Microwave and open vessel digestion methods for biochar

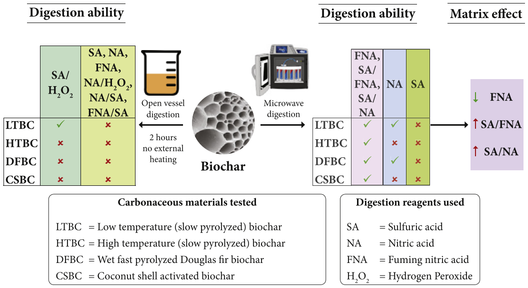
Pathum D. Wathudura [a], Chathuri Peiris [a, b], Chanaka M. Navarathna [c], Todd E. Mlsna [c], M.N. Kaumal [b], Meththika Vithanage [d], Sameera R. Gunatilake [a, *]

[a] *College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya, CO 10107, Sri Lanka*
[b] *Department of Chemistry, University of Colombo, CO 00300, Sri Lanka*
[c] *Department of Chemistry, Mississippi State University, MS 39762, USA*
[d] *Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, CO 10250, Sri Lanka*

HIGHLIGHTS

- Seven digestion reagents were tested to digest nine different biochars.
- H_2SO_4/H_2O_2 mixture was best suited for open vessel digestion of biochar.
- Microwave digestion with fuming nitric acid digested all tested biochar types.
- Low matrix effects and acceptable recoveries were obtained by fuming nitric acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Digestion of biomass derived carbonaceous materials such as biochar (BC) can be challenging due to their high chemical recalcitrance and vast variations in composition. Reports on the development of specific sample digestion methods for such materials remain inadequate and thus require considerable attention. Nine different carbonaceous materials; slow-pyrolyzed tea-waste and king coconut BC produced at 300 °C, 500 °C and 700 °C, sludge waste BC produced at 700 °C, wet fast-pyrolyzed Douglas-Fir BC and steam activated coconut shell BC have been tested to evaluate a relatively fast and convenient open-vessel digestion method using seven digestion reagents including nitric acid (NA), fuming nitric acid (FNA), sulfuric acid (SA), NA/SA, FNA/SA, NA/H_2O_2 and SA/H_2O_2 mixtures. From the tested digestion reagents, SA/H_2O_2 mixture dissolved low temperature produced BC (LTBC) within 2 h with occasional shaking and no external heating. Except peroxide mixtures, the other reagents were used to evaluate microwave digestion (MWD) efficiency. Nitric acid mixture was capable of only completely digesting LTBC in the MWD procedure whereas FNA, NA/SA and FNA/SA mixtures resulted in the successful dissolution of all tested carbonaceous materials. Amongst them, FNA provided the least matrix effect in the quantification of the four metals tested using flame atomic absorption spectrophotometry. Tested recoveries for FNA were satisfactory as well. It was concluded that FNA is a preferable reagent for microwave digestion of BC.

1. Introduction

Biomass-derived carbonaceous adsorbents, having resulted from the thermal degradation of superfluous plant and animal

Abbreviations

AAS	Atomic absorption spectrophotometer
BC	Biochar
CRM	Certified reference material
CSBC	Steam activated coconut shell biochar
DFBC	Wet fast pyrolyzed Douglas fir biochar
EDX	Energy dispersive X-Ray spectroscopy
FAAS	Flame atomic absorption spectrophotometer
FNA	Fuming nitric Acid
HA	Hydrochloric acid
KC	King coconut
KC300	King coconut husk biochar produced at 300 °C
KC500	King coconut husk biochar produced at 500 °C
KC700	King coconut husk biochar produced at 700 °C
LTBC	Low temperature produced biochar
MWD	Microwave digestion
NA	Nitric acid
OVD	Open vessel digestion
SA	Sulfuric acid
SW700	Sludge waste biochar produced at 700 °C
TW	Tea waste
TW300	Tea waste biochar produced at 300 °C
TW500	Tea waste biochar produced at 500 °C
TW700	Tea waste biochar produced at 700 °C
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

based matter, are abundant in carbon (Ahmad et al., 2014; Peiris et al., 2017). The high porosity and the large surface area possessed by these adsorbents make them beneficial for the sorption of inorganic and organic adsorbates (Ahmad et al., 2014; Karunanayake et al., 2017, 2018; Peiris et al., 2019b). Biochar (BC) is a biomass-derived carbonaceous adsorbent which can be produced by several methods such as, slow and fast pyrolysis, gasification, hydrothermal conversion and torrefaction (Ahmad et al., 2014; Peiris et al., 2017). These materials have received enormous research focus during recent years owing to their cost effective remedial and agricultural soil amendment applications (Ahmad et al., 2014; Peiris et al., 2017, 2019a; Jayawardhana et al., 2019).

The composition of metallic substances is an important characteristic of a carbonous adsorbent. Even though state-of-the-art techniques such as Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are available for metal composition determination, traditional atomic spectroscopic techniques are still frequently utilized (1) for the determination of the exact concentration (by mass) of each metal ion of interest, (2) for the exact determination of specific metal ion concentration because the results represent an entire sample aliquot and (3) due to the relatively high availability of instruments.

However, commonly used atomic spectroscopic methods require the complete dissolution of the sample into solution. Although both wet-digestion and dry-ashing techniques are available for sample preparation, wet-digestion methods are preferable because the dry-ashing of BC can be problematic as they may resist thermal decomposition at commonly used temperatures. It is important to note that, the recalcitrant nature and the high stability of the biomass-derived carbonaceous adsorbents can make wet-digestion challenging (Enders and Lehmann, 2012). The undigested matter can cause erroneous results by (1) altering nebulization efficiency, (2) increasing matrix interferences and (3) providing biased results as the reading does not represent the entire aliquot (Wasilewska et al., 2002; Enders and Lehmann, 2012).

Microwave digestion (MWD) methods offer significant advantages over open vessel digestion (OVD) techniques. Reduced time consumption, simultaneous digestion of multiple samples, operation at elevated temperatures, less reagent usage, less volatilization of analyte, lesser risk of contamination etc. are amongst these. However, traditional OVDs are still been utilized due to the low cost and unavailability of instruments (Lamble and Hill, 1998).

To the best of our knowledge, all reported digestion methods for BC recommends ultrapure grade reagents, namely, HCl (HA), HNO_3 (NA), H_2SO_4 (SA) and H_2O_2 with strengths of 30–40%, 68–70%, 95–98% and 30–32% respectively. Most studies have utilized US EPA 3052, 3051A and 3050B methods for BC digestion (Hristovski et al., 2009; Agrafioti et al., 2013; Lucchini et al., 2014; Song et al., 2014). The EPA 3051A (microwave) method uses NA or a mixture of NA and HA (USEPA, 2007). Method 3052 (microwave) mainly uses a mixture of NA and HF whereas a mixture of nitric acid and H_2O_2 is used in the OVD method 3050B (USEPA, 1996a, b). It is important to note that EPA method 3052 was originally designed for siliceous and organically based matrices whereas methods 3051A and 3050B were originally designed for sediments, sludges and soils.

In addition to EPA methods, several other approaches have also been reported for this purpose. A two-step approach of digesting wood based biochar was reported by Komkiene and Baltrenaite (2016). The method was originally used elsewhere for the digestion of soil and wood (Pundytė et al., 2011). Dried BC particles were fired to ash and followed by a MWD with an aqua regia solution. The use of oxidizing agents in the digestion of activated charcoal have also been reported (Lepri et al., 2010). The material has been soaked with H_2O_2 in microwave vessels for 24 h prior to MWD with NA. The utilization of methods such as centrifugation or filtration through nylon syringe filters, glass fiber filter papers or Whatman filter papers after digesting to eliminate the remaining particles, it is inferred that incomplete digestion is a major drawback in the above procedures (Kurth et al., 2006; Song and Guo, 2012; Lucchini et al., 2014).

A mixture of $HClO_4$ and NA has been established for OVD of plant materials which was later incorporated for BC digestion (Miller and Kalra, 1998; Namgay et al., 2010; Singh et al., 2010). However, the usage of $HClO_4$ has largely been avoided due to violent reactions with organic compounds in addition to the possibility of catching fire during digestion and explosions when dry (Adeloju et al., 1984; Novozamsky et al., 1993). Enders et al. reported a customized wet digestion method for BC which involved refluxing with NA and H_2O_2 for an extensive period of time (193 h) (Enders and Lehmann, 2012).

The above information suggests that although several EPA methods are utilized for digestion procedures, they had been originally developed for the digestion of other sample matrices and are not specifically for biomass derived carbonaceous adsorbents. Digestion methods reported for BC are meagre and involve discrepancies relating to the time taken for complete digestion, the acid mixtures used which pose a consequential safety hazard and refluxing.

The first objective of the presented study was to evaluate relatively simple and fast OVD methods for carbonous material. In addition to the orthodox mixtures used before, fuming nitric acid

(FNA), SA/FNA and SA/H_2O_2 mixtures have being used to obtain complete digestion within a time period less than 2 h without supplying external heat. The second objective was the successful development of a MWD method to digest BC. For this purpose, SA/FNA and FNA mixtures have being used together with traditional acid mixtures to optimize a MWD method that would achieve a complete digestion cycle within about an hour. To represent a wide variety of feedstock and production methods, nine biomass derived carbonaceous material were selected. Slow-pyrolyzed BC were produced using tea-waste and king coconut husk (at 300 °C, 500 °C and 700 °C), activated dairy industry sludge (at 700 °C) alongside wet fast-pyrolyzed wood based (Douglas-Fir) BC and coconut shell activated carbon were the adsorbents used in the study. The outcomes of this study become beneficial when optimizing methods that are required for the digestion of adsorbent samples of interest.

2. Materials and methods

2.1. Reagents, solutions, apparatus and equipment

Nitric, sulfuric and hydrochloric acids (ultra-pure grade) as well as hydrogen peroxide (ultra-trace analysis grade) were purchased from Fisher scientific (Hampton, NH). Fuming nitric acid was prepared in-house by distilling a 1:1 ratio mixture of NA (69% w/w) and SA (98% w/w). Calibration standards (Cadmium, Copper, lead and Zinc) for the atomic absorption spectrophotometer (AAS) were purchased from Inorganic ventures (Christiansburg, VA). Milestone Ethos easy microwave digester was used for the sample digestion and Hitachi ZA3000 Zeeman polarized atomic absorption spectrophotometer was used for the metal analysis in the spiked samples. Turbidity was measured using HACH 2100Q portable turbidimeter.

Tea-waste (TW) BC was prepared in-house at three different temperatures 300 °C, 500 °C and 700 °C (abbreviated as TW300, TW500 and TW700 respectively) by heating dried biomass in a muffle furnace under oxygen deficient conditions. King coconut (KC) BC were also produced in the same manner under the same temperatures (abbreviated as KC300, KC500 and KC700 respectively). Dairy sludge was collected from a wastewater treatment plant and subjected to slow pylolysis, as per previously mentioned method for TW and KC, at 700 °C to obtain sludge waste biochar (SW700). Wet fast-pyrolyzed Douglas fir BC (DFBC) were obtained from Biochar Supreme LLC (Everson, WA) and commercially available steam activated coconut shell biochar (CSBC) were obtained from the Sri Lankan market. All carbonaceous materials were ground and sieved to obtain the below 0.25 mm mesh fraction required.

2.2. Digestion reagents and mixtures

Seven different digestion reagents/mixtures, SA (20 mL), SA/H_2O_2(15 mL/5 mL), NA (20 mL), NA/H_2O_2 (16 mL/4 mL), NA/SA (14 mL/6 mL), FNA (20 mL), FNA/SA (14 mL/6 mL) were tested to evaluate the efficiency of open vessel digestion. Microwave digestion efficiency of the five digestion reagents/mixtures, SA (13 mL), NA (13 mL), NA/SA (9 mL/4 mL), FNA (13 mL), FNA/SA (9 mL/4 mL) were tested.

2.3. Open vessel and microwave digestion

Open vessel digestions were carried out by transferring 0.1 g portions of carbonaceous material into 100 mL conical flasks and treating them with desired digestion reagent/mixture for 2 h with occasional shaking. For MWDs, 0.1 g portions of BC were treated with desired digestion reagent/mixture in Teflon vessels at a maximum wattage of 1800 W. The temperature was raised to 180 °C at a rate of 10 °C/min, maintained for 15 min and allowed to cool down to room temperature (RT).

2.4. Turbidity measurements

Following OVDs, approximately 10 mL portions of each digestion mixture was placed in sample vessels and the turbidity was measured. Digestion mixtures resulting from MWDs were quantitatively transferred to 25 mL volumetric flasks, topped up with deionized water and the turbidity measured according to the above-mentioned procedure.

2.5. Evaluation of matrix effects

Matrix interferences in the solution can alter the sensitivity of the calibration curve. The extent of the matrix effect was evaluated by generating matrix matched calibration curves and comparing the sensitivities of their respective non-matrix matched calibration curves (calibration curves using neat standards). The detailed procedure can be found in the supplementary information S1. The matrix effects were calculated using the following equation,

$$M\% = \frac{(S_{\text{neat}} - S_{\text{spiked}})}{S_{\text{neat}}} \times 100\%$$

where, M% is the percent matrix effect, S_{spiked} is the slope of the calibration curve for an analyte in a matrix and S_{neat} is the slope of the calibration curve for an analyte dissolved in a neat solvent. A zero M% is an indication of no resultant matrix effect which gives identical slopes for both calibration curves (Gunatilake et al., 2013, 2014). A calculated negative matrix effect indicates an enhanced sensitivity by the matrix, whereas a positive value indicates a suppressed sensitivity in the presence of matrix components.

2.6. Evaluation of percent recoveries

Recovery tests were performed with the purpose of evaluating digestion efficiencies of the tested reagents/mixtures. Due to the unavailability of certified reference materials (CRMs) of tested material, metal loaded carbon particles were used for recovery tests. Metal ion solutions of known concentrations were shaken with a known mass of the material interested for 4 h in a shaking water bath at RT. Remaining metal concentrations were determined and hence amounts adsorbed per unit mass of the material were determined. Prior to digestions, metal loaded carbonaceous materials were subjected to oven drying at 60 °C for 6 h (further details can be found in the supplementary information S2). A graphical representation of the experimental sequence of the recovery procedure is shown in Fig. 1. Recoveries were calculated using the following equation.

$$R\% = \frac{(S - U)}{T} \times 100\%$$

where, R% is the computed percent recovery, S is the observed amounts of the metal loaded material, U is the observed amounts of the material without metal loading, and T is the amount of the metal loaded.

3. Results and discussion

3.1. Turbidity measurements

Turbidity measurements were carried out to obtain a preliminary understanding of the successfulness of dissolution. In

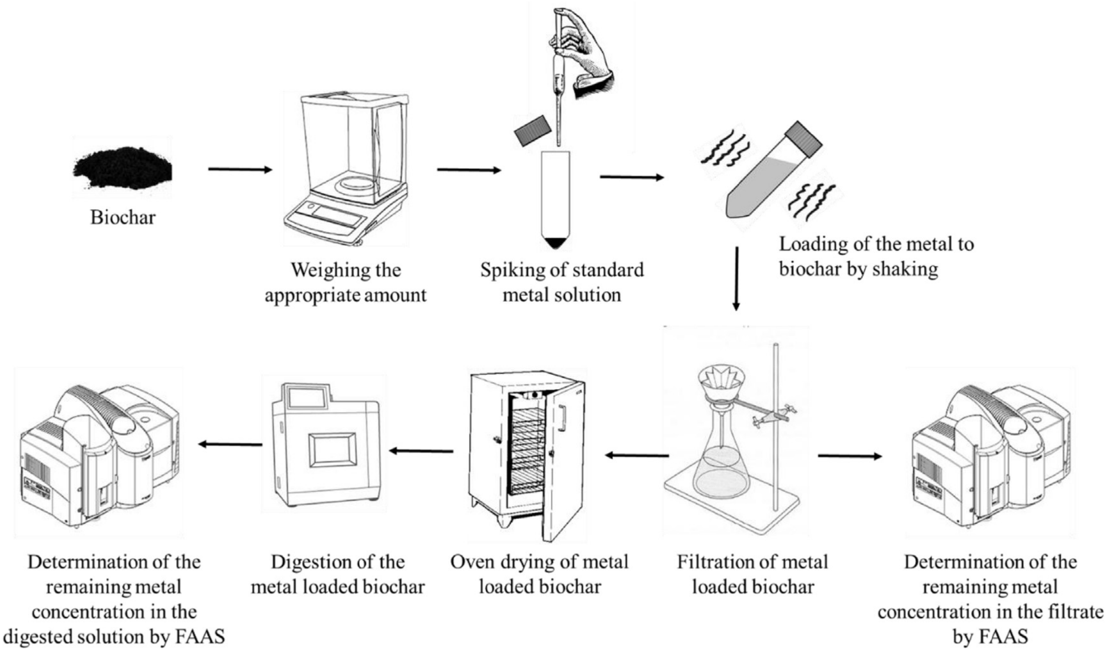

Fig. 1. The sequence of metal loading to biochar, the subsequent digestion and quantification.

addition, individual mixtures were subjected to careful eye observations, which were also considered when coming to conclusions. For instance, low turbidity values were observed for certain materials simply because the larger undigested particles have settled down at the bottom of the container without contributing to the experiment.

3.1.1. *Turbidity measurements of open vessel digestion methods*

Except H_2O_2 containing digestion mixtures, all tested reagents and mixtures resulted in highly turbid solutions. Several reasons can be responsible for this observation, (1) stability of the carbonaceous structures where the digestion reagent may not be capable of a complete dissolution, (2) due to high carbon contents per unit mass of sample where the amount of acid may be insufficient for a total digestion, (3) time allowed (2 h) for the digestion can be inadequate to complete the reactions involved, and (4) elevated temperatures may be required to provide sufficient energy for a comprehensive destruction of the material. Karunanayake et al. reported the OVD of DFBC where a 0.1 g of sample was treated with 50 mL of 1:1 95% SA:70% NA for 24 h with continuous stirring (Karunanayake et al., 2018). This provides evidence for enhanced digestion efficiency in the presence of higher amounts of reagent and longer digestion time. However, elevated temperatures, high reagent volumes and longer durations were not tested in the present study considering its relevance to the objectives and to maintain the same conditions with H_2O_2 utilized digestions.

With respect to turbidity measurements and eye observations, both NA/H_2O_2 and SA/H_2O_2 systems have showed improved digestion capabilities when compared to acid-only systems. Nitrous acid molecules formed in the NA/H_2O_2 system (Reaction 1, 2) (Chlistunoff et al., 1999) can promote the production of peroxynitrous acid (Reaction 3) (Koppenol et al., 1992) whereas SA/H_2O_2 system is capable of generating peroxymonosulfuric acid (Reaction 4) (Martin, 2005). Peroxynitrous acid is capable of forming nitro radicals (Reaction 5) (Pfeiffer et al., 1997) which are sufficiently reactive toward arene structures such as fullerenes whereas peroxymonosulfuric acid can introduce radical oxygens into the medium, contributing towards the digestion process in addition to the effect of the acid (Reaction 6) (Mattox, 1994).

$$2HNO_3 \rightleftharpoons H_2O + 2NO_2 + \frac{1}{2}O_2 \quad \text{Reaction 1}$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \quad \text{Reaction 2}$$

$$HNO_2 + H_2O_2 \rightarrow ONOOH + H_2O \quad \text{Reaction 3}$$

$$H_2SO_4 + H_2O_2 \rightarrow H_2SO_5 + H_2O \quad \text{Reaction 4}$$

$$ONOOH \rightarrow \dot{N}O_2 + \dot{O}H \quad \text{Reaction 5}$$

$$H_2SO_5 \rightarrow H_2SO_4 + \dot{O} \quad \text{Reaction 6}$$

The SA/H_2O_2 system, which is also referred to as “piranha solution” provided best turbidity results in the open vessel experiment. Three possible factors responsible for this observation are, (1) the process of extracting water from H_2O_2 by SA which catalyzes the atomic oxygen formation, (2) generation of hydroxyl cations ($OH+$) which can attack carbon-carbon double bonds (Zhang et al., 2003) and (3) the comparatively higher heat generated by the piranha solution can be an added advantage to dissolve elemental carbon which is immensely resistant to aqueous reactions (Saddow, 2012).

The SA/H_2O_2 system was able to fully digest both TW300 and KC300. It can be seen that the digestion process became more difficult as the pyrolysis temperature of BC increased. The carbon percentage of BC increases with pyrolysis temperature due to the decomposition of oxygenated and nitro moieties. Further, higher temperatures produce BC with larger aromatic domains with more ordered structures which can also be a factor contributing to their digestibility.

It is important to note that the function of peroxide is in full effect for the first 30 min as strong bubbling is observed, and diminishes approximately after an hour. Therefore, peroxide mixtures are recommended for short-timed (1–2 h) open vessel digestions (Table 1). Matrix effects and recoveries for OVD were not evaluated as no satisfactory dissolutions were obtained for most of the tested material under the conditions utilized.

3.1.2. *Turbidity measurements of microwave digestion methods*

Microwave digestions were not carried out for the digestion mixtures containing peroxide as the extreme heat and the high pressure that can be generated may damage Teflon vessels. Hence, the experiments were performed only for the remaining five acid reagents/mixtures described in 2.2. Except SA and NA, the successful dissolution of all tested carbonaceous samples were achieved by all digestion reagents/mixtures; NA/SA, FNA and FNA/SA.

In accordance with results obtained in OVD experiments, SA showed the least digestion efficiency. The extreme turbidity of the resultant solutions provided validation for this. Sulfuric acid itself is a non-oxidizing agent and is mostly used in the digestions of petroleum products, minerals, ores and plastics due it its charring ability and the formation of soluble sulfates (Flores, 2014). Hence, poor digestion efficiency of SA can be explained by the insufficient oxygen and hydrogen content in the material as well as the acid's incompetence in oxidizing graphitic carbon structure.

Being an oxidizing agent, NA showed better dissolving abilities than SA. Eventhough NA microwave digestions resulted in acceptably low turbidities, a trace of small undigested particles remained in the solutions containing TW700, KC700, CSBC and SW700.

In contrast to NA, in house distilled FNA caused a complete dissolution of tested carbonaceous materials. During extraction, water present in NA is retained by SA due to its hygroscopic nature allowing the selective evaporation of NA from its otherwise azeotropic mixture. Following distillation, FNA was subjected to standardization by neutralization titration of diluted solution and the strength was found to be 98% (w/w) in each occasion (measured density = 1.5 g/mL). The extra strength of FNA can be considered as a legitimate reason for enhanced digestion ability when compared with NA.

Acid mixtures, NA/SA and FNA/SA were also capable of producing satisfactory dissolutions of tested material. The NA/SA system is capable of producing nitronium ions, a reactive electrophile which has enough stability to exist under normal conditions. Yantasee et al. (2004) and Yang and Jiang (2014) reported the nitration of the aromatic rings in activated carbon and biochar surfaces respectively (Yantasee et al., 2004; Yang and Jiang, 2014). It may be worth mentioning that in-spite of yielding poor digestion with no external heating in open vessel experiments, NA/SA caused excellent dissolution in the presence of heat provided by microwave radiation. It can be hypothesized that the reagent causes nitration of aromatic surface, further stabilizing the arene ring. However, it causes further oxidation at higher temperatures which result in ring opening reactions. It can be concluded that when a sulfuric mixture was used, NA was capable of adequate digestion of tested material, and hence in a standpoint of turbidity measurements, there is no special requirement of using FNA (Table 1). Please note that since our preliminary work did not provide satisfactory digestions with HA, it was excluded from presented experiments. Upon identifying the dissolution efficiency of biochar after digestion, the resulting mixtures were subjected to quantification using AAS and the matrix interferences evaluated.

3.2. *Matrix effects*

Matrix effects were calculated for flame atomic absorption spectrophotometric (FAAS) quantifications of four metals, Cd, Cu, Pb and Zn. Five carbonaceous particles, TW300, TW700, DFBC, SW700 and CSBC were digested using the best four digestion reagents/mixtures mentioned in 3.1.2. (Eventhough a trace amount of undigested particles were retained in NA, the filtered solution was used to evaluate matrix effects with the intention of understanding the influence of different matrix components).

It can be seen that nitric-only digestions (NA and FNA) results in considerably lower matrix effects for all four metals tested than SA containing digestions. Hence, the results provide conclusive evidence for suppressed FAAS sensitivity in the presence of SA.

Negligible matrix effects were seen for Pb matrix matched calibration curves for NA and FNA digestions (2.4–12.5 and 1.6–8.3 respectively). However, Pb showed secondary precipitate formation with SA containing matrices, making quantifications impossible. The noticeable suppression of Pb absorbance in the presence of SA in matrix is also reported in literature (Tinggi et al., 1992).

For Cd calibration curves, minimum and negligible matrix effects (−0.7 to −4.8) were obtained for FNA digested samples. Minimum matrix effects for Cu was observed for NA digestions (2.4–6.5), However, FNA also provided insignificant deviation of sensitivities (2.4–7.6). Among the four metal ions tested, Zn showed the highest matrix effect (7.6–60.7). However, in accordance with Cd and Cu, nitric-only systems showed the lowest matrix effect for Zn as well (7.6–23.6). The computed matrix effects are shown in Table 2 and the generated matrix-matched calibration curves are shown in supplementary information S3–S6.

Table 1

Turbidity measurements of resulting solutions after different open vessel and microwave digestions.

Digestion mixture	Turbidity measurements for open vessel digestions/FNU (n = 3)								
	TW300	TW500	TW700	KC300	KC500	KC700	DFBC	CSBC	SW700
SA	t/h	t/h	t/h	t/h	t/h	t/h	t/h	236.00 (35.00)	t/h
SA/H_2O_2	7.90 (2.30)	t/h	t/h	2.04 (0.05)	45.77 (32.50)	t/h	t/h	136.73 (73.11)	172.23 (26.74)
NA	271.67 (71.67)	203.67 (7.57)	376.00 (34.39)	596.33 (51.07)	t/h	t/h	t/h	87.23 (27.64)	t/h
NA/H_2O_2	66.67 (8.56)	t/h	t/h	58.63 (7.59)	t/h	t/h	t/h	102.43 (10.36)	99.48 (56.45)
NA/SA	773.33 (68.86)	t/h	t/h	t/h	t/h	t/h	t/h	87.57 (17.72)	t/h
FNA	144.00 (45.18)	t/h	t/h	153.00 (41.07)	t/h	t/h	t/h	83.87 (28.67)	t/h
FNA/SA	134.87 (50.98)	t/h	t/h	36.03 (8.78)	t/h	t/h	t/h	12.73 (21.34)	t/h
	Turbidity measurements for microwave digestions/FNU (n = 3)								SW700
	TW300	TW500	TW700	KC300	KC500	KC700	DFBC	CSBC	
SA	t/h	t/h	t/h	t/h	t/h	t/h	t/h	256.67 (20.53)	273.02 (25.03)
NA	9.02 (0.99)	21.13 (1.21)	4.32 (1.03)	4.09 (0.17)	8.80 (1.17)	4.23 (0.99)	8.39 (1.76)	2.48 (0.10)	2.77 (0.33)
NA/SA	4.30 (0.66)	6.15 (3.19)	2.83 (1.14)	3.52 (0.91)	3.84 (0.42)	3.24 (0.17)	5.65 (1.54)	5.43 (0.73)	2.73 (1.02)
FNA	8.63 (1.18)	20.97 (7.84)	6.33 (0.98)	6.48 (1.09)	8.20 (1.28)	6.07 (1.01)	8.10 (0.67)	3.33 (0.75)	6.25 (0.78)
FNA/SA	2.53 (0.44)	3.17 (0.47)	3.70 (0.18)	1.58 (0.26)	3.86 (0.32)	4.15 (0.03)	3.29 (0.66)	2.44 (0.26)	3.52 (0.88)

Table 2
Computed percent matrix effects for tested digestion.

Digestion Mixture	Spiked Metal	Matrix effect (%) for each carbonaceous material				
		TW300	TW700	DFBC	CSBC	SW700
NA	Cd	8.3	14.9	12.5	13.7	1.1
	Cu	2.4	2.4	4.8	−2.4	6.5
	Zn	18.8	20.3	7.6	14.2	12.4
	Pb	12.5	8.3	2.4	4.8	3.1
FNA	Cd	2.4	1.8	−4.8	−1.2	−0.7
	Cu	7.1	2.4	7.1	2.4	7.6
	Zn	20.0	17.6	23.6	20.3	8.5
	Pb	4.8	2.4	7.1	8.3	1.6
NA/SA	Cd	8.3	8.9	8.3	5.4	4.0
	Cu	19.0	19.0	16.7	11.9	11.1
	Zn	37.3	40.3	37.9	36.4	58.8
	Pb	–	–	–	–	–
FNA/SA	Cd	25.0	23.2	16.7	23.8	5.0
	Cu	33.3	35.7	31.0	31.0	14.1
	Zn	31.5	30.3	37.0	37.9	60.7
	Pb	–	–	–	–	–

3.3. *Recovery tests*

When both turbidity measurements and matrix effects were considered, microwave digestion with FNA showed the best digesting capabilities for tested material. Therefore, recovery was carried out for FNA digestion using Cd and Pb as dummy metals. Recovery tests were performed with the intention of obtaining a rough understanding of digestion efficiency.

It is important to note that, the accuracies of metal contents in metal loaded carbon materials may not be comparable with that of a CRM as the loaded amounts were calculated only using initial and final concentrations of the metal in shaking solution. The homogeneous loading of metal is also not guaranteed and the metal adsorption occurs on the surface rather than at the core of a particle. For all five carbonous material tested, FNA provided acceptable percent recoveries as shown in Fig. 2. Further, the exact values are given in Table S7, in the supplementary information.

4. Conclusions

Regarding open vessel digestions, it can be concluded that SA/H_2O_2 mixtures are capable of dissolving low temperature produced BC within a short duration (1–2 h) without external heating. However, high temperature BC may require more reagent, temperature and reaction time for a complete dissolution. It is important to mention that the activity of H_2O_2 in digestion solution lasts for a maximum of a couple of hours and therefore no additional advantage is provided for long duration digestions.

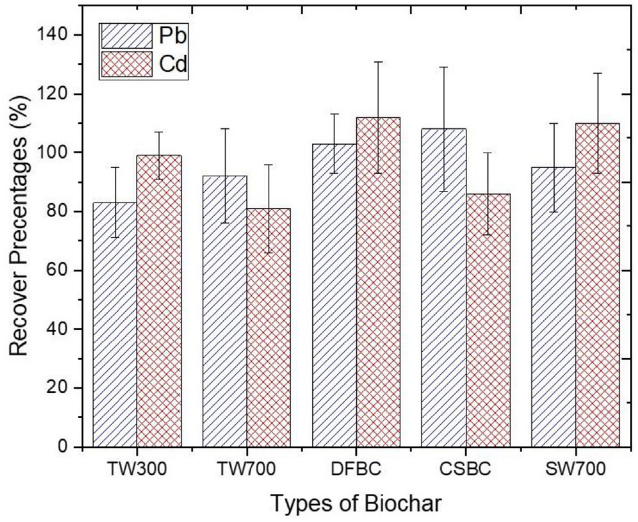

Fig. 2. Recovery Percentages for metal loaded sample digestion.

Regarding microwave digestions, NA is capable of dissolving low temperature BC fully, though a 100% dissolution may not be obtained for CSBC and all other high temperature BC. There is a high chance to completely digest carbonaceous particles (including low and high temperature slow-pyrolyzed, fast-pyrolyzed and steam activated BC) by using FNA, NA/SA and FNA/SA. However, considerable losses in sensitivity is observed when SA is present in the matrix. Furthermore, secondary precipitate formation in SA matrix is also possible for certain metals (Example: Pb) depending on the content. It is also worth mentioning that H_2O_2 containing acid mixtures are not recommended for microwave digestions of BC considering the safety and the durability of Teflon vessels due to the high heat and the pressure produced. By considering all observations, in general, FNA can be considered as the preferred reagent for the digestion of BC. Computed recovery percentages for FNA can also be considered satisfactory. Due to extreme strength of FNA, it is recommended to perform an appropriate dilution before the FAAS analysis and must be handled with extreme caution.

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Appendix A. Supplementary data

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