

## THE EFFECT OF ADSORBENT AGENTS: SILICA, ANDISOL, LECA, ANTHRACITE, AND ACTIVATED CARBON ON POLLUTANT UPTAKE IN THE CITARUM RIVER

*(Pengaruh agen penjerap silika, andisol, LECA, antrasit, dan karbon aktif terhadap penyerapan polutan di Sungai Citarum)*

Fahriya Puspita Sari<sup>1\*</sup>, Nissa Nurfajrin Solihat<sup>1</sup>, Muhammad Sholeh<sup>2,3</sup>, Lucky Risanto<sup>1</sup>, Fitria<sup>1</sup>, Faizatul Falah<sup>1</sup>, Widya Fatriasari<sup>1</sup>

<sup>1</sup>Research Center for Biomaterials, National Research and Innovation Agency, Cibinong, Indonesia

<sup>2</sup>Perusahaan Daerah Air Minum Tirta Tarum Karawang, Indonesia

<sup>3</sup>Doctoral Program of Environmental Science, Department of Environmental Science, Universitas Sebelas Maret, Surakarta, Indonesia

Email : [fahriya.ps07@gmail.com](mailto:fahriya.ps07@gmail.com)

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### ABSTRACT

*Citarum is the longest and largest river in West Java-Indonesia which plays a critical role in the water supply. Water treatment is needed to process the Citarum water due to its pollutants have been over standard for human consumption. Nowadays, the adsorption process is still popular in water treatment process because of its effectiveness. In this study, the effectivity of five adsorbents on Citarum water treatment: silica, andisol, LECA (Light Expanded Clay Aggregate), anthracite, and activated carbon has been evaluated with variable contact time and solid loading. After treatment, turbidity and heavy metal of filtrate were analyzed. Surface characteristics, functional group, and surface area of five adsorbents were done by FE-SEM (Field Emission - Scanning Electron Microscopes), FTIR (Fourier Transform Infrared Spectroscopy), and BET (Brunauer-Emmett-Teller) surface area analysis, respectively. The result showed that andisol and LECA decreased turbidity of Citarum water from 21.30 NTU (Nephelometric Turbidity Unit) to 1.23 and 2.52 NTU after 10 min contact time. Activated carbon was taking another 10 min longer to decrease turbidity to 2.26 NTU yet it has the highest surface area, 548.31 (m<sup>2</sup>/g). Surface area was in correlation with FE-SEM result where activated carbon has a more regular and larger pore size compared to others adsorbent. In general, andisol, LECA, activated carbon were successful to decrease turbidity of Citarum water which correlated to their particles' surface area.*

**Keywords:** *adsorption; Citarum water river; adsorbents; pore size*

### ABSTRAK

Sungai Citarum merupakan sungai terpanjang dan terbesar di Jawa Barat, Indonesia yang mempunyai fungsi vital sebagai sumber air. Pengolahan air sungai Citarum sebelum

disalurkan ke masyarakat diperlukan untuk menghilangkan pengotor karena kandungan pengotor pada air sungai Citarum melebihi batas ambang yang dipersyaratkan untuk air konsumsi. Saat ini proses penjerapan atau adsorpsi merupakan proses yang umum digunakan pada perusahaan pengolahan air karena efektifitasnya. Pada penelitian ini, efektifitas lima agen penjerap yaitu silika, andisol, hidroton, antrasit, karbon aktif telah dievaluasi dengan perbedaan rasio padatan dan larutan, dan waktu kontak. Setelah pengolahan, kekeruhan dan logam berat dalam air dianalisa. Karakteristik permukaan, gugus fungsi, dan luas permukaan dari kelima agen penjerap dianalisa masing-masing menggunakan FE-SEM (*Field Emission - Scanning Electron Microscopes*), FTIR (*Fourier Transform Infrared Spectroscopy*), dan analisa luas permukaan BET (*Brunauer-Emmett-Teller*). Hasil analisa menunjukkan bahwa masing-masing andisol dan LECA menurunkan kekeruhan dari air Citarum dari 21.30 NTU (*Nephelometric Turbidity Unit*) menjadi 1.23 dan 2.52 NTU setelah waktu kontak 10 menit. Karbon aktif membutuhkan waktu 10 menit lebih lama untuk menurunkan kekeruhan menjadi 2.26 NTU akan tetapi karbon aktif memiliki luas permukaan yang paling tinggi yaitu 548.31 (m<sup>2</sup>/g). Luas permukaan berkaitan dengan hasil FE-SEM dimana karbon aktif memiliki pori yang teratur dan berukuran besar. Pada umumnya, andisol, LECA, dan karbon aktif telah berhasil menurunkan kekeruhan air Sungai Citarum yang berkaitan dengan luas permukaan partikelnya.

**Kata kunci: agen penjerap; air sungai Citarum; penjerapan; luas permukaan**

## I. INTRODUCTION

One of the goals of watershed management is to ensure the availability of clean water for living things. Water is one of the crucial needs for all living things to survive and for socio-economic activities. The high population and economic growth in Indonesia make human and industrial activities expanding rapidly. As a result, the environment is increasingly being threatened by inevitable waste water production. Pollution of water resources can be caused not only by synthetic and natural chemicals but also heavy metals as toxic and dangerous pollutants. The pollutants are considered being a hazard for human beings (Piccin, Cadaval, De Pinto, & Dotto, 2017; Belinawati, Soesilo, Asteria, & Harmain, 2018; Seliem et al., 2020).

Citarum River is one of the natural water supply which has a flow length of about 300 km and the downstream located in Karawang Regency, West Java, Indonesia (Shara, Moersidik, & Soesilo, 2021). In Karawang, Citarum River has vital functions to supply water for irrigation, electricity generation, fisheries, reservoir water, and drinking water where the water river was treated by Perusahaan Daerah Air Minum (PDAM) Karawang (Sholeh, Pranoto, Budiastuti, & Sutarno, 2018). Despite the important role of Citarum River, the accumulation rate of solid and liquid waste in the Citarum River and its tributaries has caused an intolerable impact in environmental feasibility and human health. In 2019, more than 1,600 industries dominated by the textile, pulp and paper, and

electroplanting industries have operated along the Citarum River. Only about 400 industries carry out wastewater treatment and the rest are discharged directly into wastewater without proper treatment into the Citarum River (Widyawati, Notodarmojo, Hidayat, & Helmy, 2019; Sholeh, Pranoto, Budiastuti, & Sutarno, 2018). Therefore, the water quality of Citarum River such as watercolor, heavy metal (commonly Fe and Mn), biological oxygen demand (BOD), chemical oxygen demand (COD), and high turbidity are the main obstacles at PDAM water plant treatment Energy Dispersive X-Ray.

Different technologies and methods for wastewater treatment have been extensively reported and developed. In general, the technologies and methods used to remove contaminants from wastewater include anaerobic treatment, coagulation, flocculation, flotation, filtration, ion exchange, membrane separation, and advanced oxidation (Da'na, 2017). Nevertheless, they have their restrictions and are still considered a challenge. The adsorption process is considered the most effective and affordable method for wastewater treatment (Piccin, Cadaval, De Pinto, & Dotto, 2017). It is affected by temperature, adsorbate and adsorbent properties, the presence of other pollutants, and atmospheric and experimental conditions such as pH, concentration of pollutants, dosage, contact time, and particle size of the adsorbent (Ali & Gupta, 2007). Currently, PDAM Karawang treats Citarum water through coagulation, flocculation,

sedimentation, filtration, and disinfection (Suhartono, 2020). Filtration is one of the crucial steps in this process due to the adsorption of light particles and heavy metals that can not precipitated until the sedimentation step (Barakat, 2011). Therefore, selecting the best adsorbent during the filtration process is crucial, as well.

The essential criteria for adsorbent are its abundance and sustainability because it impacts the treatment budget and environment. Recently, natural adsorbents are popular in Water Treatment Plants (WTP), such as activated carbon from biomass and clay or soil-based adsorbent. Activated carbon has been recognized as the most widely used adsorbent due to its immense ability to remove various pollutants such as heavy metals, metalloids, halogens, dyes, pharmaceuticals, organic pollutants, toxins, etc (Bonilla-Petriciolet, Mendoza-Castillo, & Reynel-Ávila, 2017).

One of clay-based adsorbent which has extensively been used is Light Expanded Clay Aggregate (LECA). LECA is a highly porous material that has a low density, natural pH, and thermal resistance up to 1000 °C. It has a uniform pore structure so it can adsorb environmental pollutants and not lost significantly during the backwash process (Mohammadi, Yetilmezsoy, & Uygur, 2013; Sepehr et al., 2014). Andisol is a kind of soil that has a large amount of non-crystalline materials such as imogolite, allophane, Al/Fe-humus and ferrihydrite complexes, and the accumulation of organic carbon. This material is highly porous and have large

specific surface areas (Babel & Opiso, 2010). As well as other adsorbents, silica also a porous material that potential for adsorbents to remove pollutants (Cashin, Eldridge, Yu, & Zhao, 2018). Mesoporous silica can adsorb n-pentane (Gor et al., 2013) and heavy metals with modification (Da'na, 2017). Anthracite is a type of coal that is compact, hard, has a high luster, and high carbon content (Rahman, Azam, & Alam, 2012). Some studies reported that anthracite is an effective adsorbent to remove pollutant such as Mn (VII) and Cr (VI) (Seliem et al., 2020), quinoline (Xu et al., 2019), and phosphate ion (Rahman, Azam, & Alam, 2012).

Anthracite and silica are common adsorbents in water plant treatment. Nevertheless, these adsorbents have not optimal to adsorb pollutants and heavy metals. The concentration of Fe and Mn, also turbidity are relatively high even after complete treatment (Analysis Report PDAM (unpublished data), 2020). In this study, we compared anthracite and silica with other potential adsorbents such as andisol, activated carbon, and LECA. The purpose of this study was to investigate the effect of activated carbon, LECA, andisol, silica, and anthracite to remove pollutants from Citarum River. The influence of adsorbent properties such as functional groups, surface area, and morphological features on the water treatment was also investigated.

## II. MATERIALS AND METHODS

### A. Time and Location

This research was conducted in Karawang Regency. The water sample was

taken from the main canal of North Tarum (west branch) during the rainy season. Figure 1 shows water sampling location.

### B. Materials

Andisol, LECA, silica, and anthracite were purchased from local companies in Karawang, West Java, Indonesia. Meanwhile, activated carbon from OPEFB (Oil Palm Empty Fruit Bunches) was prepared by one-step process of carbonization and continued by activation according to Sari, Yanto, & Pari (2019). Andisol, silica, and anthracite were ground into small particles then sieved into particles size of 10-14 mesh while activated carbon into 180 mesh. The LECA sample was selected with a particle size up to 10 mm. All adsorbent materials were presented in Figure 2.

### C. Methods

#### 1. Batch experiment

The batch study was conducted to determine the adsorption capacity of each adsorbent materials. 100 ml of Citarum water samples was put into 250 ml erlenmeyer flasks and stirred at 250 rpm for 10, 20, and 30 minutes with solid loading 1: 10 (gr/ml) for antracite, silica, andisol, and LECA, and 1:100 (gr/ml) for activated carbon. After that, it was filtered using 0.45 um filter paper. Prior to that turbidity (HACH 2100Q, USA), and AAS analysis (XplorAA, GBC USA) were performed to determine Fe and Mn concentration. This experiment was arried out three replications for each adsorbent.



Figure 1. The location of water sample at main canal of North Tarum (West Branch), Karawang Regency  
Source: Google Maps (2021)



Figure 2. The visual appearance of the adsorbents: anthracite (a), andisol (b), LECA (c), silica (d), and activated carbon (e)

Source: Visualization of materials (2020)

## 2. Adsorbent Characterization and Analysis

### a. FTIR analysis

Attenuated Total Reflectance -Fourier Transform Infra-Red (ATR-FTIR) analysis (Spectrum two-Perkin Elmer, USA) was used to characterize the functional groups of adsorbent materials. About 1 gr of adsorbents were placed on a diamond plate and then IR spectra were recorded in absorption mode with a scan count of 4 per sample and a resolution of 4.0 cm in the wave number range of 4000 to 400

cm<sup>-1</sup> at room temperature using spectrum two Perkin Elmer software.

### b. SEM and BET analysis

The micrograph of the adsorbents was obtained by Field Emission Scanning Electron Microscopy (FE-SEM) using FE-SEM Thermo Scientific - Quattro S (USA). The samples were fixed on a specimen holder with tape and each sample was examined at 500-fold magnification. The specific surface area and pore structure characteristic of the adsorbents were determined by adsorption-desorption isotherms of nitrogen at 196 °C using

automated gas adsorption analyzer namely AUTOSORB-1 (Quantachrome Instruments, USA). Before analysis, degassing of samples was conducted at 300 °C for 3 hours. Brunauer-Emmet-Teller (BET) method was used to calculate the surface area of samples. The average pore diameter and pore volume of the adsorbents were determined by Barret-Joymer-Halenda (BJH) model.

### III. RESULTS AND DISCUSSION

#### 1. Influence of adsorbents on turbidity

The causes of high levels of turbidity are the accumulation of sedimentation over the years and the impact of household waste disposal. The level of pollution can be vary depending on the source of the pollutant, seasonal turbidity during rainy season, and the river flow itself (Sholeh, Pranoto, Budiastuti, & Sutarno, 2018). According to Babur & Kara (2017), water treatment is one of the important step in integrated watershed management to produce clean water. One of the effective water treatment is adsorption process.

In this study, the turbidity of the Citarum river is 21.30 NTU (Figure 3) while

according to Indonesian Minister of Health Regulation no. 492 the quality standard of turbidity for water supply is less than 5 NTU. In Figure 3, it clearly showed that after the treatment process the best adsorbent to decrease turbidity is Andisol which can decrease significantly to 1.23 NTU and then LECA to 2.52 in 10 minutes. Nevertheless, turbidity increased after 20 minutes of stirring for LECA and andisol and 30 minutes for silica. The use of LECA and silica as adsorbent significantly increased the turbidity from 2.52 to 23.40 NTU and 8.98 to 33.10 NTU, respectively. Activated carbon consistently decreases the turbidity until 2.26 NTU for 30 minutes. However, it needs more time than LECA and andisol in absorbing the pollutant. The partial dissolution of adsorbent in the solution can have an impact on the decreasing adsorption capacity. Adsorbent hardness is one of the factors to determine the suitable adsorbent material (Mohammadi, Yetilmezsoy, & Uygur, 2013; Sepehr et al., 2014).

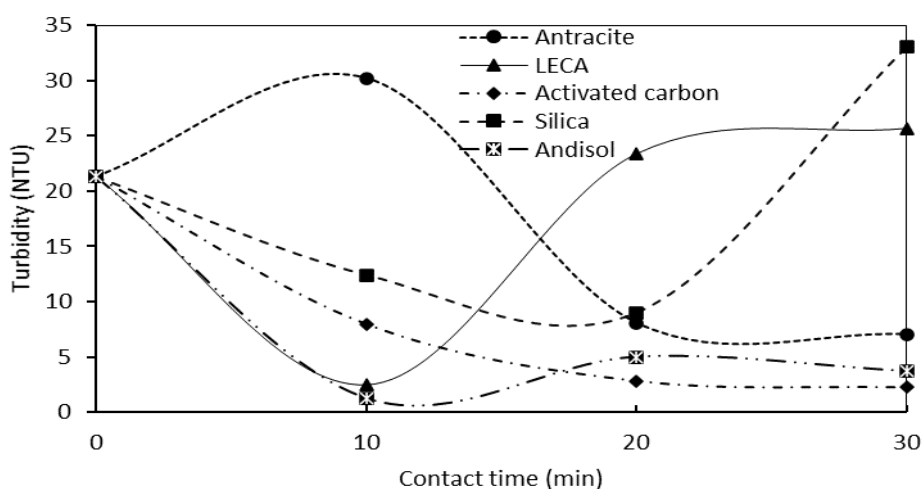


Figure 3. Influence of adsorbent and contact time on the water turbidity of Citarum River  
Source: Analisis Result (2021)

Table 1. The concentration of Fe and Mn before and after treatment using different adsorbents

Adsorbents	Fe (mg/kg)	Mn (mg/kg)
(before treatment)	Nd*	Nd*
Anthracite	625.94	5.31
Andisol	Nd*	Nd*
LECA	Nd*	Nd*
Silica	Nd*	Nd*
Activated Carbon	Nd*	Nd*

\*not detected

Source: Analysis Result (2021)

## 2. Influence of adsorbents on heavy metals adsorption

Table 1 shows the concentration of Fe and Mn before and after treatment. Before treatment, the sample did not contain Fe or Mn. This finding is different with previous report by Sholeh, Pranoto, Budiastuti, & Sutarno (2020b) The raw water quality depends on the domestic waste, sedimentation, and industry's effluent, as well as the current season (Hasbiah & Kurniasih, 2019). The experiment from Sholeh, Pranoto, Budiastuti, & Sutarno (2020b) with the same water resources showed that the concentration of Mn and Fe in the water before treatment was 0.005-0.02 ppm and 0.015-0.03 ppm, respectively. The concentration of Mn and Fe have been below the threshold recommended by Permenker RI number 32 of 2017 of 0.5 and 1 ppm, respectively. Because of sampling in the rainy season, Mn and Fe's concentration in this research became very low or not detected.

Furthermore, after 30 minutes of treatment using andisol, LECA, silica, and activated carbon were also not detected. Meanwhile, Fe and Mn were detected using anthracite after 30 minute of

treatment. Fe concentration was very high up to 625.94 mg/kg, while Mn concentration was 5.31 mg/kg. This condition affected the filtrate color after treatment. The yellowish color observed in the filtrate after treatment with anthracite can be attributed to the release of Fe and Mn ions which were loaded during the stirring process. Hence it shows that anthracite is not an effective adsorbent. This condition is caused by the presence of iron which is one of the metal components in anthracite (Ribeiro, DaBoit, Flores, Kronbauer, & Silva, 2013). Further study is needed to investigate the elemental composition of adsorbents.

## 3. Adsorbents Characterization

### a. Functional groups of adsorbents by FTIR

FTIR spectra is available in Figure 4 while the interpretation of data can be seen in Table 2. Figure 4 shows that silica, andisol, and LECA have the same strong bands at  $1081\text{ cm}^{-1}$  (3),  $800\text{ cm}^{-1}$  (5), and  $462\text{ cm}^{-1}$  (7) which can be interpreted as asymmetric vibration of siloxane (Si-O-Si), deformation of Si-O peak in  $\text{SiO}_4$ , and Si-O from amorphous silica (Noverliana & Asmi, 2015; Shokri, 2020).

Table 2. Interpretation of the FTIR bands of silica, andisol, LECA, anthracite, and activated carbon

No	Bands (cm <sup>-1</sup> )	Interpretation
1	2928	aliphatic (-CH <sub>2</sub> ) (He, Liu, Nie, & Song, 2017; Zhang et al., 2015)
2	1611	carbonyl (C=O) (He, Liu, Nie, & Song, 2017; Zhang et al., 2015)
3	1031	siloxane (Si-O-Si)
4	1010	Si-O-C (Noverliana & Asmi, 2015; Shokri, 2020)
5	800	Deformation Si-O in SiO <sub>4</sub> (Noverliana & Asmi, 2015; Shokri, 2020)
6	687	C-H in aromatic ring (Zhang et al., 2015)
7	462	Amorphous silica (Si-O) (Zhang et al., 2015)

Source: Analysis Result (2020)

However, shapes of these peaks are sharper in Silica than the peak of andisol and LECA which may relate to silica content in the adsorbent. The observed functional group of silica in this study was slightly different from Adam, Chew, & Andas' (2011) study. The band around 3440 cm<sup>-1</sup> which corresponds to hydroxyl stretching in silanol (Si-OH), was not detected in this study. Andisol soil is formed from volcanic rocks, and it usually is found at altitude 700-1500 m above sea level. Due to the main compound of andisol that is amorphous silica or aluminum (Park, Hyun, & Koo, 2020), many research reported utilization of andisol as an adsorbent for the drinking water process (Pranoto, Inayati, & Firmansyah, 2018). Besides vibration of siloxane, FTIR spectra of andisol at 1081 cm<sup>-1</sup> also corresponds to alumina (Al-O-Al). However, stretching vibration both Al-OH and Si-OH at the range of 3400-3500 cm<sup>-1</sup> is not detected in this research (Pranoto, Martini, & Maharditya, 2020). It may be because the different locations of andisol soil have the different chemical composition (Zebua, Guchi, & Sembiring, 2020). Unlike andisol, SiO<sub>2</sub> is the main mineral in LECA, and all the functional groups correspond to SiO<sub>2</sub>, which was

detected in the FTIR spectra (Sohrabi & Akhlaghian, 2016).

Anthracite is a type of coal that consists of fixed carbon and organic matter. The appearance of stretching vibration at 2928 cm<sup>-1</sup> (1) represents the existence of an aliphatic structure that commonly presents in anthracite (He, Liu, Nie, & Song, 2017). Stretching of carbonyl group appeared at 1611 cm<sup>-1</sup> band (2) while C-H stretching in aromatic rings appears at 687 cm<sup>-1</sup> band (6). According to FTIR spectra in Figure 3, the use of anthracite in this study consists of mineral silica that exists at bands of 1031 cm<sup>-1</sup> (3), 1010 cm<sup>-1</sup> (4), 800 cm<sup>-1</sup>(5), 462 cm<sup>-1</sup> (7) (Zhang et al., 2015). Unlike others adsorbents, activated carbon has no observed peak due to vaporized volatile material during the thermal process in activated carbon production (Sari, Yanto, & Pari, 2019). Therefore, functional groups of lignocellulose as the raw material disappears and remains 99% carbon.

#### b. Morphology of Adsorbents

The micrographs from SEM at the magnification 500 times of adsorbents anthracite, silica, andisol, activated carbon, and LECA is available in Figure 5. Morphology of anthracite in Figure 5a



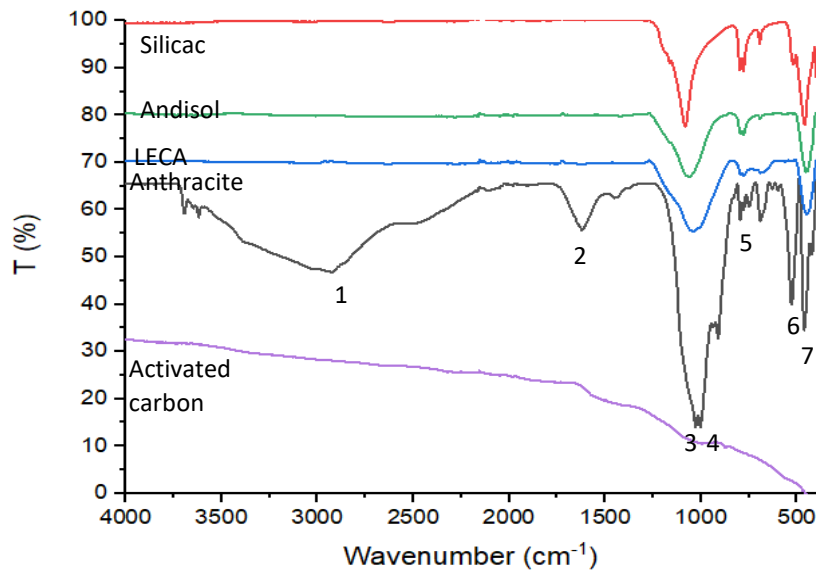


Figure 4. FTIR spectra of silica, andisol, LECA, anthracite, and activated carbon  
Source: Analysis Result (2020)

shows inhomogeneous pore distribution with wedge-shaped and ruptures because of the impact process of coalification where the surface of anthracite contains some crystalline and amorphous phases (Liu, Zhang, Choi, & Lu, 2018). According to EDS report, anthracite contains 85% carbon 8% titanium and iron, and 7% amorphous phase (Ribeiro, DaBoit, Flores, Kronbauer, & Silva, 2013). However, silica has smooth morphological surface with seldom pore (Figure 5b). Rosalia, Asmi, & Ginting (2016) investigated effect of calcination on silica's surface that increasing temperature of calcination decreased pore size of morphological silica. Besides that silica, zinc and silver were also included as mineral component in silica by EDX (Energy Dispersive X-Ray) analysis (Colboc et al., 2016).

Rupture and irregular pore are identified in surface graph of andisol (Figure 5c). SEM image shows the existence of micro- and mesoporous particle that can retain particles and

minerals such as Fe. Pranoto, Martini, & Maharditya (2020) investigated the adsorption of Fe on andisol trapped on the pore of andisol. After Fe adsorption, the pore size of andisol was smaller compared to the pore size before adsorption which indicated that Fe embedding on the pore (Pranoto, Martini, & Maharditya, 2020). Others results showed that the pore can entrap bacterial such as Coliform total dan *E. Coli* (Sholeh, Pranoto, Budiastuti, & Sutarno, 2020a) and also decreased BOD and COD (Sholeh, Pranoto, Budiastuti, & Sutarno, 2020b).

The activated carbon micrograph in Figure 5d showed regular and larger pores (macro size) compared to others adsorbents which are typically observed in activated carbon. The macro-pore (size ~50 nm) was a result of diffusion and reaction of steam with carbon as a treatment for the synthesis of activated carbon (Sari, Yanto, & Pari, 2019). The

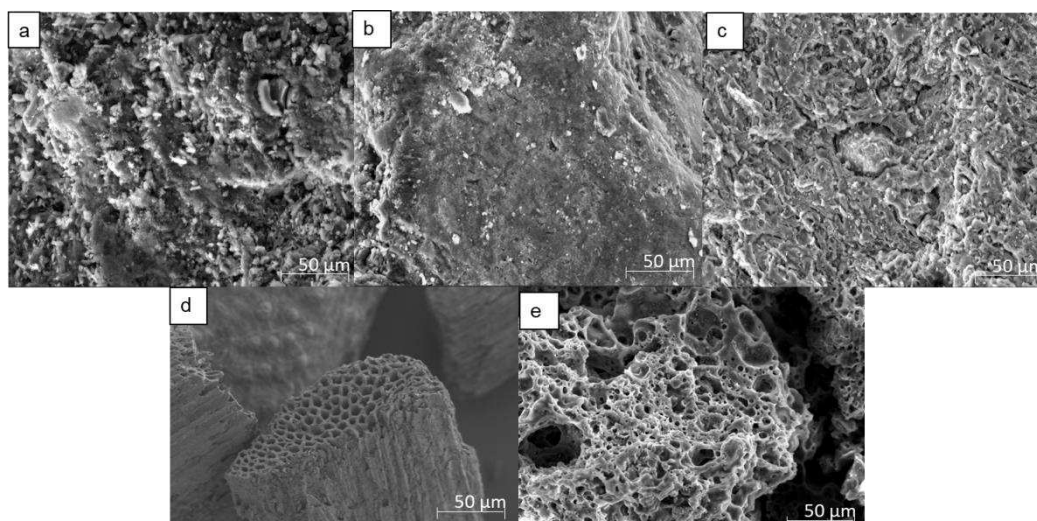


Figure 5. The micrographs from SEM at the magnification 500 times of adsorbents: anthracite (a), silica (b), andisol (c), active carbon (d), and LECA (e)  
 Source: Analysis Result (2020)

Table 3. The pore characteristics of the adsorbents

Adsorbents	BET surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Average pore diameter (Å)
Silica	114.405	0.183	17.082
Andisol	172.204	0.303	17.126
LECA	119.574	0.209	17.151
Anthracite	229.523	0.393	17.057
Activated carbon	548.310	0.948	17.034

Source: Analysis Result (2021)

pores size of the activated carbon can force adsorption of impurities which have been widely used in water the treatment plant (Jiang et al., 2019; Jin, Jin, Wang, Feng, & Wang, 2013). According to EDS report by Sari, Yanto, & Pari (2019), activated carbon contained 100% carbon without others element.

Surface of LECA in Figure 5e presented the irregular porous surfaces. Even though the chemical component by FTIR of LECA was similar to the chemical component of andisol, the pores are typically different. These pores are able to trap contaminant in water such as phosphor (Mlih et al., 2020). In addition, the detail of the

surface pore of each adsorbent is available in the BET section.

Nitrogen adsorption is a procedure to determine the porosity of the adsorbents. The surface area, pore-volume, and average pore diameter of silica, andisol, LECA, anthracite, and activated carbon are in Table 3. According to The International Union of Pure and Applied Chemistry (IUPAC) classification, the average pores diameter of the adsorbents indicate that the pores are classified into micro-porous (less than 20 Å). The higher surface area and porosity of the adsorbents may be attributed to the high sorption efficiency (Rout, Bhunia, & Dash, 2015). Table 3

shows that activated carbon has the highest surface area and pore volume, while silica has the lowest. The results of these pore characteristics are related to the turbidity of the solution where silica is only able to reduce the turbidity up to 8.98 NTU. Even though activated carbon has the highest surface area, the adsorption rate based on turbidity is lower than the adsorption rate of LECA and andisol. It occurred because the solid loading of the activated carbon is only 1:100 (w/v) while the others are 1:10 (w/v). Therefore, the activated carbon needs more time to adsorb the pollutant.

This research findings are essential and in line with one of the goals in watershed management, that is to ensure the availability of clean water for human life. The availability of clean water can be obtained through some water treatments as explained above; however, the prevention of river water from pollution is better than preserving nature. .

#### IV. CONCLUSION

Before the adsorption process, the turbidity of Citarum water was 21.30 NTU which was not eligible for human consumption. The turbidity was successfully decreased to below 5 NTU after the treatment using andisol and LECA for 10 minutes with a solid loading of 1:10 (gr/mL). Activated carbon took 10 minutes longer than the time of andisol and LECA to decrease turbidity due to its lower solid loading ratio. Silica has the lowest adsorption rate that may correlate to its pore size. The adsorption rate of the adsorbents was greater for the higher pore size. According to BET analysis, the

order of surface area was activated carbon>anthracite>andisol>LECA>silica. The pore size by BET corresponds to the surface image by FE-SEM analysis where activated carbon has regular and larger pores compares to others pores. In general, all the used adsorbents, except active carbon, have similar functional groups such as siloxane and amorphous silica at the band of  $1031\text{ cm}^{-1}$  and  $462\text{ cm}^{-1}$ . We concluded that active carbon, LECA, and andisol are suitable to purify water due to their large surface area. However, the effectiveness of the combination of five adsorbents in water treatment need to evaluated further.

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#### AUTHORS CONTRIBUTION

Fahriya Puspita Sari: Conceptualization, methodology, data analysis, data curation, writing – original draft preparation, review and editing. Nissa Nurfajrin Solihat: Conceptualization, methodology, data analysis, data curation, writing – original

draft preparation, review and editing. Muhammad Sholeh: Methodology, validation, supervision. Lucky Risanto: Methodology, data curation. Fitria: Methodology, editing, validation. Faizatul Falah: Methodology, data curation. Widya Fatriasari: Methodology, validation, reviewing, editing, supervision.

## REFERENCES

- Adam, F., Chew, T. S., & Andas, J. (2011). A simple template-free sol-gel synthesis of spherical nanosilica from agricultural biomass. *Journal of Sol-Gel Science and Technology*, 59(3), 580–583. <https://doi.org/10.1007/s10971-011-2531-7>
- Ali, I., & Gupta, V. K. (2007). Advances in water treatment by adsorption technology. *Nature Protocols*, 1(6), 2661–2667. <https://doi.org/10.1038/nprot.2006.370>
- Babel, S., & Opiso, E. M. (2010). Utilisation of andisols as possible low-cost adsorbent to remove Cr (VI) from aqueous solution. *International Journal of Environmental Technology and Management*, 12(2–4), 277–293. <https://doi.org/10.1504/IJETM.2010.031533>
- Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4(4), 361–377. <https://doi.org/10.1016/j.arabjc.2010.07.019>
- Belinawati, R. A. P., Soesilo, T. E. B., Asteria, D., & Harmain, R. (2018). Sustainability: Citarum River, government role on the face of SDGs (water and sanitation). *E3S Web of Conferences*, 52, 1–7. <https://doi.org/10.1051/e3sconf/20185200038>
- Bonilla-Petriciolet, A., Mendoza-Castillo, D. I., & Reynel-Ávila, H. E. (2017). Adsorption processes for water treatment and purification. *Adsorption Processes for Water Treatment and Purification*, 1–256. <https://doi.org/10.1007/978-3-319-58136-1>
- Cashin, V. B., Eldridge, D. S., Yu, A., & Zhao, D. (2018). Surface functionalization and manipulation of mesoporous silica adsorbents for improved removal of pollutants: A review. *Environmental Science: Water Research and Technology*, 4(2), 110–128. <https://doi.org/10.1039/c7ew00322f>
- Colboc, H., Bazin, D., Moguelet, P., Frochot, V., Weil, R., Letavernier, E., ... Daudon, M. (2016). Detection of silica and calcium carbonate deposits in granulomatous areas of skin sarcoidosis by  $\mu$ Fourier transform infrared spectroscopy and Field Emission Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy analysis. *Comptes Rendus Chimie*, 19(11–12), 1631–1641. <https://doi.org/10.1016/j.crci.2016.05.007>

- Da'na, E. (2017). Adsorption of heavy metals on functionalized-mesoporous silica: A review. *Microporous and Mesoporous Materials*, 247, 145–157. <https://doi.org/10.1016/j.micromeso.2017.03.050>
- Gor, G. Y., Paris, O., Prass, J., Alexandra, P., Lopes, M., Carrott, R., ... GmbH, T. (2013). Adsorption of n-Pentane on Mesoporous Silica and Adsorbent Deformation Adsorption of n-Pentane on Mesoporous Silica and Adsorbent Deformation Department of Civil and Environmental Engineering. <https://doi.org/10.1021/la401513n>
- Hasbiah, A. W., & Kurniasih, D. (2019). Analysis of water supply and demand management in Bandung City Indonesia. *IOP Conference Series: Earth and Environmental Science*, 245(1). <https://doi.org/10.1088/1755-1315/245/1/012030>
- He, X., Liu, X., Nie, B., & Song, D. (2017). FTIR and Raman spectroscopy characterization of functional groups in various rank coals. *Fuel*, 206, 555–563. <https://doi.org/10.1016/j.fuel.2017.05.101>
- Jiang, C., Cui, S., Han, Q., Li, P., Zhang, Q., Song, J., & Li, M. (2019). Study on Application of Activated Carbon in Water Treatment. *IOP Conference Series: Earth and Environmental Science*, 237(2), 0–5. <https://doi.org/10.1088/1755-1315/237/2/022049>
- Jin, P., Jin, X., Wang, X., Feng, Y., & Wang, X. C. (2013). Biological Activated Carbon Treatment Process for Advanced Water and Wastewater Treatment. *Biomass Now - Cultivation and Utilization*. <https://doi.org/10.5772/52021>
- Liu, Z., Zhang, Z., Choi, S. K., & Lu, Y. (2018). Surface properties and pore structure of anthracite, bituminous coal and lignite. *Energies*, 11(6). <https://doi.org/10.3390/en11061502>
- Mlih, R., Bydalek, F., Klumpp, E., Yaghi, N., Bol, R., Wenk, J., ... Str, W. J. (2020). Light-expanded clay aggregate ( LECA ) as a substrate in constructed wetlands – A review. *Ecological Engineering*, 148(March), 105783. <https://doi.org/10.1016/j.ecoleng.2020.105783>
- Mohammadi, E., Yetilmezsoy, K., & Uygur, N. (2013). Applied Surface Science Modeling of adsorption of toxic chromium on natural and surface modified lightweight expanded clay aggregate ( LECA ). *Applied Surface Science*, 287, 428–442. <https://doi.org/10.1016/j.apsusc.2013.09.175>
- Noverliana, N., & Asmi, D. (2015). Sintesis Keramik Silika Daun Bambu Dengan Metode Sol-Gel Dan Karakterisasi Pada Suhu Kalsinasi 500 OC, 600 OC, dan 700 OC. *JURNAL Teori Dan Aplikasi Fisika*, 03(01), 17–23.

- Park, W. P., Hyun, H. N., & Koo, B. J. (2020). Silicon fractionation of soluble silicon in volcanic ash soils that may affect groundwater silicon content on jeju island, korea. *Water (Switzerland)*, 12(10), 1–17. <https://doi.org/10.3390/w12102686>
- Piccin, J. S., Cadaval, T. R. S. A., De Pinto, L. A. A., & Dotto, G. L. (2017). *Adsorption isotherms in liquid phase: Experimental, modeling, and interpretations. Adsorption Processes for Water Treatment and Purification*. [https://doi.org/10.1007/978-3-319-58136-1\\_2](https://doi.org/10.1007/978-3-319-58136-1_2)
- Pranoto, Inayati, & Firmansyah, F. (2018). Effectiveness Study of Drinking Water Treatment Using Clays/Andisol Adsorbent in Lariat Heavy Metal Cadmium (Cd) and Bacterial Pathogens. *IOP Conference Series: Materials Science and Engineering*, 349(1). <https://doi.org/10.1088/1757-899X/349/1/012047>
- Pranoto, P., Martini, T., & Maharditya, W. (2020). Uji Efektivitas dan Karakterisasi Komposit Tanah Andisol/Arang Tempurung Kelapa Untuk Adsorpsi Logam Berat Besi (Fe). *ALCHEMY Jurnal Penelitian Kimia*, 16(1), 50. <https://doi.org/10.20961/alchemy.16.1.33286.50-66>
- Rahman, M. A., Azam, T., & Alam, A. M. S. (2012). Removal of Phosphate Ions from Aqueous Solution Using Anthracite. *Dhaka University Journal of Science*, 60(2), 181–184. <https://doi.org/10.3329/dujs.v60i2.11490>
- Ribeiro, J., DaBoit, K., Flores, D., Kronbauer, M. A., & Silva, L. F. O. (2013). Extensive FE-SEM/EDS, HR-TEM/EDS and ToF-SIMS studies of micron- to nano-particles in anthracite fly ash. *Science of the Total Environment*, 452–453, 98–107. <https://doi.org/10.1016/j.scitotenv.2013.02.010>
- Rosalia, R., Asmi, D., & Ginting, E. (2016). Preparasi dan Karakterisasi Keramik Silika (SiO<sub>2</sub>) Sekam Padi dengan Suhu Kasinasi 800oC - 1000oC. *Jurnal Teoro Dan Aplikasi Fisika*, 04(01), 101–106.
- Rout, P. R., Bhunia, P., & Dash, R. R. (2015). A mechanistic approach to evaluate the effectiveness of red soil as a natural adsorbent for phosphate removal from wastewater. *Desalination and Water Treatment*, 54(2), 358–373. <https://doi.org/10.1080/19443994.2014.881752>
- Sari, F. P., Yanto, D. H. Y., & Pari, G. (2019). Activated Carbon Derived From OPEFB by One Step Steam Activation and Its Application for Dye Adsorption: Kinetics and Isothermal Studies. *Reaktor*, 19(2), 68–76. <https://doi.org/10.14710/reaktor.19.2.68-76>
- Seliem, M. K., Mobarak, M., Selim, A. Q., Mohamed, E. A., Halfaya, R. A., Gomaa, H. K., ... Dotto, G. L.

- (2020). A novel multifunctional adsorbent of pomegranate peel extract and activated anthracite for Mn(VII) and Cr(VI) uptake from solutions: Experiments and theoretical treatment. *Journal of Molecular Liquids*, 311(Vii), 113169.  
<https://doi.org/10.1016/j.molliq.2020.113169>
- Sepehr, M. N., Kazemian, H., Ghahramani, E., Amrane, A., Sivasankar, V., & Zarrabi, M. (2014). Defluoridation of water via Light Weight Expanded Clay Aggregate (LECA): Adsorbent characterization, competing ions, chemical regeneration, equilibrium and kinetic modeling. *Journal of the Taiwan Institute of Chemical Engineers*, 45(4), 1821–1834.  
<https://doi.org/10.1016/j.jtice.2014.02.009>
- Shara, S., Moersidik, S. S., & Soesilo, T. E. B. (2021). Potential health risks of heavy metals pollution in the Downstream of Citarum River. *IOP Conference Series: Earth and Environmental Science*, 623, 012061.  
<https://doi.org/10.1088/1755-1315/623/1/012061>
- Shokri, A. (2020). Using Mn based on lightweight expanded clay aggregate (LECA) as an original catalyst for the removal of NO<sub>2</sub> pollutant in aqueous environment. *Surfaces and Interfaces*, 21(September), 100705.  
<https://doi.org/10.1016/j.surfin.2020.100705>
- Sholeh, M., Pranoto, Budiastuti, S., & Sutarno. (2020a). Effect of adsorbent composition variation quartz sand/andisol soil/zeolite/activated carbon toward Cu, Pb, coliform total and E. coli treatments on the citarum river. *Systematic Reviews in Pharmacy*, 11(9), 169–177.  
<https://doi.org/10.31838/srp.2020.9.29>
- Sholeh, M., Pranoto, Budiastuti, S., & Sutarno. (2020b). The Effect of Adsorbent Composition: Quartz Sand/Andisol Soil/Zeolite/Activated Carbon against Mn, Fe, BOD, and COD in Citarum River Eater Cleaning Progress. *Systematic Reviews in Pharmacy*, 11(10), 645–652.  
<https://doi.org/10.31838/srp.2020.10.97>
- Sholeh, M., Pranoto, P., Budiastuti, S., & Sutarno, S. (2018). Analysis of Citarum River pollution indicator using chemical, physical, and bacteriological methods. *AIP Conference Proceedings*, 2049(December).  
<https://doi.org/10.1063/1.5082473>
- Sohrabi, S., & Akhlaghian, F. (2016). Light expanded clay aggregate (LECA) as a support for TiO<sub>2</sub>, Fe/TiO<sub>2</sub>, and Cu/TiO<sub>2</sub> nanocrystalline photocatalysts: a comparative study on the structure, morphology, and activity. *Journal of the Iranian Chemical Society*,

- 13(10), 1785–1796.  
<https://doi.org/10.1007/s13738-016-0896-9>
- Suhartono, Y. (2020). Proses Pengolahan Air PDAM Cabang Karawang. Retrieved from <https://www.pdamkarawang.id/blog/posting/proses-pengolahan-air-pdam-cabang-karawang/>
- Widyawati, Y. R., Notodarmojo, S., Hidayat, S., & Helmy, Q. (2019). Removal of Hexavalent Chromium from Raw Drinking Water by Zeolite-FeO Composite Supported Carbon: Case Study Citarum River. *IOP Conference Series: Materials Science and Engineering*, 536(1). <https://doi.org/10.1088/1757-899X/536/1/012067>
- Xu, H., Sun, X., Yu, Y., Liu, G., Ma, L., & Huang, G. (2019). Removal of quinoline using various particle sizes anthracite: Adsorption kinetics and adsorption isotherms. *Physicochemical Problems of Mineral Processing*, 55(1), 196–207.  
<https://doi.org/10.5277/ppmp18121>
- Zebua, A. C., Guchi, H., & Sembiring, M. (2020). Isolation of non-symbiotic Nitrogen-fixing bacteria on andisol land affected by Sinabung eruption. *IOP Conference Series: Earth and Environmental Science*, 454(1). <https://doi.org/10.1088/1755-1315/454/1/012167>
- Zhang, W., Jiang, S., Wang, K., Wang, L., Xu, Y., Wu, Z., ... Miao, M. (2015). Thermogravimetric dynamics and FTIR analysis on oxidation properties of low-rank coal at low and moderate temperatures. *International Journal of Coal Preparation and Utilization*, 35(1), 39–50.  
<https://doi.org/10.1080/19392699.2013.873421>