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Evaluating the surface functional groups on banana leaf petioles and the resultant biochar for potential adsorbance

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Abstract
The presence of surface functional groups is key to the performance of an adsorbent material. The aim of this study was to evaluate the presence of functional groups on banana leaf petiole and on biochar made from banana leaf petiole. These functional groups assist in determining the potential of the material as an adsorbent for pollutants and heavy metals in waste water. Banana leaf petioles were collected from a single plantation and analyzed using the Fourier transform infrared spectroscopy. The material was then pyrolyzed at pyrolytic temperatures of 300°C, 400°C and 500°C, and the resulting biochars were analyzed to identify the surface functional group. The results showed the presence of hydroxyl and carboxyl functional groups on the banana leaf petiole before pyrolysis. The biochars also showed presence of hydroxyl and carboxyl functional groups whose presence and abundance reduced with increase in pyrolytic temperature. The presence of hydroxyl and carboxyl functional groups in a material has been related to its ability to adsorb metals in waste water and thus the banana leaf petiole as well as its resulting biochar would be a promising adsorbent for waste water remediation.

1. Introduction
Adsorption technique is a popular method in reducing the amounts of environmental pollutants and researchers are focusing on developing low cost adsorbents from cheap sources to replace the costly adsorbents [1-4]. The process of adsorption is dependent on several factors such as the nature of the adsorbent, the adsorption conditions and the adsorbate. The adsorbent's characteristics may include the surface area, hydrophobicity and the presence of functional groups on the surface of the adsorbing material [5-7]. The surface chemistry of an adsorbent is as a result of presence of heteroatoms such as oxygen, nitrogen, hydrogen and phosphates which form ketones, carboxyl, phenols, ethers, lactones, amines, nitro groups and phosphates [8,9]. The presence of functional groups plays an important role in the adsorption process and molecules that interact with an adsorbent that has functional groups will experience greater adsorption [6,10]
Biochar is produced through Pyrolysis which is an inexpensive technology that can result in thermochemical decomposition of organic materials [11-13]. The pyrolysis process involves a thermochemical conversion technology that operates in the absence or limited oxygen and results in end products such as bio-oils, biochar and gases [14]. Biochar has been considered as a potential surrogate for activated carbon in environmental remediation and water treatment due to its low cost, relative abundance and comparative sorption abilities [15]. Biochar has been shown to exhibit a greater ability

and potential in remediation of contaminated waters than other adsorbents as it contains micro- and/or meso-porous structures, different surface functional groups which include carboxylic groups, hydroxyl groups, carbonyl groups, alcoholic and lactone groups, and inorganic mineral species [16,17,18]. In order to examine the presence of these functional groups on biomass and biochar, Fourier Transform Infrared (FTIR) spectroscopy technique is used. The FTIR spectra produced is used to depict the possible changes in abundance of the surface functional moieties of biomass when compared with the product biochar [19-21]. Pyrolysis has been identified to have a significant effect on the present functional groups in biochars [20].

Various parts of the banana plant have been studied as adsorbents against cationic, anionic and neutral pollutants [2,22,23]. This is due to their advantages which include being readily available, low cost and protecting the environment by preventing methane and carbon dioxide formation where the wastes are dumped in wetlands or burned [2]. Low et al. [24] studied the removal of metal from electroplating waste and synthetic solution using banana pith biochar. Anwar et al. [25] used banana peels biochar to remove lead and cadmium from water. Memon et al. [26] further studied banana peels for the selective removal of Chromium (VI) from industrial waste water. Banana pseudo stem was studied for the removal of colour and Chemical Oxygen Demand (COD) from landfill leachate [27]. Banana trunk activated carbon was studied for remediation of methylene blue contaminated water [23]. Banana peduncle biochar at different pyrolytic temperatures was also studied for the removal of Chromium (VI) [28]. The potential of banana leaf petioles as a potential adsorbent has not been studied. The objective of this study was to evaluate the presence of functional groups responsible for adsorption of organic and inorganic pollutants on the banana petioles and on the biochar prepared from the banana petiole material.

2. Material and Methods

2.1 Banana Leaf Petiole Collection and Preparation

The Banana leaf petioles for use in this study were collected from a banana plantation in Embu, Kenya. The sample was collected from a single banana species (*Mussa acuminata*). The petioles were harvested and separated from the sheath and leaf parts of the banana plant. These were then washed with tap water to remove dirt on their surfaces and later rinsed with deionized water to remove the metal ions on the surfaces. They were then sun dried to remove the surface water. The leaf petioles were then sliced into small pieces (<2 cm) to increase their surface area for drying and also to fit in the crucibles used in the pyrolysis process.

2.2 Preparation of Banana Stalks Samples for Fourier Transform Infrared (FTIR) Spectroscopic Analysis

The sliced banana leaf petioles (<2 cm) were oven dried at a temperature of 105° C to constant mass in order to remove the moisture content. A sample of the dry material was ground using a high-speed universal disintegrator (model FW80-I, China) into powder form and a sample of 10 grams stored in air tight Ziplock bag for use in Fourier Transform Infrared (FTIR) spectroscopy analysis.

2.3 Biochar Production

The dried banana leaf petiole material was packed in three crucibles each holding a mass of 35 g of the material and then pyrolyzed using a muffle furnace (Model LH 15/14, Nabertherm, Germany). The muffle furnace was programmed to rise to a temperature of either 300°C, 400°C or 500°C. The temperature rise was maintained at 10°C/min. The holding time for the different pyrolytic temperature was one hour after which the furnace was allowed to cool down to room temperature. The biochar produced in each pyrolysis process was weighed and the mass recorded. The biochar was then packed into air-tight plastic Ziplock bags. This process was replicated seven times.

2.4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Analysis for the functional groups present on the samples of dried banana leaf petiole powder and biochars produced at temperatures 300°C, 400°C and 500°C was conducted using an FTIR machine (Model: Jasco, Japan) in attenuated total reflectance (ATR) mode [29, 30]. The scans were conducted from a wavelength of 4000 cm^{-1} to 500 cm^{-1} at a scan rate of 50 conducted at a resolution of 4 cm^{-1}. The infra-red (IR) spectra for each sample was obtained electronically. The samples were analyzed in triplicates.

3. Results and discussion

The Infrared spectra depicted in Figures 1, 2, 3 and 4 shows the surface functional groups present in raw banana leaf petiole, biochar pyrolyzed at 300°C, biochar pyrolyzed at 400°C and biochar pyrolyzed at 500°C, respectively.
The raw banana leaf petioles FTIR (Figure 1) showed peaks at wavelengths 3294 cm^{-1} and other peaks at 2923 cm^{-1},1644 cm^{-1},1538 cm^{-1}, 1427 cm^{-1} and 1016 cm^{-1}. These peaks correspond to O-H, C-H stretching, C=O, N-O, O-H bending and C-O surface functional groups respectively. These results corroborate with a study by Dos Santos et al. [31] on functional groups present in raw banana fibre who noted the presence of O-H, C-H stretching, O-H bending, C=O and C-O surface functional groups. The presence of O-H, C-H, C-O, C=O functional groups has also been reported in banana peel FTIR [32].

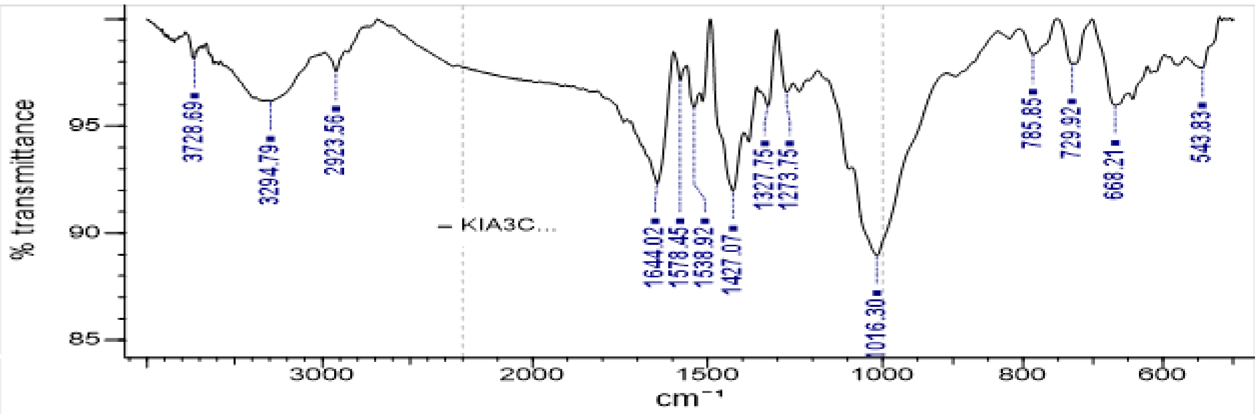

Figure 1: Fourier Transform Infrared (FTIR) spectrum of raw banana leaf petiole powder before pyrolysis

The peaks identified on biochar 300°C (Figure 2) were at wavelengths 3625 cm^{-1}, 2912cm^{-1}, 1609 cm^{-1},1314 cm^{-1} and 1053 cm^{-1}. These peaks correspond to free O-H, aldehyde C-H, conjugated C=C, amine C-N and stretching C-O groups, respectively. In biochar 300°C, the band shift from 2923 cm^{-1} before pyrolysis to 2912 cm-1 after pyrolysis, and 1016 cm^{-1} to 1053cm^{-1}, respectively, for the C-H and C-O groups was observed. A similar trend was observed in a different study of banana fibre pyrolyzed at 300°C which showed the presence of O-H, C-H stretching, C=C and C-O groups in biochar [31, 33, 34]. A shift in functional group band after pyrolysis was also confirmed by Li et al. [34], where they reported a shift in C-O peaks after increasing pyrolysis temperature.
The main peaks identified on the surface of biochar 400°C (Figure 3) were at wavelength 3620cm^{-1}, 2878cm^{-1}, 1607 cm^{-1} and 1315 cm^{-1}. The peaks correspond to free O-H, C-H, conjugated C=C and amine C-N groups respectively. A band shift was also noted for the C-H group from 2923 cm^{-1} before pyrolysis to 2878 cm^{-1} after pyrolysis. The presence of O-H, C-H, C=C functional groups in biochar 400°C was also reported by Dos Santos et al. [31].

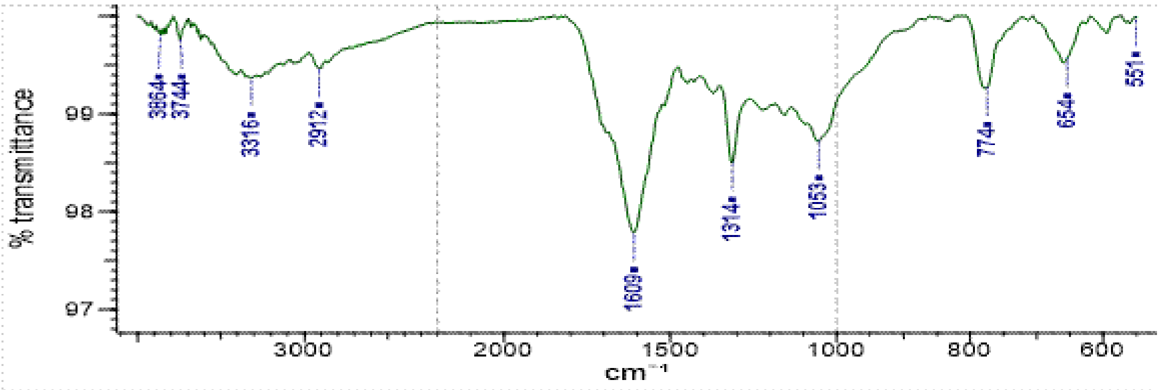

Figure 2: Fourier Transform Infrared (FTIR) spectrum of banana leaf petioles pyrolyzed at Temperature 300°C (Biochar 300°C)

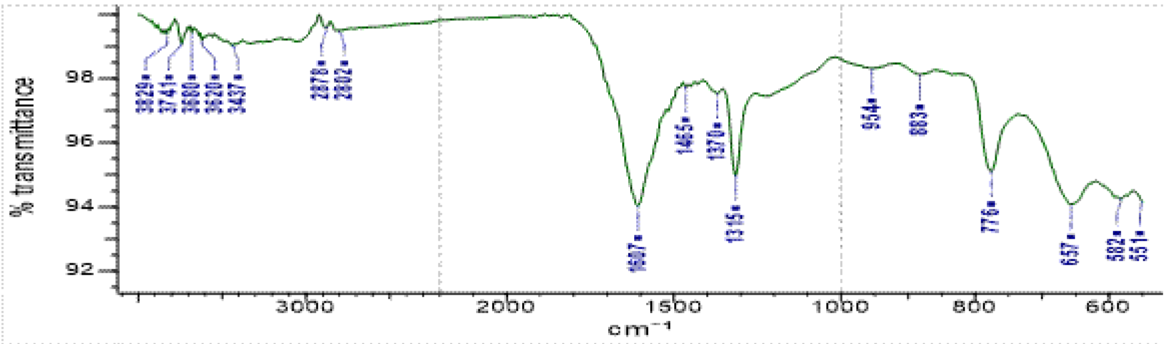

Figure 3: Fourier Transform Infrared (FTIR) spectrum of banana stalks pyrolyzed at temperature 400°C (Biochar 400°C)

Figure 4 shows the identified surface functional groups were the O-H functional group at 3217cm^{-1}, a nitro NO2 at 1565 cm^{-1}, a C-O stretching group at 1221 cm^{-1} and a peak at 1408 cm^{-1} which could be attributed to S=O stretching sulfate/sulfonyl chloride or O-H bending alcohol or carboxylic acid group. A band shift for the C-O group from 1016 cm^{-1} before pyrolysis to 1221 cm^{-1} after pyrolysis, carboxylic O-H group from 3294 cm^{-1} before pyrolysis to 3217 cm^{-1} after pyrolysis, the O-H bending from 1427 cm^{-1} before pyrolysis to 1408 cm^{-1} after pyrolysis, was observed on biochar 500°C. The presence of O-H, C-H, C=C functional groups in biochar 500°C was reported by Dos Santos et al. [31].

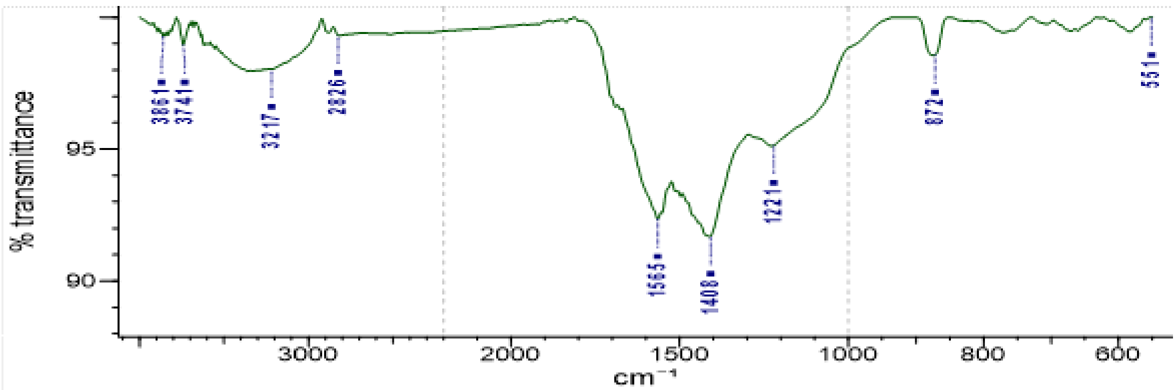

Figure 4: Fourier Transform Infrared (FTIR) spectrum of banana leaf petioles pyrolyzed at temperature 500°C (Biochar 500°C)

The above observations showed that after pyrolysis of the banana leaf petiole stalks, the identified hydroxyl O-H stretching vibrations and the C-O stretching vibrations were attenuated. This indicates that most of the O2- containing functional groups such as polysaccharides diminished after pyrolysis

[11, 35]. The functional group C-O which was pronounced in the raw banana leaf petioles FTIR spectrum was noted to have significantly reduced in intensity at biochar 300°C and was missing in both biochar 400°C and 500°C. This change could be attributed to the loss of C-O or C-OH functional groups as a result of dehydration and rearrangement of molecules at high pyrolytic temperatures [33, 36]. Pyrolysis therefore can lead to alternation of carbon to oxygen, hydrogen to carbon and carbon to nitrogen ratios and may modify functional groups leading to instances such as increase in aromatic C=C or a decrease in O-H and C-H [29] a case observed on biochar 300°C and biochar 400°C in this study.

Conclusion

The banana leaf petiole powder and resultant biochar prepared at different pyrolytic temperatures showed the presence of hydroxyl and carboxyl surface functional groups. The presence of these surface moieties is related to the ability of the material to adsorb metals and pollutants, and thus, banana leaf petiole powder and its biochar can be considered as a promising adsorbent.

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References

1. S. Wong, N. Ngadi, I. M. Inuwa, O. Hassan, Recent advances in applications of activated carbon from biowaste for wastewater treatment: a short review, *Journal of Cleaner Production*, 175 (2018): 361-375. https://doi.org/10.1016/j.jclepro.2017.12.059
2. T. Ahmad, M. Danish, Prospects of banana waste utilization in wastewater treatment: A review, *Journal of Environmental Management*, 206 (2018) 330-348. https://doi.org/10.1016/j.jenvman.2017.10.061
3. M. Danish, T. Ahmad, A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application, *Renewable and Sustainable Energy Reviews*, 87 (2018): 1-21. https://doi.org/10.1016/j.rser.2018.02.003
4. M. Rafatullah, T. Ahmad, A. Ghazali, O. Sulaiman, M. Danish, R. Hashim, Oil palm biomass as a precursor of activated carbons: a review. *Critical reviews in environmental science and technology*, 43, (2013): 1117-1161. https://doi.org/10.1080/10934529.2011.627039
5. I. I. Salame, T. J. Bandosz, Role of surface chemistry in adsorption of phenol on activated carbons, *Journal of Colloid and Interface Science*, 264, no. 2 (2003): 307-312. https://doi.org/10.1016/S0021-9797(03)00420-X
6. M. Danish, R. Hashim, M. N. Ibrahim, O. Sulaiman, Effect of acidic activating agents on surface area and surface functional groups of activated carbons produced from Acacia mangium wood, *journal of Analytical and Applied Pyrolysis*, 104 (2013): 418-425. https://doi.org/10.1016/j.jaap.2013.06.003
7. M. Danish, T. Ahmad, R. Hashim, N. Said, M. N. Akhtar, J. M. Saleh, O. Sulaiman, Comparison of surface properties of wood biomass activated carbons and their application against rhodamine B and methylene blue dye, *Surfaces and Interfaces*, 11 (2018): 1-13. https://doi.org/10.1016/j.surfin.2018.02.001
8. H. P. Boehm, Chemical identification of surface groups, In *Advances in catalysis*, vol. 16, pp. 179-274. Academic Press, (1966). https://doi.org/10.1016/S0360-0564(08)60354-5
9. B. R. Puri, Surface complexes on carbons, *Chemistry and physics of carbon*, 6 (1970): 191-282.
10. B. R. Puri, P. L. Walker, Chemistry and physics of carbon, Marcel Dekker, New York, (1970) 191-282.

11. S. M. Shaheen, N. K. Niazi, N. E. E Hassan, I. Bibi, H. Wang, D. C. W. Tsang, Y. S. Ok, N. Bolan, J. Rinklebe, Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review, *International Materials Reviews*, 64, no. 4 (2019): 216-247. https://doi.org/10.1080/09506608.2018.1473096
12. M. Ahmad, A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S. S. Lee, Y. S. Ok, Biochar as a sorbent for contaminant management in soil and water: a review, *Chemosphere*, 99 (2014): 19-33. https://doi.org/10.1016/j.chemosphere.2013.10.071
13. J. J. Manyà, Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs, *Environmental Science & technology*, 46, no. 15 (2012): 7939-7954. https://pubs.acs.org/doi/abs/10.1021/es301029g
14. S. Nanda, A. K. Dalai, F. Berruti, J. A. Kozinski, Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials, *Waste and Biomass Valorization*, 7, no. 2 (2016): 201-235.https://link.springer.com/article/10.1007/s12649-015-9459-z
15. J. P. Kearns, L. S. Wellborn, R. S. Summers, D. R. U. Knappe, 2, 4-D adsorption to biochars: Effect of preparation conditions on equilibrium adsorption capacity and comparison with commercial activated carbon literature data, *Water Research*, 62 (2014): 20-28. https://doi.org/10.1016/j.watres.2014.05.023
16. D. Rehrah, R. R. Bansode, O. Hassan, M. Ahmedna, Physico-chemical characterization of biochars from solid municipal waste for use in soil amendment, *Journal of analytical and applied pyrolysis*, 118 (2016): 42-53. https://doi.org/10.1016/j.jaap.2015.12.022
17. Y. Han, A. A. Boateng, P. X. Qi, I. M. Lima, J. Chang, Heavy metal and phenol adsorptive properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties, *Journal of Environmental Management*, 118 (2013): 196-204. https://doi.org/10.1016/j.jenvman.2013.01.001
18. F. Ronsse, S. V. Hecke, D. Dickinson, W. Prins, Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions, *Gcb Bioenergy*, 5, no. 2 (2013): 104-115. https://doi.org/10.1111/gcbb.12018
19. E. F. Zama, Y. G. Zhu, B. J. Reid, G. X. Sun, The role of biochar properties in influencing the sorption and desorption of Pb (II), Cd (II) and As (III) in aqueous solution, *Journal of Cleaner Production*, 148 (2017): 127-136. https://doi.org/10.1016/j.jclepro.2017.01.125
20. S. F. Vaughn, J. A. Kenar, F. J. Eller, B. R. Moser, M. A. Jackson, S. C. Peterson, Physical and chemical characterization of biochars produced from coppiced wood of thirteen tree species for use in horticultural substrates, *Industrial Crops and Products*, 66 (2015) 44-51. https://doi.org/10.1016/j.indcrop.2014.12.026
21. T. Ahmad, M. Danish, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim, M. N. M. Ibrahim, The use of date palm as a potential adsorbent for wastewater treatment: a review, Environmental *Science and Pollution Research*, 19, no. 5 (2012) 1464-1484. https://link.springer.com/article/10.1007/s11356-011-0709-8
22. N. Abdullah, F. Sulaiman, R. M. Taib, Characterization of banana (Musa spp.) plantation wastes as a potential renewable energy source, In *AIP Conference Proceedings*, 1528(1) (2013) 325-330. https://doi.org/10.1063/1.4803618
23. N. Abdullah, F. Sulaiman, R. M. Taib, Characterization of banana (Musa spp.) plantation wastes as a potential renewable energy source, In *AIP Conference Proceedings*, 1528(1) (2013) 325-330. https://doi.org/10.1063/1.4803618
24. K. S. Low, C. K. Lee, A. C. Leo, Removal of metals from electroplating wastes using banana pith, *Bioresource Technology*, 51(2-3) (1995) 227-231. https://doi.org/10.1016/0960-8524(94)00123-I
25. J. Anwar, U. Shafique, M. Salman, A. Dar, S. Anwar, Removal of Pb (II) and Cd (II) from water by adsorption on peels of banana, *Bioresource technology*, 101(6) (2010) 1752-1755. https://doi.org/10.1016/j.biortech.2009.10.021

26. J. R. Memon, S. Q. Memon, M. I. Bhanger, A. E. Turki, K. R. Hallam, G. C. Allen, Banana peel: a green and economical sorbent for the selective removal of Cr (VI) from industrial wastewater, *Colloids and surfaces B: Biointerfaces*, 70, no. 2 (2009): 232-237. https://doi.org/10.1016/j.colsurfb.2008.12.032
27. Z. A. Ghani, M. S. Yusoff, N. Q. Zaman, M. F. M. A. Zamri, J. Andas, Optimization of preparation conditions for activated carbon from banana pseudo-stem using response surface methodology on removal of color and COD from landfill leachate, *Waste Management*, 62 (2017): 177-187. https://doi.org/10.1016/j.wasman.2017.02.026
28. A.A. Karim, M. Kumar, S. Mohapatra, C. R. Panda, A. Singh, Banana peduncle biochar: characteristics and adsorption of hexavalent chromium from aqueous solution, International *Research Journal of Pure and Applied Chemistry*, 7(1) (2015) 1-10. https://doi.org/10.9734/IRJPAC/2015/16163
29. F. M. Ferraz, Q. Yuan, Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon, *Sustainable Materials and Technologies*, 23 (2020) e00141. https://doi.org/10.1016/j.susmat.2019.e00141
30. J. J. Zhao, X. J. Shen, X. Domene, J. M. Alcañiz, X. Liao, C. Palet, Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions, *Scientific Reports*, 9, no. 1 (2019) 1-12. https://www.nature.com/articles/s41598-019-46234-4
31. D. D. S. Dias, F. A. Faria, L. Mattiolli, M. V. Capela, J. M. V. Capela, M. S. Crespi, C. A. Ribeiro, Moisture sorption of biochar from banana pseudostem fibers according to the pyrolysis temperature, *Journal of Thermal Analysis and Calorimetry*, 138, no. 5 (2019) 3825-3832. https://link.springer.com/article/10.1007/s10973-019-08141-8
32. B. DeMessie, E. S. Demessie, G. A. Sorial, Cleaning water contaminated with heavy metal ions using pyrolyzed biochar adsorbents, *Separation Science and Technology*, 50, no. 16 (2015) 2448-2457. https://doi.org/10.1080/01496395.2015.1064134
33. M. D. Y. Milani, D.S. Samarawickrama, G. P. C. A Dharmasiri, I. R. M. Kottegoda, Study the structure, morphology, and thermal behavior of banana fiber and its charcoal derivative from selected banana varieties, *Journal of Natural Fibers*, 13, no. 3 (2016) 332-342. https://doi.org/10.1080/15440478.2015.1029195
34. H. Li, X. Dong, E. B. da Silva, L. M. de Oliveira, Y. Chen, L. Q. Ma, Mechanisms of metal sorption by biochars: biochar characteristics and modifications, *Chemosphere*, 178 (2017) 466-478. https://doi.org/10.1016/j.chemosphere.2017.03.072
35. S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M. H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, *Journal of environmental quality*, 41, no. 4 (2012) 990-1000. https://doi:10.2134/jeq2011.0070
36. W. Ding, X. Dong, I. M. Ime, B. Gao, L. Q. Ma, Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars, *Chemosphere*, 105 (2014) 68-74. https://doi.org/10.1016/j.chemosphere.2013.12.042

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