IRON ADSORPTION IN PEAT WATER BY SAGO WASTE ACTIVATED CARBON

Awali Sir Kautsar Harivram¹), Isna Syauqiah^{1,2)*}, Muthia Elma^{1,3)}, Erdina Lulu Atika Rampun³⁾, Dina Amryna Chairul Putri¹), Namira Ghina Safitri¹

 ¹⁾ Chemical Engineering Department,Lambung Mangkurat University (ULM) JL.A. Yani KM 36, Banjarbaru, South Kalimantan 70714, Indonesia
²⁾ Wetland Based Materials Research Center, Lambung Mangkurat University (ULM) JL.A. Yani KM 36, Banjarbaru, South Kalimantan 70714, Indonesia
³⁾ Materials and membranes Research Group (M2ReG), Lambung Mangkurat University JL.A.Yani KM 36, Banjarbaru, South Kalimantan 70714, Indonesia

* E-mail corresponding author: isna_tk@ulm.ac.id

ARTICLE INFO	ABSTRACT
Article history:	In South Kalimantan, peat water is the main water sources for
Received: 26-08-2022	local people. But peat water has high iron content. It cannot be
Received in revised form: 06-09-	consumed directly and need further treatment. Adsorption is the most
2022	common technology to treat peat water. The goal of this research is to
Accepted: 21-10-2022	study sago waste adsorbent for iron removal in peat water. Citric acid
Published: 25-10-2022	was employed as activating agent in the sago waste activated carbon
	adsorbent fabrication. Carbonization process was done at 300 °C with
Keywords:	70, 80, 90, 100, 110 and 120 minutes of time variation. After treatment
Activated carbon	using the adsorbent, iron content was tested via Atomic Absorption
Adsorption	Spectrophotometry (AAS). While, Fourier Transform Infra-Red (FTIR)
Iron	were carried out to investigate the functional groups of sago pith waste
Peat water	activated carbon (SPWAC) and sago pith waste unactivated carbon
Sago pith waste	(SPWUC). The experiment results show iron could be removed until
	82% with iron concentration of 0.05 mg/l at 80 minutes. SPWAC and
	SPWUC have functional groups such as alkenes (C-H and $C=C$),
	carbonyl ($C=O$ and $C-O$) and hydroxyl ($O-H$). Fe concentrations are
	still meet water quality standard according to No.
	492/Menkes/PER/IV/2010 which is 0.3 mg/L. Therefore, adsorption
	uses sago pith waste activated carbon is an effective and inexpensive
	water treatment

ADSORPSI BESI PADA AIR GAMBUT DENGAN KARBON AKTIF

Abstrak- Di Kalimantan Selatan, air gambut adalah sumber air utama untuk penduduk lokal. Akan Tetapi air gambut memiliki kandungan besi yang tinggi. Air tersebut tidak dapat dikonsumsi secara langsung dan perlu adanya pengolahan lebih lanjut. Adsorpsi adalah teknologi yang umum dalam mengolah air gambut. Tujuan penelitian ini adalah mempelajari adsorben ampas sagu untuk menghilangkan zat besi dalam air gambut. Asam sitrat digunakan sebagai agen pengaktivasi dalam pembuatan adsorben. Proses karbonisasi dilakukan pada suhu 300 °C dengan variasi waktu 70, 80, 90, 100, 110 dan 120 menit. Setelah pengolahan menggunakan adsorben, kadar besi diuji via *Atomic Absorption Spectrophotometry (AAS)*. Sedangkan, *Fourier Transform Infra-Red (FTIR)* dilakukan untuk menginvestigasi gugus fungsi dari karbon aktif ampas sagu (SPWAC) dan ampas sagu adsorben tanpa aktivasi (SPWUC). Hasil eksperimen menunjukkan zat besi dapat direjeksi sampai 82% dan konsentrasi besi sebesar 0.05 mg/L pada 80 menit. SPWAC dan SPWUC memiliki gugus fungsi seperti alkene (C-H dan C=C), karbonil (C=O dan C-O) and hidroksil (O-H). Konsentrasi Fe telah memenuhi standar kualitas air menurut No. 492/Menkes/PER/IV/2010 yaitu 0.3 mg/L. Oleh karena itu, adosrpsi menggunakan karbon aktif ampas sagu ini merupakan pengolahan efektif dan murah.

Kata kunci : adsorpsi, air gambut, ampas sagu, besi, karbon aktif.

BACKGROUND

Indonesia has 149,056 km² of peatland. It is located in remote regions and nearby major population centers in Sumatra, Kalimantan and Papua. (Kalimantan: 28-32%; Papua: 25-38%; and Sumatra: 34-43%)(Warren et al., 2017). Peatlands deliver water and forest sources to local people.

Water stored in peatland is known as peat water. Peat water contains natural organic matter (NOM) including humic acid and acidic compounds (Mahmud et al., 2020). Besides the NOM, it also has a large amount of iron and manganese (Rakhmina et al., 2018). A high iron content may cause diarrhea, vomiting, poisoning and intestinal damage. Generally, peat water cannot be consumed because it exceeds the maximum Indonesian water quality standard through Minister of Health No. RI. 416/Menkes/PER/IX/1990. But, the local people especially in South Kalimantan has utilized the peat water due to their large quantity and inaccessible clean water from PDAM.

Several researches such as coagulation, flocculation, adsorption, filtration, membrane(Apriani et al., 2016), two stages adsorption-ultrafiltration (Mahmud et al., 2020), oxidation-filtration(Arifianingsih et al., 2020) coagulation-adsorption-ultrafiltration (Elma et al., 2022) have been attempted for peat water treatment. Among them, the most commonly applied is adsorption.

As a highly porous carbon based adsorbent, activated carbon (AC) is known for its high reactivity, surface chemistry and developed porosity. It is effective for removing heavy metals in water (Fan et al., 2018). Commercial adsorbent mostly made from coal, wood and petroleum residues. These all are expensive.

In recent years, research has focused on finding alternative low-cost adsorbent. Rakhmina et al. (2018) has developed AC from robusta coffee waste for peat water treatment. It reduced iron until 65.4%. Another research has produced pine bark AC. It removed 100% heavy metals (Cu, Pb, Zn, Ni and Cd)(Paradelo et al., 2016).

Sago waste is relatively waste that obtained from starch processing (Leatemia et al., 2013). The sago waste is usually used as animal feed supplement but its potential uses have not been fully explored. It can be bioadsorbent derived from waste. Previous research has fabricated a sago waste activated carbon by H_2SO_4 and $(NH_4)_2S_2O_8$ activation addition (Kadirvelu et al., 2004). Therefore, this research is needed to study sago waste adsorbent for iron removal in peat water. In this study, citric acid has chosen as activating agent because of their carboxylic functional group presence and availability (Rashid and Bezbaruah, 2020).

MATERIALS & METHOD

1. Materials

Sago waste from sago industry in Sungai Tabuk, peat water was collected in Gambut Subdistrict, Banjar district, distilled water, 0.1 M citric acid ($C_6H_8O_7$), furnace, oven, 120 mesh shieve shaker.

2. Fabrication of activated cabon from sago waste

Sago waste was washed to remove the dirt and dried it under the sun. The sago waste was then mashed to accelerate the carbonization process. Meshed sago waste was calcined in air at 300 °C for 120 minutes to remove water content, volatile, and ash. The result is known as carbonaceous sago pith waste (CSPW). After that, the same process was done for every carbonization time variation (70, 80, 90, 100, 110 minutes). The CSPW was sifted to 120 mesh size. The CSPW was activated using 0.1 M citric acid and stirred for 2 h. Sago pith waste activated carbon (SPWAC) was filtered and then dried again in the oven at 100 °C for 2 h. Until the pH reaches neutral, it is washed with distilled water and dried in the oven at 80 °C for 2 h. Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red (FTIR) were used to investigate the morphology of SPWAC and the functional groups, respectively. In addition, FTIR deconvolution confirmed via Fityk software based on Gaussian line.

3. Adsorption process of iron in peat water

Lastly, 1 gram of SPWAC and unactivated sago pith waste was stirred up in 100 mL of peat water for 90 min at 300 rpm speed. Followed by filtering the filtrate before it is analyzed to Atomic Absorption Spectrophotometry (AAS). Iron removal is then obtained.

RESULTS AND DISCUSSION

1. Functional groups of sago pith waste activated carbon

The prepared sago pith waste activated carbon (SPWAC) and sago pith waste unactivated carbon (SPWUC) at 80 minutes carbonization time were analyzed by FTIR. The FTIR was carried out to identify functional groups. The functional groups were investigated within range 4000-600 cm⁻¹ wavelength numbers.

Based on figure 1, there are two peaks at 1600 and 1700 cm⁻¹ referring to region of alkene (C=C) and carbonyl (C=O), respectively (Maulina and Mentari, 2019). It indicates carbon presence in

the SPWAC and SPWUC. There is a slightly difference between the SPWAC and SPWUC absorption peaks in these regions. There is an increase in carbonyl after carbon activation by citric acid addition. Carboxyl in citric acid as organic acid gives proton (H+) and configures into stable complexes with several ions by forming a negatively charged carboxyl group(Faizul et al., 2013). As a result of the citric acid presence, a few new sites are formed, thereby enhance the adsorption capacity.

The Figure 1 also illustrates the absorbance peaks around ~784 cm⁻¹. It is reported that 995-675 cm⁻¹ attributed to alkenes (C-H) for SPWAC and SPWUC (Skoog et al., 1998). This is in accordance with previous research which found C-H in sago waste activated carbon with phosphoric acid and potassium hydroxide activation (Togibasa et al., 2021).

Carboxylic acids (R-COOH) consist of carbonyl (C=O) and hydroxyl (O-H) groups at around 1700 cm⁻¹ and 3600-2500 cm⁻¹ (Munajad and Subroto, 2018). As explained before, the C=O peaks appear at ~1703, while the peaks at ~3300 cm⁻¹ represent the O-H groups. The absorbance peaks for C-H, C=O, and O-H show the similar patterns. Because of it, Fityk software is required to deconvolute the peaks.



Figure 1. FTIR spectra of sago pith waste activated carbon (SPWAC) and sago pith waste unactivated carbon (SPWUC)

In Fityk, selected parameters can be quantified and analyzed across different types of experimental data as shown from the Table 1 (Wojdyr, 2010). The C-H, C=C, C=O, and O-H functional groups are slightly decreased except C-O group after citric acid activation. It is due to dehydration reaction of activation. The acid presence facilitates the O-H groups as water to be removed. The decomposition during activation also led to C=O reduction (Louarrat et al., 2019). The weak organic acid is known can modify pore size distribution of activated carbon because it removes easy leaving group (Bergna et al., 2018). While, the C-O group declined because the oxygen content enhanced on the SPWAC surface using citric acid activation. It is in line accordance to previous research which produce activated carbon with KOH(Bergna et al., 2022).

Table 1. FTIR dec	onvolution usi	ng Fityk Softwa	re
Adsorbent	Functional	Fityk area	

$\begin{tabular}{ c c c c } \hline Group \\ \hline SPWAC & C-H & 0.54 \\ C-O & 9.40 \\ C=C & 1.18 \\ C=O & 1.07 \\ O-H & 8.38 \\ \hline SPWUC & C-H & 0.64 \\ C-O & 5.15 \\ C=C & 1.57 \\ C=O & 1.50 \\ O-H & 11.54 \\ \hline \end{tabular}$	Ausorbent	Functional	Fityk arca
SPWAC C-H 0.54 C-O 9.40 C=C 1.18 C=O 1.07 O-H 8.38 SPWUC C-H 0.64 C-O 5.15 C=C 1.57 C=O 1.50 O-H 11.54		Group	
$\begin{array}{cccc} C-O & 9.40 \\ C=C & 1.18 \\ C=O & 1.07 \\ O-H & 8.38 \\ \textbf{SPWUC} & C-H & 0.64 \\ C-O & 5.15 \\ C=C & 1.57 \\ C=O & 1.50 \\ O-H & 11.54 \\ \end{array}$	SPWAC	C-H	0.54
$\begin{array}{cccc} C=C & 1.18 \\ C=O & 1.07 \\ O-H & 8.38 \\ \textbf{SPWUC} & C-H & 0.64 \\ C-O & 5.15 \\ C=C & 1.57 \\ C=O & 1.50 \\ O-H & 11.54 \\ \end{array}$		C-0	9.40
$\begin{array}{cccc} C=O & 1.07 \\ O-H & 8.38 \\ \textbf{SPWUC} & C-H & 0.64 \\ C-O & 5.15 \\ C=C & 1.57 \\ C=O & 1.50 \\ O-H & 11.54 \end{array}$		C=C	1.18
O-H 8.38 SPWUC C-H 0.64 C-O 5.15 C=C 1.57 C=O 1.50 O-H 11.54		C=O	1.07
SPWUC C-H 0.64 C-O 5.15 C=C 1.57 C=O 1.50 O-H 11.54		O-H	8.38
C-O 5.15 C=C 1.57 C=O 1.50 O-H 11.54	SPWUC	C-H	0.64
C=C 1.57 C=O 1.50 O-H 11.54		C-0	5.15
C=O 1.50 O-H 11.54		C=C	1.57
О-Н 11.54		C=O	1.50
		O-H	11.54

2. Sago pith waste activated carbon for iron removal

Carbonization time will affect the absorption of activated carbon to the solution. In this study, the carbonization time variations of 70, 80, 90, 100, 110 and 120 minutes are determined as shown in Figure 2 and Figure 3. It reveals the highest Fe rejection was achieved on 80 minutes of carbonization time until 82% with maximum Fe concentration of 0.05 mg/L. Noncarbon elements are removed in the carbonization stage (Sun et al., 2005). This is also due to the activation of sago waste activated carbon with 0.1 M citric acid which can increase the surface area, absorption area and pore volume of the adsorbent (Siswoyo et al., 2014). The results are accordance with previous research by Kadirvelu et al. (2004) that reject mercury using sago activated carbon with H₂SO₄ and (NH₄)₂S₂O₈. There are a number of potential mechanisms for surface adsorption, such as covalent bonds, Coulomb interactions, hydrogen bonds, and $\pi \rightarrow \pi$ interactions (Tong et al., 2019). Heavy metal cations are chemically bound to carboxyl and hydroxyl in activated carbon, as a consequence the heavy metal can be rejected (Hadjittofi et al., 2014). Fe concentrations in peat water after treatment are still meets the water quality standards No. which is 0.3 mg/L 492/Menkes/PER/IV/2010 (Permenkes, 2010).



Figure 2. Fe concentration trend after sago pith waste activated carbon (SPWAC) treatment



Figure 3. Fe rejection trend after sago pith waste activated carbon (SPWAC) treatment

Conclusion

In conclusion, sago pith waste activated carbon to remove iron (Fe) in peat water in have been examined. It has functional groups such as C-H, C-O, C=C, C=O and O-H. The highest Fe rejection is 82% at 80 minutes of carbonization time. Fe concentrations are still meet water quality standard according to No. 492/Menkes/PER/IV/2010. Therefore, adsorption uses sago pith waste activated carbon is an effective and inexpensive water treatment.

ACKNOWLEDGEMENT

Thanks to LPPM, Universitas Lambung Mangkurat (ULM)'s laboratory as well as Materials and Membranes Research Group's (M2ReG) Laboratory for providing PDWM grant and facilities.

REFERENCES

- APRIANI, M., MASDUQI, A. & HADI, W. 2016. Degradation of Organic, Iron, Color and Turbidity from Peat Water. ARPN Journal of Engineering Applied Sciences, 11, 8132-8138.
- ARIFIANINGSIH, N. N., ZEVI, Y., HELMY, Q., NOTODARMOJO, S., FUJITA, H., SHIMAYAMA, Y. & KIRIHARA, M. Peat water treatment using oxidation and physical filtration system and its performance in reducing iron (Fe), turbidity, and color. E3S Web of Conferences, 2020. EDP Sciences, 07011.
- BERGNA, D., ROMAR, H. & LASSI, U. 2018. Physical activation of wooden chips and the effect of particle size, initial humidity, and acetic acid extraction on the properties of activated carbons. *Journal of carbon research*, 4, 66.
- BERGNA, D., VARILA, T., ROMAR, H. & LASSI, U. 2022. Activated carbon from hydrolysis lignin: Effect of activation method on carbon properties. *Biomass and Bioenergy*, 159, 106387.
- ELMA, M., PRATIWI, A. E., RAHMA, A., RAMPUN, E. L. A., MAHMUD, M., ABDI, C., ROSADI, R., YANTO, D. H. Y. & BILAD, M. R. 2022. Combination of Coagulation, Adsorption, and Ultrafiltration Processes for Organic Matter Removal from Peat Water. *Sustainability*, 14, 370.
- FAIZUL, C., ABDULLAH, C. & FAZLUL, B. 2013. Extraction of silica from palm ashvia citric acid leaching treatment. Advances in Environmental Biology, 7, 3690-3695.
- FAN, C., LI, K., HE, Y., WANG, Y., QIAN, X. & JIA, J. 2018. Evaluation of magnetic chitosan beads for adsorption of heavy metal ions. *Sci Total Environ*, 627, 1396-1403.
- HADJITTOFI, L., PRODROMOU, M. & PASHALIDIS, I. 2014. Activated biochar derived from cactus fibres--preparation, characterization and application on Cu(II) removal from aqueous solutions. *Bioresour Technol*, 159, 460-4.
- KADIRVELU, K., KAVIPRIYA, M., KARTHIKA, C., VENNILAMANI, N. & PATTABHI, S. 2004. Mercury (II) adsorption by activated carbon made from sago waste. *Carbon*, 42, 745-752.
- LEATEMIA, M., SILAHOOY, C. & JACOB, A. 2013. The impact analysis of piled of sago pith waste on river water quality around the location of sago processing in waisamu

village, kairatu sub district, West Ceram district. *Jurnal Budidaya Pertanian*, 9, 86-91.

- LOUARRAT, M., ENAIME, G., BAÇAOUI, A., YAACOUBI, A., BLIN, J. & MARTIN, L. 2019. Optimization of conditions for the preparation of activated carbon from olive stones for application in gold recovery. *Journal of the Southern African Institute of Mining Metallurgy*, 119, 297-306.
- MAHMUD, ELMA, M., RAMPUN, E. L. A., RAHMA, A., PRATIWI, A. E., ABDI, C. & ROSSADI, R. 2020. Effect of Two Stages Adsorption as Pre-Treatment of Natural Organic Matter Removal in Ultrafiltration Process for Peat Water Treatment. *Materials Science Forum*, 988, 114-121.
- MAULINA, S. & MENTARI, V. A. Comparison of Functional Group and Morphological Surface of Activated Carbon from Oil Palm Fronds Using Phosphoric Acid (H3PO4) and Nitric Acid (HNO3) as an Activator. IOP Conference Series: Materials Science and Engineering, 2019. IOP Publishing, 012023.
- MUNAJAD, A. & SUBROTO, C. 2018. Fourier transform infrared (FTIR) spectroscopy analysis of transformer paper in mineral oilpaper composite insulation under accelerated thermal aging. *Energies*, 11, 364.
- PARADELO, R., CUTILLAS-BARREIRO, L., SOTO-GÓMEZ, D., NÓVOA-MUÑOZ, J. C., ARIAS-ESTÉVEZ, M., FERNÁNDEZ-SANJURJO, M. J., ÁLVAREZ-RODRÍGUEZ, E. & NÚÑEZ-DELGADO, A. 2016. Study of metal transport through pine bark for reutilization as a biosorbent. *Chemosphere*, 149, 146-153.
- PERMENKES 2010. Drinking water quality standard.
- RAKHMINA, D., MULANOVA, R. & HAITAMI, H. 2018. Effect of Active Carbon of Coffee Robusta Waste (Coffea robusta Lindl.) in Reducing Iron of Peat Water. *Medical Laboratory Technology Journal*, 4, 12-15.
- RASHID, U. S. & BEZBARUAH, A. N. 2020. Citric acid modified granular activated carbon for enhanced defluoridation. *Chemosphere*, 252, 126639.
- SISWOYO, E., ENDO, N., MIHARA, Y. & TANAKA, S. 2014. Agar-encapsulated adsorbent based on leaf of platanus sp. to adsorb cadmium ion in water. *Water science technology*, 70, 89-94.
- SKOOG, D. A., HOLLER, F. J. & NIEMAN, T. A. 1998. Principle of Instrumental Analysis, Philadelphia.

- SUN, J., WU, G. & WANG, Q. 2005. The effects of carbonization time on the properties and structure of PAN-based activated carbon hollow fiber. *Journal of Materials Science*, 40, 663-668.
- TOGIBASA, O., ANSANAY, Y. O., DAHLAN, K. & ERARI, M. 2021. Identification of surface functional group on activated carbon from waste sago. *Journal of Physics: Theories Applications*, 5, 1-8.
- TONG, Y., MCNAMARA, P. J. & MAYER, B. K. 2019. Adsorption of organic micropollutants onto biochar: a review of relevant kinetics, mechanisms and equilibrium. *Environmental Science: Water Research Technology*, 5, 821-838.
- WARREN, M., HERGOUALC'H, K., KAUFFMAN, J. B., MURDIYARSO, D. & KOLKA, R. 2017. An appraisal of Indonesia's immense peat carbon stock using national peatland maps: uncertainties and potential losses from conversion. *Carbon balance management*, 12, 1-12.
- WOJDYR, M. 2010. Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography*, 43, 1126-1128.