur-Doped AC

3.2.1 Elemental Analysis

Table 3 shows the elemental composition of lignite and the obtained AC product. The AC showed a decrease in carbon content after the activation. Sulphur content in the AC is significantly higher than that in the raw lignite, which may result from the decrease of carbon during the carbonisation and activation. It may suggest that sulphur may not be lost during such process. Lignite used in this work is suitable for the S-doped AC production.

Table 3: Elemental analysis of lignite and ACs prepared from lignite

Material	Ratio	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulphur (wt%)
Lignite	-	36.80	2.50	1.35	4.40
Lignite: KOH	1 : 1	13.01	0.16	0.20	14.34

3.3 Nitrogen-Sorption Analysis

Table 4 shows SSA of the ACs prepared from lignite, which decreases significantly when the amount of activating agent (KOH) increases. Possible explanation would be the decomposition of KOH at high temperature to form K_2CO_3 , which may lead to the pore blockage. At the highest ratio of 1 : 4, the excess KOH would be decomposed and were not able to characterise the sample. The lignite to KOH ratio of 1 : 1 gives the highest SSA of ca. $650 \text{ m}^2/\text{g}$, which is comparable to the commercial ACs ($400 - 1,500 \text{ m}^2/\text{g}$) together with a high sulphur content of 14.3 wt%.

The authors have recently found that the lignite from Mae Moh contains a large amount of ash (ca. 40 wt% by TGA analysis). This could explain why the SSA of AC products are relatively low. The ashes in lignite are mainly calcium carbonate, silica, and alumina. As previously mentioned, calcium carbonate can decompose to calcium oxide and carbon dioxide at high temperature according to the reaction below.



Calcium carbonate can be removed easily by acid washing, as shown in Eq(2). The lignite was pre-washed with 10 M HCl at $50 \text{ }^\circ\text{C}$ for 30 min. As expected, the ash content of lignite after the acid washing decreased to ca. 20 wt%. The SSA of AC can be expected to be higher than $1,200 \text{ m}^2/\text{g}$. If the ash is completely removed from the lignite, the SSA can reach $2,000 \text{ m}^2/\text{g}$ reasonably.



Table 4: Specific surface area of AC prepared from lignite

Material	Ratio	Specific Surface Area (m^2/g)
Lignite: KOH	1 : 1	650
	1 : 2	200
	1 : 4	-

4. Conclusion

In conclusion, N-doped activated carbon from crab and shrimp shells, and S-doped activated carbon from lignite, were successfully prepared with a cleaner and environmentally friendly strategy – the selection of biomass precursors. Due to insufficient carbon content in both crab and shrimp shells, lignin was added and served as a carbon source. Shrimp shell contained higher carbon and nitrogen contents than that of crab shell. It is a more suitable precursor for the N-doped AC production rather than crab shell. Specific surface area of the AC prepared from shrimp shell was $2,100 \text{ m}^2$, which was significantly higher than that of commercial AC, together with a moderate nitrogen content of 1.4 wt%. S-doped AC prepared from lignite had high sulphur content (14.3 wt%) and commercial comparable specific surface area ($650 \text{ m}^2/\text{g}$), which can be further increased by the acid washing of the lignite precursor. The raw materials used in this work are thus viable for the production of heteroatom decorated AC without the harmful and environmental burden processes.

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