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Effectiveness of Raw versus Activated Coconut Shells for Removing Arsenic and Mercury from Water

Ismaila Emahi[1], Patrick O. Sakyi[1], Pennante Bruce-Vanderpuije[2], & Abdul Rashid Issifu[1]

[1] Department of Chemical Sciences, University of Energy and Natural Resources, Sunyani, Ghana

[2] CSIR Water Research Institute, P. O. Box AH 38, Achimota, Accra, Ghana

Correspondence: Ismaila Emahi, Department of Chemical Sciences, University of Energy and Natural Resources, P. O. Box 214, Sunyani, Ghana. Tel: 233-20-924-7259. E-mail: ismaila.emahi@uenr.edu.gh

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Abstract

Relatively inexpensive biosorbents, made from coconut shell, were explored as alternatives to high-quality activated carbon for use in small-scale, wastewater treatment in developing economies. Simple charring and activation procedures were followed to produce $CaCl_2$-activated coconut shell charcoal and its effectiveness was compared with raw coconut shell powder for removal of mercury (Hg) and arsenic (As) from contaminated water. From atomic absorption spectroscopy analyses, the removal efficiency of As and Hg with the use of activated charcoal were 67% (vs 65% for the raw form), and 53% (vs 49% for the raw form), respectively, from their corresponding "artificially"-contaminated wastewater. These results suggest that despite the slightly improved removal efficiencies recorded for activated coconut shells, the raw version could equally be used in treating wastewater towards the removal of the toxic metals- As and Hg. In order to understand the chemistry of the adsorption processes, FT-IR spectroscopy was employed to study similarities and differences in chemical compositions of the raw versus activated coconut shells before and after the biofiltration processes. To further investigate the effect of this biofiltration process on the overall quality of water, the physicochemical parameters (pH, conductivity, colour, turbidity, TDS and TSS) were measured on river water samples, pre-treated with the biosorbents. For both the raw and activated coconut shell, there was general improvement although the conductivity of the water treated with the activated version was slightly elevated, likely due to leaching of $CaCl_2$ that was used for activation.

Keywords: Activated Charcoal, Arsenic, Biofiltration, Biosorbent, Mercury, Raw Coconut Shell Powder

1. Introduction

Activated charcoal or carbon is widely used across the globe as an effective adsorbent for treating wastewater of various contaminants, including heavy metals (Martin, 1980; Mohammad-khah & Ansari, 2009). Activated carbon produced from coconut shells is considerd as one of the best grades of activated carbons (Mohammad-khah & Ansari, 2009). The superior property of these activated carbon materials is due to their ability to provide high adsorption capacity resulting from their large surface area and high pore volumes. Despite these benefits, the process of producing high-quality activated charcoal, which involves controlled pyrolysis at very high temperatures makes it an expensive and unsafe process to produce for small-scale use in developing countries. Several researchers have, therefore, attempted to produce relatively inexpensive chemically activated carbon alternatives, using a variety of agricultural waste materials (Dias et al., 2007). Although the quality of activated carbon produced is largely influenced by the source of the carbon material used, recent works involving the use of agricultural waste, in successfully removing pollutants from water, suggests the practicality of this approach. For example, Cobb et al. (2012) produced low-tech activated charcoal from coconut shells using calcium chloride ($CaCl_2$), zinc chloride ($ZnCl_2$), and common salt [sodium chloride (NaCl)] as chemical activating agents, instead of high steam activation. They reported up to 70% removal efficiency for atrazine in water (Cobb et al., 2012). Similarly, in the work by Ocreto et al. (2019), activated carbon chemically modified with phosphoric acid (H_3PO_4) from bamboo was reported to have excellent removal efficiencies for the heavy metals: copper, cadmium and lead in water (Ocreto et al., 2019). For extensive review of other low-tech chemically-activated carbon from readily available agricultural waste products, the reader is referred to the reviews by Dias et al. (2019) and Yahya et al. (2015).

The use of chemical activating agents, has no doubt, simplified the carbon-activation process and offered relatively inexpenive options to the steam activation method. However, there is still a possibility and need to continuously explore relatively inexpensive, yet effective alternatives. A critical review of the literature on the chemical composition of coconut shell reveals that it is primarily composed of hemicellulose, cellulose, and lignin (Hasanah et al., 2012; Iqbaldin et al., 2013; Leman et al., 2016; Liyanage & Pieris, 2015). All these compounds contain the key functional groups - carboxyl (-COOH) and hydroxyl (-OH) groups, which can be very important for metal adsorption when present. The aim of this work was therefore to prepare low-cost $CaCl_2$-activated coconut shell powder, and to compare its effectiveness to raw (chemically-unmodified) form towards the removal of the toxic metals: mercury (Hg) and arsenic (As) in water. Arsenic and Hg were selected for this key study as they are two of the most toxic heavy metals that are mostly detected in drinking water sources (Kim et al., 2016; Phan et al., 2010). Results of this work will therefore provide future research opportunities to explore low-tech, low-cost, biomass materials for removing toxic contamaminants from the environment.

2. Method

2.1 Reagents and Solutions

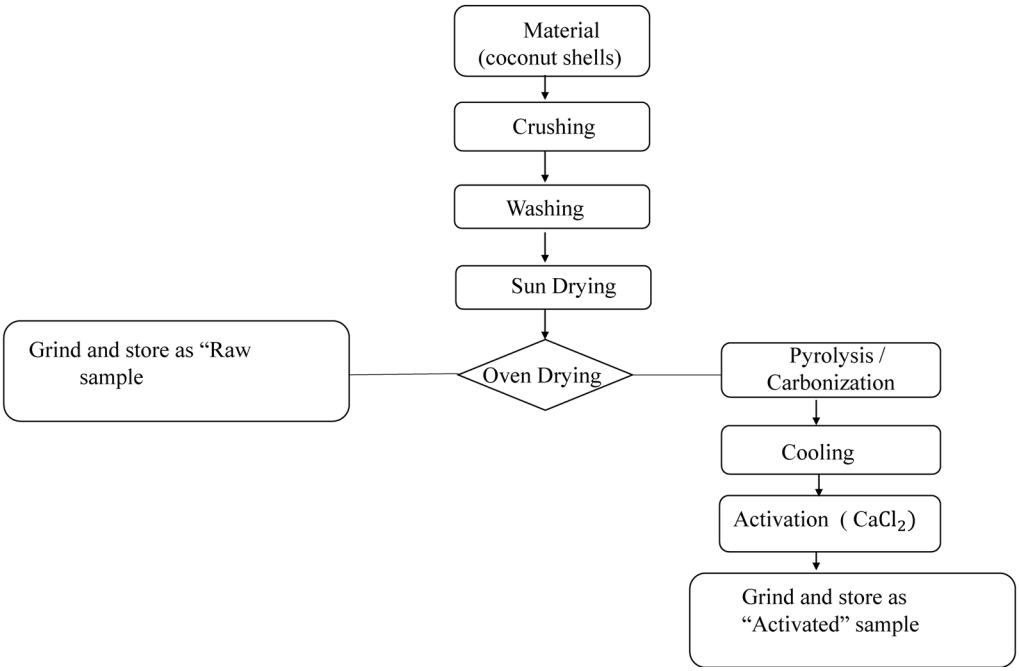
All reagents used were of analytical grade standard. Arsenous oxide (As_2O_3) and Hg (II) sulphate ($HgSO_4$) were purchased from BDH Laboratory, England, and used without further purification. Solutions of Arsenic (As^{2+}), and Mercury (Hg^{2+}) metal ions were prepared through appropriate dilutions from 1000 ppm stocks. The solutions were prepared with deionized water and supplemented with 10% (v/v) nitric acid (HNO_3) to facilitate complete dissolution and to stabilize the metal ions in solution.

2.2 Biomass Material

Freshly-emptied coconut shells were collected directly from a street coconut vendor near the campus of University of Energy and Natural Resources in Sunyani, Ghana. The shells were thoroughly washed with tap water followed by distilled water afterwhich it was sun dried for 45 min. The shells were crushed into smaller pieces and dried in the oven at 105^{o}C for 24 h.

2.3 Preparation of Coconut Shell Adsorbent

The oven-dried coconut shells were divided into two, and processed into raw and activated forms as outlined in Scheme 1, and further described in sections 2.3.1 and 2.3.2 below.



Scheme 1. Summary of steps in preparation of the raw and activated coconut shell samples

2.3.1 Preparation of Raw Powdered Coconut Shell Adsorbent

Half of the dried, crushed coconut shells were ground to fine powder using a kitchen-type mechanical blender. The powdered sample was then transferred into zip-lock bags and stored airtight at 4^{o}C until ready for use.

2.3.2 Preparation of Activated (Coconut Shell) Charcoal Adsorbent

The remaining half of the dried coconut shells were charred using the procedure described by Cobb et al. (2012), with slight modifications (Cobb et al., 2012). Specifically, the combustion process lasted for about 4 h, afterwhich the resulting charcoal was allowed to cool and washed with deionized water to remove ash and other unwanted debris. The charcoal was further pulverized using a kitchen-type blender. The "clean", powdered charcoal was then activated by soaking in 25% (v/v) solution of ($CaCl_2$) for 18 h before draining the $CaCl_2$. The $CaCl_2$-activated charcoal was further rinsed with deionized water and spread on a clean tray to further dry at 110^{o}C in the oven for 3h. The dried final product was transferred into a zip-lock bag and stored at 4^{o}C until use.

2.4 Biofiltration Experiments

The ability of each biosorbent (raw coconut shell powder and activated coconut shell charcoal) to remove As and Hg from wastewater, were carried out through biofiltration experiments using 100ppm solutions of As and Hg in separate experiments. This solution is hereby referred to as artificially contaminated water since it was made to purposively contain the said toxic metals. In each experiment, 0.1g of the biosorbent was added to 20ml of the metal solution in a pre-treated flask. The flask was then incubated at 40^{o}C for 1 h with gentle agitation. Filter paper (Whatman No. 1) and funnel were used to separate the solid from the solution. The filtrates were then analyzed using the atomic absorption spectrophotometer (Analytik Jena AAS Model AA400p instrument, Germany). Equation 1 was used to evaluate the extent of heavy metal removal or adsorption by the biosorbents.

$$\% \text{ Removal} = [(C_a - C_b)/C_a] \times 100 \quad (1)$$

Where C_a is the initial metal ion concentration, and C_b is the concentration of metal ion remaining after biofiltration.

2.5 IR Characterization

To characterize the functional groups present on the biosorbents, and the roles played in the adsorption process (raw coconut shell powder and activated coconut shell charcoal), dried, powdered samples of each biosorbent before and after biofiltration were analyzed via Fourier-Transform Infra Red spectroscopy (FT-IR).

2.6 Study of the Biosorbents to Improve Water Quality

The ability of the biosorbents to improve the physicochemical quality of water was also tested on water samples collected from the Kwabrafo River in Obuasi, a well-known mining town in Ghana. The Kwabrafo River is reportedly contaminated with solid waste from the Obuasi Township, in addition to possible heavy metal pollution from sorrrounding illegal mining activities (CHRAJ, 2008). The biofiltration process, described in section 2.4 above, was repeated using river water sample as the "contaminated" water. After biofiltration, the filtrate was analyzed for the physicochemical parameters pH, electrical conductivity, turbidity, colour, total dissolved solids and total suspended solids. The Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured using E-1 portable EC / TDS meter (Newly Digital, China). The pH of the sample was measured with a pH meter (pH901, Bante Instruments, China). The remaining parameters were analyzed using standard protocols.

3. Results and Discussions

3.1 Removal Efficiencies

Using equation 1 above, the results of the AAS experiments were analyzed to determine the removal efficiency of the activated charcoal in adsorbing each metal compared with the raw form. The results are summarized in Figure 1. As clearly depicted by the figure, the activated charcoal was able to remove approximately 67% and 53% of the initial As and Hg, respectively, from their corresponding artificially-contaminated waste water. The performance of the raw form was statistically not different from the activated form. The raw form was able to remove approximately 65% and 49%, respectively, for As and Hg. This may likely indicate the presence of cellulose, hemicellulose and lignin, which are chiefly responsible for metal adsorption in the case of both the activated and raw forms. The fact that both biosorbents showed slightly greater ability to remove As than Hg, is consistent with the results of FT-IR studies discussed in section 3.2 below. It is also not surprising that the activated charcoal did not markedly outperform the raw (chemically-unmodified) coconut powder form in removing the toxic metals from water. Pyrolysis of carbon materials during activated charcoal formation causes loss of the cellulose,

hemicellulose and lignin present on the biomaterial, and the introduction of acidic/polar oxygen functional groups (Sencan & Kilic, 2015), which become the "new" sites for adsorbing or removing contaminants. Various oxidizing post treatments are carried out to stimulate new functional groups that can adsorb a variety of contaminants (Sencan & Kilic, 2015). The use of chemicals such as $CaCl_2$ during the chemical activation process, renders the surface of the activated charcoal to contain more porous structures, and net large surface area to facililate the adsorption of contaminants (Girgis & El-Hendawy, 2002; Yin et al., 2007). Losing all the celluloses, hemicelluloses and lignins, however, may only be achieved at high temperature pyrolosis (ca 1000^{o}C), which was not achieavable in this study that sought to employ low-tech, low-cost materials for easy adoption by developing economies. It is therefore highly probable that charring of the coconut shells was incomplete, rendering most of the celluloses, hemicelluloses and lignins still available for interacting with the metal ions, as is likely the case for the raw coconut shell powder samples. The slightly higher percent removal values recorded for the activated charcoal over the raw samples, is a strong indication that thoroughly charred and chemically activated charcoal presents superior properties of removing contaminants from aqueous solutions.

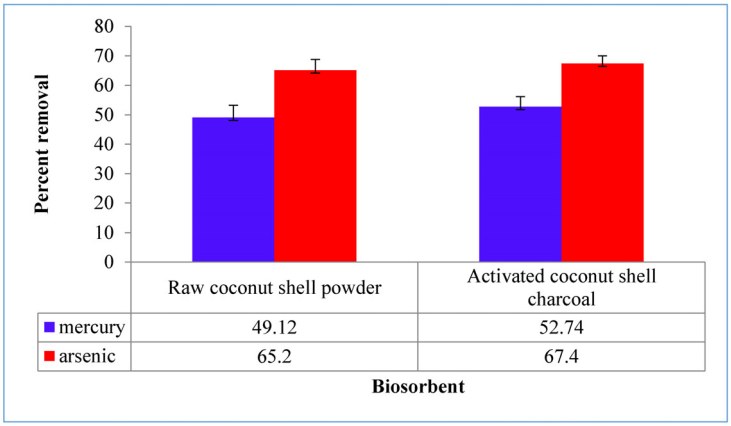


Figure 1. Evaluation of the performance of the raw coconut shell powder versus activated coconut shell charcoal in the removal of arsenic and mercury from 100 ppm artificially contaminated solutions

3.2 Characterization via FT-IR Spectroscopy

3.2.1 Comparison of the Chemistry of Raw Versus Activated Coconut Shell Powder

The FT-IR spectra of the raw and activated coconut were carried out to determine the functional groups capable of adsorbing the heavy metals- Hg and As. Generally, agricultural residues are made up of similar functional groups including phenol, aldehydes, carboxyl groups, ether, alcohols and ketones which bind to pollutants (Pagnanelli et al., 2003). A broad and strong band at 3200 – 3500cm^{-1} in the FT-IR spectrum of the activated coconut shell powder, as seen in Figure 2, is due to the O-H stretching vibrations of either phenol, alcohols or carboxylic acids. This same band was also observed for the raw coconut shell powder, though it was found to be weak with a reduced intensity. Meanwhile, the absorption peak at 2900cm^{-1} for the raw coconut, which is due to C-H stretching vibrations was completely absent in the FT-IR of the activated coconut shell. The peak at 1719cm^{-1} for the raw coconut is due to the presence of C=O; this is expected from the lignin network (Chang et al., 2012). This peak was absent in the activated coconut shell possibly because of its volatility (Bakti & Gareso, 2018). The peak around 1600cm^{-1} in both spectra is due to C=C vibration of aromatic rings. The strong peak around 1033cm^{-1} of raw coconut is due to the presence of C-O stretching vibration of alcohol or ether. This peak was absent in activated coconut because it is also volatile, hence lost during activation process.

3.2.2 Comparison of the Chemistry of Activated Charcoal vs Raw Coconut Shell Powder before and after Biofiltration

The FT-IR spectra in Figure 3(A) show the chemical characteristics of the activated coconut charcoal before and after the biofiltration with As and Hg; while Figure 3(B) gives the chemical characteristics of the raw coconut shell powder before and after biofiltration. The IR spectrum of the raw coconut shell powder was found to be similar to that of the activated charcoal after adsorption of Hg. The presence of a strong and broad band around 3200-3500cm^{-1} for the adsorption of Hg is due to the O-H stretching vibration. This peak was absent in the FT-IR

spectrum after the removal of As- suggesting a strong interaction between -OH group and the As metal ion. The peak at 1618cm^{-1}, which is due to C=C of the aromatic ring of the activated coconut shell, was found to be at a slightly higher wavenumber at 1625cm^{-1} and 1622cm^{-1} for the adsorption of Hg and As respectively. The transmittance observed was also reduced for the adsorption of the two metals. This is due to the use of the C=C in the metal-carbon interaction with the two metals. The peak at 1100cm^{-1}, which is due to C-O of either alcohol, alkanoic acid or ether of the activated coconut shell, was found to be at a slightly higher wavenumber of 1154cm^{-1} and 1509cm^{-1} for the removal of Hg and As respectively. There was a reduced transmittance for the absorption of the two metals. This confirms the use of the C-O in adsorbing the two metals.

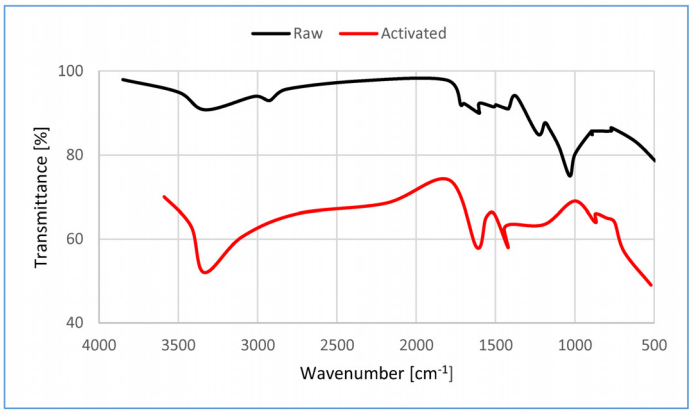


Figure 2. Comparison of the FT-IR spectra of $CaCl_2$-activated coconut shell charcoal and raw (uncharred, chemically-unmodified) coconut shell powder

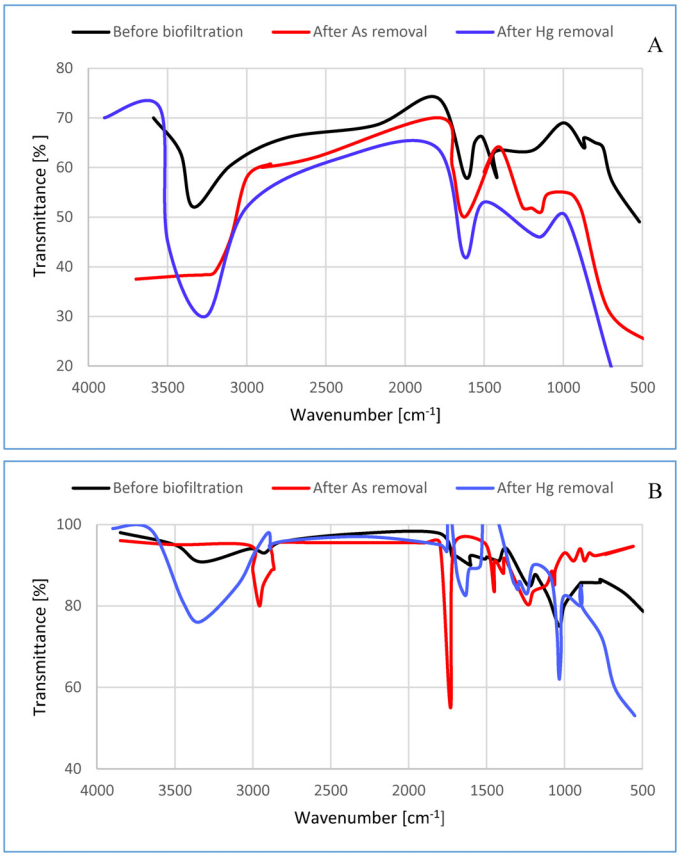


Figure 3. Comparison of the changes in FT-IR spectra before and after biofiltration of arsenic and mercury metal ions using A) $CaCl_2$-activated coconut shell charcoal; and B) raw (uncharred, chemically-unmodified) coconut shell powder

3.2.3 Similarities and Differences in the Chemical Characteristics of the Activated Charcoal vs Raw Coconut Shell Powder in Removing As and Hg

The FT-IR of both the raw and activated coconut shell powder, before and after the adsorption of Hg and As, gave useful information about the functional groups involved in the adsorption of the metals. There was no broad peak at 3200-3500cm^{-1} for As adsorption in both cases. It can therefore be confirmed that -OH group is strongly involved in adsorbing As. The broad band around 3343cm^{-1} observed after adsorption of Hg was due to the O-H stretching vibration. This peak was found to be strong and intense than the raw coconut shell before adsorption. This indicates that -OH group was involved in the adsorption of Hg as well. The C=O stretching vibration was observed at 1754cm^{-1} for Hg, and was found to be slightly higher than that observed for raw coconut shell as stated above. This peak was found to be strong and intense at 1731cm^{-1} after the adsorption of As. The presence of the claw-like peaks around 2800 to 2980cm^{-1} is due to O=C-H. This peak is prominent compared to FT-IR spectrum of the raw coconut shell powder, and implies that the O=C-H was also involved in the adsorption of As. The C=C of the aromatic ring, found to be at 1636cm^{-1} for the absorbance of Hg, was slightly higher than 1605cm^{-1} for the raw coconut shell powder. This same peak was observed at 1451cm^{-1} for the raw coconut shell after adsorbing As. The difference is due to the use of the double bond in metal-ion interactions. The peak at 1033 and 1160cm^{-1} are due to C-O stretching of the raw coconut shell powder in interacting with Hg and As respectively. The observed peak for Hg adsorption was found to be the same as that of the raw coconut shell powder. The peak observed for As was found to be strong, intense and higher than that observed for the raw coconut shell powder. This implies that the C-O was involved in adsorbing As (Lazim et al., 2015).

The above observations strongly suggest that both the raw and activated coconut shell powder possessed the key functional groups -COOH, -OH, C-O, C=C from aromatic groups, and C=O which were largely involved in the removal of As and Hg from the wastewater.

3.3 Analysis of Physicochemical Parameters on River Water Samples

Results of the physicochemical parameters tested on water samples collected from the Kwabrafo River are summarized in Table 1. Results of the raw water sample as well as after biofiltration with the two coconut biosorbents are provided for comparison. Clearly, both the activated coconut shell charcoal and raw coconut shell powder were able to remove suspended solids from the raw water, eventually clarifying the water – as evident in the measured differences in color and turbidity between the raw water sample and the coconut biosorbent-treated filtrate.

Table 1. Physicochemical properties of river water samples treated with and without the coconut shell biosorbents

Parameter	*Raw water*	*Control**	Raw water treated with biosorbent		WHO Guideline**
			Activated Carbon	Raw coconut Powder	
pH	7.4	7.7	7.7	7.7	6.5-8.5
Conductivity (µs/cm)	513	555	1629	555	200 – 800
Turbidity (NTU)	12	10	4.3	7.6	≤ 5
Color	18	7.6	10	15	≤15
TDS (ppm)	256	177	809	277	≤ 1000
TSS (mg/l)	86	71	14	8	Not mentioned

*control = raw water filtered with Whatman No. 1 filter paper without the use of biosorbent

**2017, WHO Guideline for drinking-water quality

The relatively higher conductivity and TDS values recorded for the activated charcoal in particular is likely due to the chemical activation process. Girgis and El-Hendawy (2002) have described a chemical reaction between activated carbon and $Ca(OCl)_2$ leading to the generation of chloride and hydrogen ions, which can contribute to increased dissolved ions in the solution (Girgis & El-Hendawy, 2002). Although elevated conductivity and TDS values may not necessarily imply that a particular water sample is toxic for consumption, it should be taken as a precautionary measure for activated charcoal producers to consider using relatively benign chemicals for the activation process. Generally, activated charcoal is known to adsorb relatively insoluble solids more readily than soluble organics (Cobb et al., 2012), so the trend observed for TDS and TSS values for the activated carbon option is consistent with the literature.

4. Conclusion

In this study, we produced calcium chloride ($CaCl_2$)-activated charcoal from coconut shells and compared the effectiveness of the activated version to the raw (chemically-unmodified) coconut shell powder in the removal of As and Hg from water. Although the activated charcoal version slightly outperformed the raw form in metal removal (67% [vs 65% for the raw form]; and 53% [vs 49% for the raw form]), the extent of metal adsorption/ removal by the raw (chemically-unmodified) form suggests that, depending on the contaminant of interest, charring and activation or post-chemical treatment of agricultural biomass may not always be necessary for use in wastewater treatment. Further studies via FT-IR showed that the functional groups -COOH, -OH, C-O, C=C from aromatic groups and C=O, which were present in both the activated and raw coconut shell powder were key to the metal adsoption process. These techniques, could be explored further on a large scale to identify their effectiveness in wastewater treatments in the developing world.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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