COMPARISON STUDY OF METAL REMOVAL EFFICIENCY FOR COMMERCIAL ACTIVATED CARBON AND BIOCHAR OBTAINED FROM BANANA PEELS

Mihai NEGROIU[11], Andreea A. ȚURCANU[1*], Ecaterina MATEI[1], Maria RÂPĂ[1], Andra M. PREDESCU[1], Cristian PANTILIMON[1], George COMAN[1], Cristina I. COVALIU[1] and Cristian PREDESCU[1]

An efficient and economical method used for the removal of heavy metals, organic pollutants and dyes from polluted waters is adsorption. The aim of this study was to develop a biochar from waste banana peels with improved properties and efficiency in the removal of heavy metals from water samples. The material was characterized by means of SEM and FTIR. Qualitative batch experiments were performed using Atomic Absorption Spectroscopy (AAS) and the results obtained were compared to those obtained when using a commercial activated carbon.

Keywords: biochar, activated carbon, heavy metal removal

1. Introduction

Due to the rapid industrial development around the world, a variety of toxic waste materials are constantly released into the aquatic environment, which is why one of the most concerning environmental problems of today is the pollution of waters with heavy metal ions [1,2]. Heavy metals are toxic at certain levels, tend not to be biodegradable and are bioaccumulated in the environment, and when in constant contact with living organisms they have serious effects on health [3]. There are many techniques used in this direction, like adsorption advanced oxidation, ion-exchange, membrane filtration, photo-catalysis, nanofiltration, irradiation, and precipitation [4-6]. Unfortunately, most of these methods are complicated, expensive, require qualified personnel and have only low efficiencies in removing pollutants from the waters, thus making adsorption the most efficient and economical method for the removal of heavy metals, organic pollutants and dyes from polluted waters [7].

A variety of materials have been used, such as activated carbon [8], graphene [9,10], silica [11], biopolymers [26] . Activated carbon from renewable sources such as biomass waste is an eco-friendly and inexpensive adsorbent for removing heavy metals from water. Efficient biosorbents were tested, such as

---

[1] Faculty of Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, *Corresponding author: e-mail: andreea.turcanu90@yahoo.com

peanut shells, rice husks, banana peels, orange peels, coconut shells, potato peels, corn cobs, corn leaves, microbial biomass, cocoa beans, waste palm [12,13].

Banana peel waste is of particular interest because bananas are widely grown in different countries and consumed worldwide (the second largest fruit crop in the world), so banana peel waste is available, underused and is very efficient as a biosorbent [14]. According to Shah et al [15] a total of 220t of banana waste comes from only one hectare of banana crop, thus making it a perfect material for processing into value added products. Banana peels contain a variety of chemicals that can be extracted and isolated, such as antibacterial compounds (malic acid, ß-sitosterol, 12-hydroxystrearic acid), proteins, lipids, fibers and many essential minerals (calcium, iron, manganese, potassium, sodium) [16]. Because many complex heteropolysaccharides are found in the chemical structure of the banana peels, many carboxyl groups are found, that are responsible for metal ions from aqueous solutions to bind to the structure, thus making banana peels a good precursor for developing bio-sorbents for heavy metal removal.

The aim of the present paper was to develop a biochar from waste banana peels with improved properties and efficiency in the removal of heavy metals from wastewaters.

2. Methods and experiments

Chemicals and reagents

To prepare the banana peel biochar (BPB) the next reagents and precursors were used: Sodium hydroxide, reagent grade, ≥98%, pellets (anhydrous), banana peels to obtained the biochar, commercial activated charcoal (CA) (Moisture Content < 12 %, Water Soluble Substance < 0.50 %, Acid Soluble Substance < 200 ppm).

Preparation of the BPB

A modified method proposed by Yang et al. [17] was used to obtain BPB, the banana peels were charred and then activated, using NaOH instead of KOH. Banana peel contains mainly hemicellulose, lignin, pectin, free sugars, proteins and crystalline cellulose. In the pyrolysis process, the organic components decompose, with the release of a certain amount of small molecule gases, such as CH_4 and CO, and the rest of the carbon is crosslinked with other aromatic structures. To obtain the BPB, banana peels were dried in an oven at 140°C for 4 hours. The banana peels resulted were then subjected to two-stage pyrolysis in a calcination furnace. In the first stage of pyrolysis at a temperature of 700°C, for 1h, and a heating rate of 3°C/min, amorphous coal was obtained. In order to remove partially charred intermediate compounds, the product was treated with NaOH at a weight ratio of 1:3, followed by a heating process at 800°C for 1 h.

The activation process, with NaOH, in a ratio of 3:1, was carried out according to the following chemical reactions:

$$6NaOH + 2C \longrightarrow 2Na + 3H_2 + 2Na_2CO_3 \quad (1)$$

$$Na_2CO_3 \longrightarrow Na_2O + CO_2 \quad (2)$$

$$CO_2 + C \longrightarrow 2CO \quad (3)$$

$$Na_2CO_3 + 2C \longrightarrow 2Na + 3CO \quad (4)$$

$$C + Na_2O \longrightarrow 2Na + CO \quad (5)$$

The BPB obtained was washed repeatedly with distilled water to remove the excess NaOH. This material was tested in qualitative adoption experiments to compare its efficiency with that of a commercia activated carbon in the removal of metal ions from water samples.

The structural and morphological properties of the BPB and the CA were determined using Scanning electron microscopy (SEM) coupled with EDS (QUANTA 450 FEG scanning electron microscope, equipped with a field emission gun and a 1.2 nm resolution X-ray energy dispersive spectrometer, with a resolution of 133 eV).

Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR), (Interspec 200-X Spectrophotometer, Interspectrum, Estonia) was used to characterize the BPB and the CA for comparison reasons.

Batch adsorption experiments - qualitative analysis of a multielement aqueous solution were performed by using a contrAA® 800D Atomic Absorption Spectrometry (AAS) System from Analytik Jena with acetylene flame.

3. Results and discussions

ATR-FTIR analysis

The ATR-FTIR analyses for the commercial CA and BPB are presented in figure 1 and the peak data is presented in Table 1. The spectrum for the commercial CA sample presents peaks for O–H, N–H, C–H, C=O, C=C, C–N, C–O and C–H vibrations on the surface [18] which provide sufficient surface functionality for pollutant interaction. The spectrum for the BPB sample presents a peak at 2920 cm^{-1} is attributed to the stretching vibration of CH bonds, probably originated from the decomposition of phenolic hydroxyls [19,20].

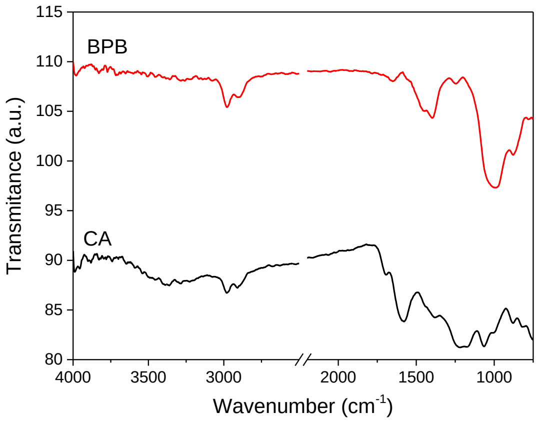


Fig. 1 ATR-FTIR analysis for commercial CA and BPB

The peaks at 1510 cm^{-1} and 1530 cm^{-1} present in the commercial CA spectrum are typical for stretching vibrations from C-H bonds [21]. These peaks were not observed for the BPB sample, this might be to the degradation during the heat treatment of the banana peels. The peaks at 1590 and 1693 cm^{-1} in the commercial CA sample are attributed to the highly conjugated C=O stretching or C–O stretching in carboxyl groups, respectively, and the peak at 1181 cm^{-1} is attributed C–O stretching of carboxylate and ether structures [22]. These peaks are not present in the BPB spectrum, due to the carbonization process. The peaks at 1065 cm^{-1} for commercial CA and at 1018 cm^{-1} for BPB are due to the aromatic C-H bond bending [19], indicating a rearrangement of the macromolecular aromatic molecules [20]. It can also be due to the stretching vibrations of C=O that originate from the partial oxidation of carbon by oxygen [21].

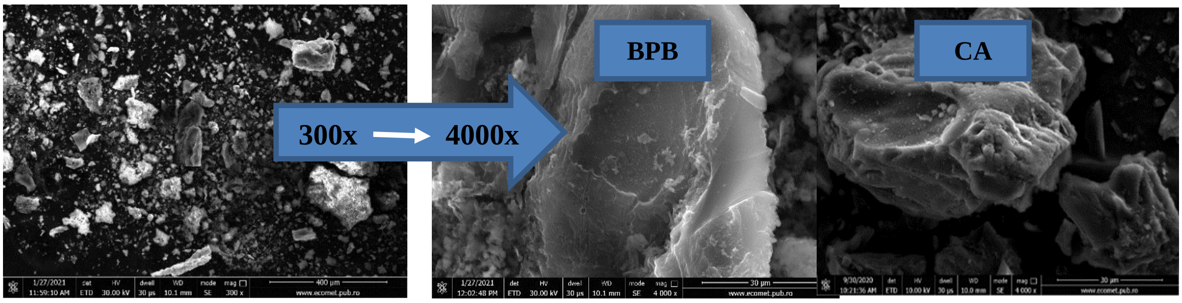
Table 1

Peak data for CA and BPB

Commercial CA		BPB	
Peak At	Assigned	Peak At	Assigned
1065	CH	1018	C-H
1181	C–O	1418 1682	C-O=C
1590	C-O=C		
1693		2909 2980	-CH
2909 2980	-CH		
3370	-OH		

SEM-EDS analysis

The morphological properties of the BPB sample were determined by SEM analysis. Figure 2 shows a porous surface (micro and macro pores), the presence of cracks and depressions, characteristics that favor adsorption.



(a) (b) (c)

Fig. 2 SEM analysis for BPB (a) and (b), commercial CA (c)

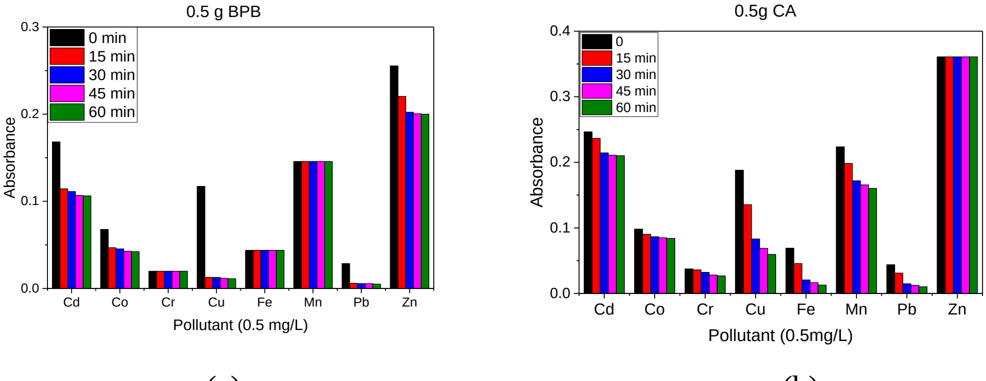
BPB exposed an agglomeration tendency of particles at magnification factor of 300 x (Figure 2 (a)), with detailed highlighting of the particle structure at 4000 x (Figure 2 (b)). As can be seen, the surfaces show much more homogeneity in the case of BPB, washing the carbonized sample of intermediate BPB with NaOH leading to the appearance of very fine, agglomerated particles by removing organic residues compared to the CA sample (Figure 2(c)).

The EDS analysis indicates the presence of the major elements C (57%) and O (36%), characteristic of the cellulosic components in the sample and a significant amount of K (approx. 4.89%), as indicated by the literature [16], and also being present in traces Cl (1.40%), Si and P below 1%.

Chemical Element	Mass weight [%]	Error [%]
C	57.04	6.65
O	36.32	11.36
Si	0.19	31.99
P	0.17	39.10
Cl	1.40	7.38
K	4.89	3.18

Batch adsorption tests

The commercial CA and BPB were tested for heavy metal removal efficiency by performing a batch experiment and AAS qualitative analysis. 0.5 g of material was put in contact with 100 ml multielement solution of 0.5 mg/L concentration. The metals studied were Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn. It can be observed from Figure 3 (a) that when using BPB in a period of 1 h, the absorbance for most metal ions slightly decreases, indicating a decrease in metal ion concentration in the water sample, excepting Mn, Fe and Cr. When commercial CA was used, a slow decrease in all metal ion concentrations can be observed in Figure 3 (b), thus indicating that BPB is a better absorbent than commercial CA.



(a) (b)

Fig. 3 Qualitative analysis on a multielement solution (concentration 0.5 mg/L) for commercial BPB (a) and CA (b)

The removal efficiencies evaluation for heavy metal ions from synthetic solution for the BPB and CA were based on qualitative analyses. Thus, the absorbance values before and after both materials contact were detected. It could be observed that the BPB material is more efficient than the commercial CA, especially Pb and Cu. For example, Cu exposed a removal efficiency over 90% beginning with 15 minutes and maintained the same after 60 minutes. For Pb, the maximum efficiency was at 79% at 15 minutes, increasing at 82% after 30 minutes and maintained at the same efficiency also at 60 minutes. For the others metal ions, the evolution has no significant impact, with 37% for Co and Cd, and about 20% for Zn. This tendency is due to the low hydration radii for Pb (4,01 Å) and Cu (4,19 Å), these ions having a higher rate of adsorption compared with the others ions: Co (4,23 Å) < Cd (4,26 Å) ~ Fe II (4,28 Å) < Zn (4,3 Å) < Cr III (4,61 Å) [24,25,26]. From the variation of the absorbances there is a decrease of the values in the order: Pb <Co <Zn <Cd <Cu. This decrease is correlated with the efficiency calculation formula leading to the conclusion that the affinity of the BPB material is high only for Cu and Pb ions respectively, compared to other competitive ions.

6. Conclusions

A comparison study was made to observe the efficiency of heavy metals removal from water samples for BPB and CA. The materials tested were characterized by using ATR-FTIR and morphology using SEM-EDS. It was observed that the BPB presented a higher number of functional groups than the commercial CA and also a more porous and rougher surface, all characteristics that indicate good adsorption properties. After a batch qualitative experiment, it was observed that the adsorption properties of the BPB are superior to those of the commercial CA, especially for Cu and Pb. Future adsorption tests will be made in order to establish adsorption mechanism and competitive ions behavior in real wastewaters.

Acknowledgments

This research was developed under Doctoral Studies Contract SD07/01.10.2018.

The FTIR analysis (on INTERSPEC 200-X Spectrophotometer) and atomic absorption spectrometry analysis (on ContrAA800D, Analytik Jena) was possible due to European Regional Development Fund through Competitiveness Operational Program 2014–2020, Priority axis 1, Project No. P_36_611, MySMIS code 107066, Innovative Technologies for Materials Quality Assurance in Health, Energy and Environmental - Center for Innovative Manufacturing Solutions of Smart Biomaterials and Biomedical Surfaces-INOVABIOMED

REFERENCES

1. K.G Akpomie, J. Conradie, “Banana peel as a biosorbent for the decontamination of water pollutants. A review.” Environmental Chemistry Letters **2020**, 18, pp. 1085-1112.
2. D.Li, M.-Q. Wang, C. Lee, “The waste treatment and recycling efficiency of industrial waste processing based on two-stage data envelopment analysis with undesirable inputs.” Journal of Cleaner Production **2020**, pp. 242.
3. R. Jain, D. Dominic, N. Jordan, E.R. Rene, S. Weiss, E.D. van Hullebusch, R. Huebner, P.N.L. Lens, “Higher Cd adsorption on biogenic elemental selenium nanoparticles.” Environmental Chemistry Letters **2016**, 14, pp. 381-386.
4. K.G. Akpomie, F.A. Dawodu, K.O. Adebowale, “Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential.” Alexandria Engineering Journal **2015**, 54, pp. 757-767.
5. P. Abbasi, B. McKevitt, D.B. Dreisinger, “The kinetics of nickel recovery from ferrous containing solutions using an Iminodiacetic acid ion exchange resin.” Hydrometallurgy **2018**, 175, pp. 333-339.
6. M.A. Barakat, “New trends in removing heavy metals from industrial wastewater.” Arabian Journal of Chemistry **2011**, 4, pp. 361-377.
7. G.A. El-Din, A.A. Amer, G. Malsh, M. Hussein, “Study on the use of banana peels for oil spill removal.” Alexandria Engineering Journal **2018**, 57, pp. 2061-2068.
8. L. Zhou, Q. Yu, Y. Cui, F. Xie, W. Li, Y. Li, M. Chen, “Adsorption properties of activated carbon from reed with a high adsorption capacity.” Ecological Engineering **2017**, 102, pp. 443-450.
9. I. Ali, A.A. Basheer, X.Y. Mbianda, A. Burakov, E. Galunin, I. Burakova, E. Mkrtchyan, A. Tkachev, V. Grachev, “Graphene based adsorbents for remediation of noxious pollutants from wastewater.” Environment International **2019**, 127, pp. 160-180.
10. I. Ali, A.E. Burakov, A.V. Melezhik, A.V. Babkin, I.V. Burakova, E.A. Neskomornaya, E.V. Galunin, A.G. Tkachev, D.V. Kuznetsov, “Removal of Copper(II) and Zinc(II) Ions in Water on a

Newly Synthesized Polyhydroquinone/Graphene Nanocomposite Material: Kinetics, Thermodynamics and Mechanism.” Chemistryselect **2019**, 4, pp. 12708-12718.

11. K.G. Akpomie, C.F. Onyeabor, C.C. Ezeofor, J.U. Ani, S.I. Eze, “Natural aluminosilicate clay obtained from south-eastern Nigeria as potential sorbent for oil spill remediation.” Journal of African Earth Sciences **2019**, 155, pp. 118-123.
12. I. Anastopoulos, I. Pashalidis, A. Hosseini-Bandegharaei, D.A. Giannakoudakis, A. Robalds, M. Usman, L. Belen Escudero, Y. Zhou, J.C. Colmenares, A. Nunez-Delgado, “Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions.” Journal of Molecular Liquids **2019**, pp. 295.
13. S. Singh, V. Kumar, S. Datta, D.S. Dhanjal, K. Sharma, J. Samuel, J. Singh, “Current advancement and future prospect of biosorbents for bioremediation.” Science of the Total Environment **2020**, pp. 709.
14. B.S. Padam, H.S. Tin, F.Y. Chye, M.I. Abdullah, “Banana by-products: an under-utilized renewable food biomass with great potential.” Journal of Food Science and Technology-Mysore **2014**, 51, pp. 3527-3545.
15. M.P. Shah, G.V. Reddy, R. Banerjee, P.R. Babu, I.L. Kothari, “Microbial degradation of banana waste under solid state bioprocessing using two lignocellulolytic fungi (Phylosticta spp. MPS-001 and Aspergillus spp. MPS-002).” Process Biochemistry **2005**, 40, pp. 445-451.
16. B.A. Anhwange, T.J.U., T.D. Nyiaataher, “Chemical Composition of Musa sepientum (Banana) Peels.” Electronic Journal of Environmental, Agricultural and Food Chemistry, **2009**; 8, pp. 437-442.
17. K. Yang, Q. Gao, Y. Tan, W. Tian, W. Qian, L.C. Zhu, Yang, “Biomass-Derived Porous Carbon with Micropores and Small Mesopores for High-Performance Lithium-Sulfur Batteries.” Chemistry-a European Journal **2016**, 22, pp. 3239-3244.
18. A. Stavrinou, C.A. Aggelopoulos, C.D. Tsakiroglou, “Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: Adsorption kinetics and equilibrium isotherms as a tool.” Journal of Environmental Chemical Engineering **2018**, 6, pp. 6958-6970.
19. S.M.a.V. Udeye, “Characterization and Evaluation of Charcoal Briquettes Using Banana Peel and Banana Bunch Waste for Household Heating.” American Journal of Engineering and Applied Sciences, **2017**; 10, pp 353-365.
20. J. Cao, G. Xiao, X. Xu, D. Shen, B.Jin, “Study on carbonization of lignin by TG-FTIR and high-temperature carbonization reactor.” Fuel Processing Technology **2013**, 106, pp. 41-47.
21. K. Elyounssi, M. Halim, “An investigation on the texture and microstructure of carbonized charcoals produced by two-step pyrolysis.” Journal of Analytical and Applied Pyrolysis **2014**, 109, pp. 258-265.
22. J. Shu, S. Cheng, H. Xia, L. Zhang, J. C. Peng, Li, S. Zhang, “Copper loaded on activated carbon as an efficient adsorbent for removal of methylene blue.” Rsc Advances **2017**, 7, pp. 14395-14405.
23. A. Bashir, T. Manzoor, L. A. Malik, A. Qureashi, and A. H. Pandith, "Enhanced and selective adsorption of Zn (ii), Pb (ii), Cd (ii), and Hg (ii) ions by a dumbbell-and flower-shaped potato starch phosphate polymer: a combined experimental and DFT calculation study." ACS OMEGA **2020,** 7, pp. 4853-4867
24. J. Goel, K. Kadirvelu, C. Rajagopal, “Competitive sorption of Cu (II), Pb (II) and Hg (II) ions from aqueous solution using coconut shell-based activated carbon." Adsorption Science & Technology, **2004**, 22, pp. 257-273.
25. E. Nightingale Jr. Phenomenological theory of ion solvation. Effective radii of hydrated ions. The Journal of Physical Chemistry, **1959**, 63, pp.1381-1387.
26. B.R. Lee; K.H. Lee; E. Kang; D.S. Kim; S.H. Lee. Microfluidic wet spinning of chitosan-alginate microfibers and encapsulation of HepG2 cells in fibers. Biomicrofluidics **2011**, 5, pp. 9.