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Electrochemical Study of Demineralized Bituminous Coal by Alkali-Acid Leaching Assisted Low-Frequency Ultrasonication

Mohamad Samsul Anrokhi[1,*], Oktaviardi Bityasmawan Abdillah[1], Pipit Fitriani[1,2], Fatimah Arofiati Noor[1] & Ferry Iskandar[1,2]

[1]Department of Physiscs, Faculty of Mathematics and Natural Science,
Institut Teknologi Bandung, Bandung 40132, Jawa Barat, Indonesia.
[2]Reseach Center of Nanosceinece and nanotechnology (RCNN),
Institut Teknologi Bandung, Bandung 40132, Jawa Barat, Indonesia.
[*]Email: anrokhi@fi.itera.ac.id

Abstract. This paper describes experimental research on alkali-acid leaching treatment on bituminous coal assisted by low-frequency ultrasonication and investigates its influence on the coal's specific capacitance. In order to describe the grade of raw coal, approximate and ultimate analyses were utilised. As a leachant, NaOH and H_2SO_4 were utilised. The coal samples were leached twice with NaOH and H_2SO_4 at 37 kHz ultrasonic frequency. The concentration ratio of NaOH to H_2SO_4 was 1:2, with NaOH concentrations varying between 5 and 10 weight percent. With increasing leachant concentration, Fourier Transform Infrared (FTIR) spectroscopy revealed a rise in mineral band transmittance. Specific capacitance (CS) of leached coal in 3M KOH electrolyte increased in proportion to the concentration of leachant. Using 10% NaOH and a scan rate of 5 mV/s, the SC value of leached coal was 4.87 F/g.

Keywords: *coal; demineralization; alkali-acid leaching; electrochemical; ultrasonication.*

1 Introduction

Coal is the cheapest and most plentiful fossil fuel source on earth, and it is primarily used for electricity production [1]. In steel and iron industry, coal is used as a carbon source where coal is used as a reductant for iron ore to metal [2]. Based on coal formation, coal has heterogeneous complex structure that consists of mixture of carbon and mineral matter. [3]. The mineral matter generally consists of metals such as silicone, aluminium, titanium, and calcium etc. and non-metals such as nitrogen, sulphur, phosphorus and clorine [4]. These minerals will form ashes, non-combustible residues when coal is burned. The major ash that commonly found in the coal is silica.

Carbon content in the coal increases during the underground aging, resulting in four coal rank: lignite, subbituminous, bituminous and anthrasite [5]. Lignite with short aging age has the least amount of carbon content (65-70%) and hydroaromatic structure while antrachite with long aging age has the highest carbon content (more than 90%) and high hydroaromatic structure [6]. Bituminous coal is intermediate-rank coal that posseses different characteristics when compared with lignite, subbituminous and anthracite. It has 70-90% carbon content [6].

Coal has an abundant polyaromatic structure similar to the characteristics of the sp^2 bonds in graphene so that coal can be used as graphene-forming material [7]. However, the mineral contents in the coal will have an impact on the resulting graphene because minerals will obstruct the formation of graphene layers and will form irregular pore defects on the graphene [8].

Alkali-acid leaching is one of the chemical methods to clear away or demineralize minerals from coal by using alkali leaching followed by acid washing [9]. This method has benefit to obtain higer degree of demineralization because of unprocessed component and leftover minerals from the initial stage will be dissolved again. Common alkali substances include NaOH, KOH, $Ca(OH)_2$, and also common acids including H_2SO_4, HCl, HNO_3 and H_2O_2 [9,10]. The alkalis will react with the coal'sulphur and major minerals (silica, alumina, and clay-bearing minerals) to form hydrated alkali compound of silicate, aluminate and aluminosilicate [4,9]. The products of alkali leaching are poorly soluble and require acid treatment to be removed from coal [11]. Possible reaction between alkali and major minerals during leaching process as shown in equation 1-3 [9].

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$2NaOH + Al_2O_3 \rightarrow 2NaAlO_2 + H_2O \quad (2)$$

$$NaOH_{(aq)} + NaAl(OH)_{4(aq)} + Na_2SiO_{3(aq)} \rightarrow Na_a(AlO2)_b(SiO_2)_c NaOH.H_2 \quad (3)$$

$$[sodium\ aluminosilicate\ complex\ gel]$$

To improve leaching efficiency, ultrasonic energy has been used to assist coal cleaning process. Ultrasonic energy is energy from sound wave with frequency above 20 kHz [12]. Application of ultrasonic energy with frequency under 100 kHz will produce cavitation mechanism. This mechanism will increase the efficacy of the leaching process by accelerating the diffusion of reagents within coal particles [13].

As an intermediate product of coal processing into carbonaceous materials, the demineralized coal contains a lower impurity and higher carbon content than untreated raw coal which is expected to perform better electrochemical properties than raw coal. However, to the best of the information we have, the study of electrochemical properties of demineralized coal as a supercapacitor electrode has not been reported previously. Thus, in the present work, we reported electrochemical characteristic of demineralized bituminous coal as an electrode of supercapacitor. Cyclic voltammetry (CV) as an electrochemical characerization of the resulting samples is discussed.

2 Experimental method

2.1 Material

The coal sample was obtained from PT.Bukit Asam (PTBA), Lampung Indonesia. The composition of coal was characterized by proximate and ultimate analysis listed in Table 1. NaOH and H_2SO_4 solvents were used as leachant in this experiment. Meanwhile carbon black, polyvinylidineforide, and 1-methyl 2-pyrrolidinone were used as electrode forming materials mixed with coal.

Table 1. Proximate and ultimate analysis of coal.

Analysis	Result
Proximate	Wt %
Moisture	11.73
Volatile matter	39.57
Fix carbon	44.98
Ash	3.72
Ultimate analysis	Wt %
C	79.10
H	5.82
N	1.35
O	13.27
S	0.46

2.2 Experiment

The alkali-acid leaching experiment conducted in ultrasonic bath with specification frequency of 37 kHz. To obtain an average particle size range of roughly 212 μm, the coal sample was crushed and sieved. Coal powder was dried in oven at 105^0C for 3 hours. In this experiment, alkali-acid leaching was done by using ultrasonication. The first step coal powder sample of approximately 3 g was mixed with 50 ml of 1 wt% NaOH in erlenmeyer flask. This mixture placed in center possition of ultrasonicator bath for 2 h at temperature of 80^0C. Then, the 2 vol% of H_2SO_4 was addeed into the coal slurry sonication for 2 h at temperature of 80^0C. The coal slurry was created and then dried for three hours at 105 °C in an oven after being rinsed with hot deionized water until its pH was neutral. In the same way, H_2SO_4 with a 1:2 concentration ratio was added after NaOH concentrations of 5% and 10%. Henceforth, the resulted samples were labelled as raw coal, C-NaOH, C-H_2SO_4, C-mix 5% and C-mix 10% for raw coal, NaOH demineralized coal, H_2SO_4 demineralized coal, NaOH followed by H_2SO_4 with 5% and 10% concentratio, respectively. These steps are shown in **Fig.1**.

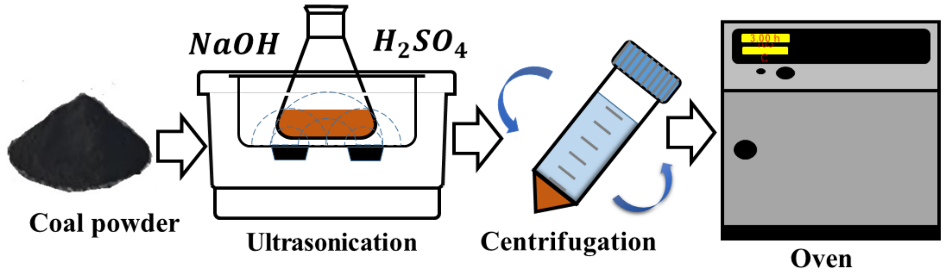

Figure 1. Schematic ilustration of demineralization of bituminous coal.

After that, an electrode based on the obtained samples was created in order to examine the electrochemical characteristics of demineralized coal. Demineralized coal powder (80% wt.), carbon black (10% wt.), polyvinylidinefloride (10% wt.), and 1-methyl 2-pyrrolidinone were combined, heated at 40°C on magnetic stirrer to generate coal slurry, and then used to make electrodes. The coal slurry was then applied on nickel foam and allowed to dry overnight at a temperature of 105°C in a vacuum oven. Three electrode cells with electrolyte solutions of 3 M potassium hydroxide (KOH) were used to characterize the electrochemical characteristics. Cyclic voltammetry (CV) measurements were investigated between 1.0 to 0.0 V at scan rate of 5 mVs^{-1}. The specific capacitance can be determined by mean of the formula [14]:

$$C_s = \frac{\int IdV}{2mv\Delta V} \quad (4)$$

Where C_s, $\int IdV$, m, v and ΔV are a specific capacitance, a cyclic voltammogram's integrated area (VA), active material's mass (g), scan rate (mV/s), and potential windows (V), respectively.

3 Result and discussion

The results of the proximate and ultimate analyses showed that the sample of coal that was utilised in this experiment was of the high-volatile bituminous-b type. This coal type has the carbon content, volatile matter, and moisture content about 78-80 %, 42-38 % and 10-12 %, respectively [5]. The mineral content of pre- and post-demineralized coal was analysed using XRF characterization, and the findings are summarised in Table 2. Based on the information in Table 2, sulphur and silicon are major elements in the raw coal sample followed by aluminium, calcium, ferrium, paladium, and the remains are trace elements. After demineralization, most of the mineral were removed especially trace elements. However, the major mineral like aluminium, silicon and sulphur were slightly reduced.

Tabel 2. Minerals composition (in At.%) in raw coal and demineralized coal from XRF characterization .

Element	Raw Coal	C-NaOH	C-H_2SO_4	C-mix 5%	C-mix 10%
Al	9.57	7.36	7.71	5.83	6.92
Si	28.91	24.39	24.27	30.20	37.71
S	41.39	22.42	58.00	58.00	52.11
K	1.61	1.56		1.19	
Ca	6.43	5.97	3.68	2.81	1.38
Ti	2.47	1.13	3.35	1.18	1.16
V	0.23	0.14	0.30	0.18	
Cr	0.24				
Eu	0.27				
Gd	0.16				
Fe	4.11	2.54	2.69		0.72
Co	0.10				
Ni	0.17				
Cu	0.22				
Pt	0.20				
Bi	0.17				
Se	0.13				
Pd	3.61				

Fig. 2 shows FTIR spectrum of raw coal and demineralized coal. It can be seen that all samples have relatively similar FTIR spectrum, demonstrating that all samples have similar functional groups. The peaks located higher than band 3624 cm^{-1} are connected with vibration of O-H in hydroxyl group of aluminosilicate or clay minerals [15]. The broad and strong band at 3427 cm^{-1} could be ascribed to hydroxyl vibration. This band is associated with water molecule that bounded to the minerals. The peaks at 2980-2845 cm^{-1} ascribed as –CH bonds that are aliphatic structure such as $–CH_2$ and $–CH_3$. Strong intensity at peak 1600 cm^{-1} are aromatic C=C vibrations indicating more carbon content. Meanwhile, the peaks at 799-473 cm^{-1} corresponds to mineral content in the sample. These bands confirmed that chemical leaching and demineralization with NaOH and H_2SO_4 did not remove these minerals.

The enclosed area of the cyclic voltametry (CV) curve for raw coal and demineralized coals tends towards pseudo-capacitive behaviour, although it is not precisely rectangular as depicted in **Fig. 3**. The specific capacitance can be calculated from Equation (4) according to the CV curve and they are about 1.00, 3.50, 3.67, 4.80 and 4.87 Fg^{-1} of raw coal, NaOH demineralization, H_2SO_4 demineralization, C-mix 5% and C-mix 10%, respectively. The greater the concentration of demineralization, the greater specific capacitance.

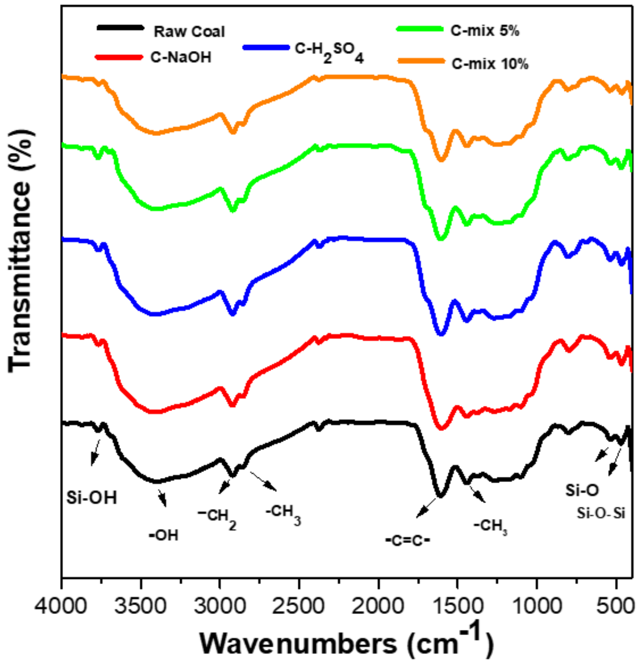

Figure 2. FTIR spectrum of coal samples.

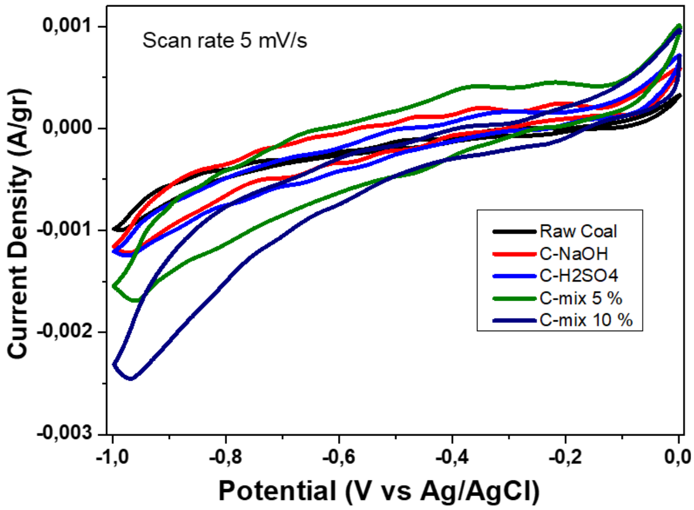

Figure 3. CV curve of all samples at 5 mVs^{-1} in 3 M KOH.

4 Conclusion

Coal has been demineralized by alkali acid leaching with ultrasonication at low frequency. FTIR spectroscopy measurement shows that intensity peaks in mineral bands lead to decrease in proportion incresing concentration of alkali acid leaching. Electrochemical properties of the demineralized coal by measurement CV in 3M KOH electrolite solution. The value of specific capacitance (SC) increased in proportion to leachan concentration. The SC value of leached coal was 4.87 F/g at scan rate of 5 mV/s by leaching 10% NaOH.

References

[1] Meshram, P., Purohit,B.K., Sinha,M.K., Sahu, S.K., and Pandey, B.D., *Demineralization of low grade coal – A review*, Renewable and Sustainable Energy Reviews, **41**, pp. 745–761, Jan. 2015.

[2] Kundu,N., Sadhukhan, D., and Sarkar, S., *Fluorescent carbon nano-materials from coal-based precursors: unveiling structure–function relationship between coal and nano-materials*, Carbon letter, **32**(3). pp.671-702. Jan. 2022.

[3] Deb Barma, S., Sathish, R., Rao, D.S. & Prakash, R. *Mechanistic investigation on the microwave- assisted leaching of low-grade coal for low-ash coal production,* Separation Science and Technology, **56**(18), pp. 3151–3166, Feb. 2021.

[4] Mukherjee S, and Borthakur PC Chemical *demineralization and desulphurization of high sulphur coal using sodium hydroxide and acid solutions*. Fuel, **80**(14), pp.2037–2040, Nov.2001.

[5] Lakhmira,M.A., Soomroa,S.A., Unara, I.N and Akhter,F. *A Review of Chemical Demineralization and Desulphurization of High Ash & High Sulphur Lignite Coal.* Jurnal Kejuruteraan **34**(3) pp.353-364. May. 2022.

[6] Li,Y., Chen,X., Zeng,Z., Dong,Y., Yuan,S., Zhao,W., Jiang,F., Yang,Y., Sun,W., and Ge, P. *Coal-Based Electrodes for Energy Storage Systems: Development, Challenges, and Prospects*, ACS Applied Energy Materials. **5**(6), pp. 7874–7888, June. 2022.

[7] Zhou, Q., Zhao, Z., Zhang, Y., Meng, B., Zhou, A. & Qiu.J. *Graphene Sheets from Graphitized Anthracite Coal: Preparation, Decoration, and Application*, Energy Fuels, **26**(8) pp.5186−5192, July. 2012.

[8] Lan, C., Tang, Y., Huan, X., and Che, Q, *Effects of Minerals in Anthracite on the Formation of Coal-Based Graphene*, ChemistrySelect, **4**(19), pp. 5937–5944, May. 2019.

[9] S.K. Behera, U. Kumari, B.C. Meikap. *A Review of chemical leaching of coal by acid and alkali solution,* Journal of Mining and Metallurgy, **54** A (1), pp. 1-24. June. 2018.

[10] Sriramoju,S.K., Dash, P.S., Suresh,A., and Ray, T., *Integrated process for coal chemical demineralization and spent caustic regeneration- A pilot scale study*, Journal of Cleaner Production, **327**, 129497, Dec.2021.

[11] Aditya,A., Suresh,A., Sriramoju,S.K., Dash,P.S., Pati,S., and Padmanabhan, N.P.H., *Optimization study of sodium hydroxide consumption in the coal demineralization process*, Mineral Processing and Extractive Metallurgy Review, **39**(4), pp. 250-257. Dec.2017.

[12] Ambedkar, B., Chintala, T.N., Nagarajan, R., and Jayanti, S., *Feasibility of using ultrasound-assisted process for sulfur and ash removal from coal*, Chemical Engineering and Processing: Process Intensification. **50**(3), pp. 236–246, March. 2011.

[13] Deb Barma,S., Sathish R, Baskey,P.K., and Biswal, S.K., *Chemical beneficiation of high ash Indian non-coking coal by alkali leaching under low-frequency ultrasonication,* Energy and fuel. **32**(2), pp.1309-1319, Jan. 2018.

[14] Abdilah, O.B., Floweri,O., Mayangsari, T.R.,Santosa,S.P., Ogi., T., and Iskandar,F., *Effect of* H_2SO_4/H_2O_2 *pre-treatment on electrochemical properties of exfoliated graphite prepared by electro-exfoliation method*, RSC Advances,**11** pp.10881-10890, march.2021.

[15] Ogunsakin,O.R., Holberg,S., Wang,X., Goroncy,A., Adams,J., Johnson, P., *Acid demineralization effect on the sonication-assisted solvent extraction of vitrinite coal of the Powder River Basin,* Fuel, **308**,121989, Jan.2022.