Modification of activated carbon with titanium dioxide as a water treatment material

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Abstract
Activated carbon is a porous material that has high absorption power which can increase the quality of drinking water. Modifying the activated carbon with Titanium Dioxide (TiO2) can increase the quality of drinking water. This experiment study used activated carbon which then immersed in a Titanium Tetraisoproxide solution, each with a concentration of 5% and 10% with a ratio of 1: 5 then stirred with a magnetic stirrer for 2 hours. The results showed that FTIR peaks at a wavelength of 700-500 cm⁻¹, as Ti-O. The diffractogram at 25°, 40°, 50°, and 55° indicates anatase. The SEM-EDX results showed 79% carbon and there was a Ti of 4%. The Chemical Oxygen Demand (COD) test results showed that COD before being treated with ACTi was 1 ppm (pH = 6). After being processed with ACTi, the water has decreased COD levels of 93.28%, which is 0.0372 ppm (pH = 7). Modification of activated carbon with TiO2 has been carried out as evidenced by the characteristics of FTIR, XRD, and SEM-EDX. Activated carbon modified with TiO2 can reduce COD levels by 93.28%.

Introduction
Industrial growing in East Java cannot be separated from environmental impacts such as pollution of the Brantas River watershed. The pollution is caused by organic and inorganic waste such as dyes, heavy metals and bacteria derived from industrial and household waste. Fabriano et al.¹ showed that there was pollution in several sources of spring water in Kediri with Macrozooobenthos organism parameters. Dahlia² Zn study was about 4 g/L, Pb 0.2 g/L, Cu 0.5 g/L, Cd 0.05 g/L, Cr 0.2 g/L; has exceeded the threshold allowed by PP No. 82/2001 (maximum Cu 0.20, Zn 2.00, Pb 1.0, Cd 0.01, Cr 1.00 mg/L). The study was supported by the study of Nasrudin et al.³ and Priatna et al.⁴ showed that the metal content of lead (Pb) in Brantas river flow was around 1.18 ppm and 0.129. The phenol content of the Bremi River is between 0-0.031 mg/l, the chromium concentration is 0.0005 mg/l while the oil concentration is 3.6-23.6 mg/l. This pollution has an impact on water quality degradation. This decrease in water quality has a negative impact on the community, especially the decline in the quality of drinking water.

Decreasing the quality of drinking water can be overcome in several ways, including with activated carbon as water treatment. Activated carbon is widely used in various applications such as petroleum processing, metal adsorbers, gas storage, drug storage, cosmetics, stomach pain medicine, and clean water treatment.⁵.⁶ Activated carbon has the advantages of easy synthesis and low raw materials and an easy synthesis process. Activated carbon can be synthesized from various kinds of raw materials such as agricultural waste such as coconut skin, cassava, peanuts, rice, and bagasse.⁷.⁸ This has the potential to develop water treatment with activated carbon, because, in addition to being supported by areas that are passed by the Brantas River, it is also an agricultural area that can be used as raw material for activated carbon.

The potential of activated carbon as water treatment has been reported in several studies. Cermakova, et al.⁹ show that activated carbon can be used as cyanobacterial adsorbents in water treatment. Bahamon et al.⁶ illustrate that activated carbon is able to take ibuprofen from water and Fu et al.¹⁰ shows that activated carbon can be used as an antibiotic adsorbent in water. Orha et al.¹¹ shows that Activated Carbon modified by TiO2 for a water treatment material so that it can be used as drinking water. This modification with TiO2 is carried out to increase the adsorbent power of activated carbon to bacterial, metal ions, and trigger pollution such as humic acid in water.¹¹.¹² On the other hand, TiO2 is a non-toxic compound, has high stability and has very high photocactivity. However, Orha’s research uses activated carbon from the industry. In this research will be Modification Of Activated Carbon With Titanium Dioxide As A Water Treatment Material.

Materials and Methods
This experiment use activated carbon from Mulyati et al. 2018. The activated carbon is then immersed in Titanium Tetraisoproxide (TTIP) solution, each with a concentration of 5% and 10% with a ratio of 1: 5 then stirred for 2 hours. The activated carbon is then immersed in Titanium Tetraisoproxide (TTIP) solution, each with a concentration of 5% and 10% with a ratio of 1: 5 then stirred for 2 hours. Then, put it in the autoclave bottle and dried in the oven at 200°C for 30 minutes. The Result characterized by Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX).

Results
The activated carbon is then immersed in Titanium Tetraisoproxide (TTIP) solution, each with a concentration of 5% and 10% with a ratio of 1: 5 then stirred for 2 hours. Then, put it in the autoclave bottle and dried in the oven at 200°C for 30 minutes. The Result characterized by Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX). Finally, the sample has used to adsorption water from river.
with a magnetic stirrer for 2 hours. Then, put it in the autoclave bottle and dried in the oven at 200°C for 30 minutes. The results were then washed with distilled water and dried at 60°C for 5 hours so called ACTi. Finally, ACTi characterized by XRD, FTIR, SEM-EDX and surface area using methylene blue.

Modification with TiO₂ aims to increase the adsorbent power of activated carbon to bacterial, metal ions, and trigger pollution in water.11,12 The greater Ti content used to modify activated carbon shows that the characteristics of TiO₂ modified activated carbon (ACTi) produced in this study are different as shown in Table 1.

The moisture and ash content test results in Table 2 show that the moisture content of the activated carbon modified with 5% TiO₂ (ACTi 5) has smaller moisture content of 10.7% compared to activated carbon (AC) which is 12.5%. This shows the nature of the modifying agent has the same properties with activator substances, namely as a water-degrading agent from the carbon surface that further reduces the water content.13 The dehydration process of water from the carbon surface shows that TiO₂ enters the surface of the active carbon to replace water so as to increase the active side of activated carbon as an adsorbent material.

The process of entering TiO₂ is also shown that activated carbon Modified TiO₂ 10% (ACTi 10) had a greater ash content of 27.3% compared to 8% of activated carbon (AC) (Table 1). According to Mulyati et al.14 and Pujiono et al.15 that ash content indicates that the number of inorganic substances or metals contained in a compound. This shows that the activated carbon ash content increases the metal scales (ie TiO₂) from activated carbon so that activated carbon contains more ash content.

The adsorption ability of ACTi was simulated by adsorbing methylene blue. The use of methyl blue on the grounds that methylene blue is often used in dyes, especially in the textile industry. This compound is very stable and dangerous for the environment because it can increase the demand for chemical oxygen (COD) which can damage the balance of the ecosystem.16 Methylene blue can be used to determine surface area. Because of absorbed in the mesopore, but also found in micropores.17

The results of the adsorption test with Methylene Blue (Table 2) showed that 10% modified TiO₂ active carbon (ACTi 5) had greater adsorption than the activated carbon (AC). This shows that the modification process can increase the adsorption power of Methylene Blue because the presence of TiO₂ increases the active side of the activated carbon so that the adsorption power increases. In addition, the increased adsorption capacity of modified activated carbon is also influenced by a larger surface area of 1477.96 m²/g compared to 1464.21 m²/g of activated carbon (Table 2). This is in accordance with Wang, et al.18 that the metal impregnation process in carbon will increase the surface area and active side of activated carbon, thereby increasing its adsorption capability. The pore shape of TiO₂-modified activated carbon can be seen in the micrograph Figure 1.

To show that activated carbon has been successfully modified with TiO₂, characterization with FTIR, XRD and EDX is carried out.

Characterization of activated carbon with FTIR aims to identify functional groups found on carbon before activation and activated carbon. Because the adsorption is not only determined by the pore size but also influenced by the chemical composition of the activated carbon, the functional group which is the active group of activated carbon.19

The FTIR spectra in Figure 2 show that there are differences in FTIR spectra between carbon before activated with activated carbon. The band at 3500-3300 cm⁻¹ which indicates the presence of O-H

![Figure 1. Micrograph of ACTi.](image-url)
groups of carbon, the activated carbon shows a decrease in the band. This happens because the role of the TiO2 modifier can reduce hydrogen bonds so that a band occurs at these wavelengths. The band at 1625-1610 cm⁻¹ indicates the existence of the aromatic C = C functional group. This band is decreasing with the process of modifying activated carbon. On the other hand, the modified activated carbon appears the band at 1450-1420 cm⁻¹ which indicates the presence of an asymmetrical C-H function group. This shows that the activation process can damage aromatic bonds to form the active side which is shown by the presence of C-H functional groups.20,21,22 Another band that supports that carbon has been successfully modified is the presence of bands in wavenumbers 700-500 cm⁻¹ which are Ti-O where ACTi 10 has a higher intensity compared to ACTi 5. This is in accordance with the XRD diffractogram pattern, where differences occur, activated carbon diffractogram before and after being modified with TiO2.

Activated carbon before and after modification is characterized by XRD at an angle of 5-70°. This aims to show that the activated carbon before and after a modification has a different structure. Figure 3 shows that the widening diffusion peaks appear at small angles of about 5 - 20° in carbon before and after modification indicates that the activated carbon structure is amorphous and has a heterogeneous surface. The difference between carbon before and after modification peak at 25°, 40°, 50°, and 55° shows the presence of anatase TiO2.23 This peak shows that TiO2 used for the modification of activated carbon has successfully occupied the surface of the activated carbon. ACTi 10 has a higher TiO2 specific peak than ACTi 5, because of more TiO2 which occupies the surface of the activated carbon so that the specific peak of amorphous carbon is lost (yellow diffractogram). This is supported by the EDX results which show that the modified carbon contains 79% carbon and there is a Ti of 4% as shown in Figure 4.

ACTi is used for the adsorption of Brantas river water with a ratio of 1:1000. Water before and after adsorption is then tested for COD. COD (Chemical Oxygen Demand) is an indicator of pollutant concentration that can be oxidized chemically. The COD results in Table 3 show that COD water before being treated with ACTi is 1 ppm (pH=6). After being processed with ACTi, the water has decreased COD levels of 93.28%, which is 0.0372 ppm (pH=7). These results indicate that ACTi can be used as a water treatment material.
Conclusions

The experiment shows that the FTIR peaks at a wavelength of 700-500 cm⁻¹ which is Ti-O. The diffractogram at 25°, 40°, 50°, and 55° which indicates anatase. The SEM-EDX results showed 79% carbon and there was a Ti of 4%. The COD test results showed that COD before being treated with ACTi was 1 ppm (pH=6). After being processed with ACTi, the water has decreased COD levels of 93.28%, which is 0.0372 ppm (pH=7).

References

1. Febrianto C, Sholikhin A, Mughofar A, et al. “Pengukuran Tingkat Pencemaran Sumber Mata Air Yang Terdapat di Kota Kediri Menggunakan Parameter Organisme Makrozoobentos”. Kediri: Universitas Nusantara PGRI; 2014.
2. Dahla, Efektivitas Bioakumulasi Tanaman Sayuran Pengiat Logam Berat dan Upaya Pemberdayaan Masyarakat. Disertasi. Jurusan Pendidikan Biologi. Pascasarjana. Malang: Universitas Negeri Malang; 2006.
3. Nasrudin, Irwan M, Sulistiono, et al. “Identifikasi Pencemaran Logam Pb Pada Tanaman Kangkung (Ipomoea aquatica) Di Sungai Brantas Kediri”. Kediri: Universitas Nusantara PGRI; 2015.
4. Priatna DE, Purnomo T, Kuswanti N. Kadar Logam Timbal (Pb) pada Air dan Ikan Bader (Barbonymus gonionotus) di Sungai Brantas. Lent Bio. 2016;5:53-58.
5. Ponkarthikeyan P, Sree, Sutha K. “A review of Activated Carbon by Chemical Activation”. Int J Civ Eng J SSRG 2017:532-524.
6. Bahamon D, Carro L, Guri, S, et al. Computational study of ibuprofen removal from water by adsorption in realistic activated carbons. J Coll and Inter Scie. 2013:498(1):334-323.
7. Bhatnagar A, Hogland W, Marques M, et al. An overview of the modification methods of activated carbon for its water treatment applications. Chem Eng J, 2013; 219:511-499.
8. Pujiono FE, Mulyati TA. Potensi Karbon Aktif Dari Limbah Pertanian Sebagai Material Pengolahan Air Limbah. J Wiyata 2017;4:46-37.
9. Cermakova L, Kopecka I, Pivokonsky M, et al. Removal of cyanobacterial amino acids in water treatment by activated carbon adsorption. Sep and Purif Tech. 2017;173:338-330.
10. Fu H, Li X, Wang J, et al. Activated Carbon Adsorption of Quinolone Antibiotics in Water: Performance, Mechanism, and Modeling. J Envi Sci. 2016;1:8-1.
11. Orhaoa C, Pode R, Manea F, et al. Titaniv oxyde-modified activated carbon for advanced drinking water treatment. Proc Safe Envi Prot. 2016;1:8-1.
12. Wang J, Zhao F, Hu Y, et al. Modification of Activated Carbon Fiber by Loading Metals and Their Performance on SO2 Removal. Chin J Chem Eng. 2006;14:485-478.
13. Buczek, Bronislaw. Preparation of Active Carbon by Additional Activation with Potassium Hydroxide and Their Performance of Their Properties. Adv. Mat. Sci. Eng. 2016; 2016:1-4.
14. Mulyati F, Pujiono F. Preparasi Dan Karakterisasi Karbon Aktif Dari Limbah Ampas Tebu Menggunakan Aktivator KOH. Ind Chem Appl J. 2018;2:5-1.
15. Pujiono F, Mulyati T. Preparasi Dan Karakterisasi Karbon Dari “Blotong” Limbah Fabrik Gula Pada Berbagai Suhu Karbonasi. J Wiyata 2018;4:179-173.
16. Ramadhani A, Muhdarina, Linggawati A. Kapasitas Adsorpsi Metilen Biru Oleh Lemung Cengar Teraktivasi Asam Sulfat. JOM FMIPA 2015;2: 239-232.
17. Tewari BB, Thornton, CO. Use Of Basic Methyline Blue Dye For Specific Surface Area Measurement of Metal Hexacyanoferrate(II) Complexes. Rev. Soc. Quim. 2010;76:336-330.
18. Wang X, Liu Y, Hu Z, et al. Degradation of methyl orange by composite photocatalyst nano-TiO2 immobilized on activated carbon of different porosities. J. Hazard. Mater. 2009;169:1067-1061.
19. García JR, Sedran U, Zaini MAA, Zakaria ZA. Preparation, characterization, and dye removal study of activated carbon prepared from palm kernel shell. Environ Sci Pollut Res Int. 2018;25:5076-5085.
20. Yagmur E, Ozmak M, Akas Z. A novel method for the production of activated carbon from waste tea by chemical activation with microwave energy. Fuel. 2008; 87: 3278–3285.
21. Budiono A, Suhartana, dan Gunawan. Pengaruh Aktivasi Arang Tempurung Kelapa Dengan Asam Sulfat dan Asam Posfat untuk Absorpsi Fenol. Semarang: Universitas Diponegoro; 2009.
22. Hidayu AR, Muda M. Preparation and Characterization of Impregnated Activated Carbon from Palm Kernel Shell and Coconut Shell for CO2 Capture. Proc. Eng. 2016; 148: 106-113.
23. Thirugnanasambandan T, Alagar M. Titanium dioxide (TiO2) Nanoparticles XRD Analyses: An Insight. Chemical Physics Journal Citation 2013. Available from: https://arxiv.org/ftp/arxiv/papers/1307/1307.1091.pdf. Accessed on: 12 August 2018.