

Comparative study on open system digestion and microwave assisted digestion methods for metal determination in shrimp sludge compost

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ABSTRACT

The aim of this work was to evaluate two different digestion methods for the determination of the total concentration of metals (Zn, Cu, Cr, Ni, Pb and Cd) in shrimp sludge compost. The compost made from shrimp aquaculture sludge co-composted with organic materials (peat, crushed bark and manure) was used as an organic growing medium for crop. Open system digestion and microwave assisted digestion procedures were employed in sample preparation. Various combinations and volumes of hydrofluoric, nitric and hydrochloric acids were evaluated for the efficiency of both methods. A certified reference material (CRM 146) was used in the comparison of these two digestion methods. The results revealed a good agreement between both procedures and the certified value. The best recoveries were found in the range between 95% and 99% for microwave assisted digestion with a mixture of 2 ml of HF, 6 ml of HNO₃ and 2 ml of HCl. This procedure was recommended as the method for digestion of the compost herein based on the recovery analysis and time taken.

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1. Introduction

Intensive farming and inadequate land management have led to a reduction in organic matter content of soils [1]. Maintenance of an adequate organic matter level in soils significantly increases soil fertility and crop production. Nowadays, application of compost is a common source of organic matter for agricultural soil. Various types of compost have been tapped from waste, such as municipal solid waste, sewage sludge [2–5] and shrimp aquaculture sludge [6].

Composting these residues is a sustainable way of reducing the amount of waste generated, which makes its management less difficult. Moreover, the produced low-cost compost could be used as an amendment in agriculture, meanwhile recycling its valuable components: organic matter, N, P and other plant nutrients [2–7]. Application of the solid waste compost to agricultural soils was previously found to improve micronutrient complex formation, which increases availability of micronutrients to plants, to simulate the presence of beneficial soil organisms and to reduce the presence of plant pathogens. Moreover, it seems to increase water holding capacity, soil buffering and cation exchange capacity and improves soil porosity [4,8–10]. The quality of such solid waste compost was found to be dependent on many factors, including the design of

the composting process, feedstock source and proportions used, composting procedure and length of maturation [10].

Concern over adverse human and ecological health effects of accumulation of heavy metal contaminants in the environment is increasing [11–14]. Heavy metal pollution accumulated in agriculture soil influences the ecosystem nearby. The toxic metals may be taken up directly by humans and animals through the inhalation of dusty soil or they may enter the food chain as a result of their uptake by edible plants and animals [15–17] or leach down to groundwater and contaminate drinking water resources, and may cause, in both cases, hazards to the health of humans and animals [12].

Although some trace elements are essential plant micronutrients [18], elevated levels of metals in soil may lead to increased uptake by plants [19] and affect the quality of agriculture products [12]. For these reasons, the monitoring of trace metals in agricultural soils is essential.

Atomic absorption spectrometry (AAS) and inductively coupled plasma-optical emission and mass spectrometry (ICP-AES and ICP-MS) are among the most common spectroscopic methods used for determination of heavy metals in environmental samples [20]. ICP-MS has emerged as a useful technique for trace analysis of soil owing to its multi elements capability, high detection power and low sample consumption [21]. The drawback of these techniques is that the solid sample required to be transformed into solution prior to the determination of the metal content [20]. Therefore, sample preparation is an important step in the analysis of soils because of the refractory nature of these materials [21].

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The speed and efficiency of instrumentation for reliable determination of trace elements in geological and environmental samples have improved dramatically over the last decades. However, sample preparation methods are still the major factor contributing to the uncertainty in the analytical results [22–25]. Conventional digestion procedures, such as wet digestion and dry ashing, are often the most time consuming stage of the analysis. These methods are labour intensive and tedious, and often have a high contamination potential [11,20].

The improvement of microwaves oven has led to their usage in analytical laboratories for sample digestion. The theory of microwave digestion has been reviewed in detail elsewhere and only brief comment is justified here [26]. The first application of microwaves for sample preparation was reported in 1975 [27]. Since that time many microwave assisted dissolution methods have been developed to include a variety of sample matrices such as soil [28], fish [29], sediments [30], sludge [31–34] and biological and environmental samples [20,35]. Microwave digestion procedures are classified according to their operational modes; open vessel microwave assisted digestion, which is more prone to sample contamination, and susceptible to losses of volatile metals and closed (pressurised) vessel procedures, which are rapid and efficient digestion techniques. On line microwave assisted digestion of solid samples and a combination with ultrasonic radiation also are known [36,37].

A large number of different acid mixtures have been used for microwave digestion. Some methods use HNO_3/HF [21]; others use $\text{HClO}_4/\text{HNO}_3$ [38]; $\text{HF}/\text{HNO}_3/\text{HCl}$ [39], HNO_3/HCl and $\text{HNO}_3/\text{H}_2\text{SO}_4$ [40]. In most cases, complete digestion of the sample is required to achieve reproducible and accurate results [40]. The addition of HF strongly influences the recovery of the microwave acid digestion of environmental samples. This acid breaks down silicates and minerals better than $\text{HClO}_4/\text{HNO}_3$ and HNO_3/HCl acid combinations. However, HF can give rise to problems in glassware and torch damage of ICP-MS or AAS. This problem can be avoided by using a small volume of HF acid and addition of saturated boric acid solution, to remove the excess of HF and dilution of samples before analysis.

In this study we report the comparison of open system digestion and microwave assisted digestion in two different composts of shrimp aquaculture sludge which used as organic growing media for crop. Our first step was to validate the methods using certified reference materials (CRMs) of soil origin and to propose a rapid, safe, and best sample preparation method. The second step was to apply the method for monitoring heavy metals content in the composts. To the best of our knowledge, this is the first research in analysis of shrimp aquaculture sludge by microwave assisted digestion using different solvent volume in the entire world.

2. Experimental

2.1. Sampling

A composite sludge samples were collected from the bottom of the drained shrimp aquaculture pond at four different locations during harvest period in 2008 at Selangor province of Malaysia. The samples were bagged, labelled and transported to the laboratory. The samples were dewatered, dried at the ambient air and ground before coned and quartered to provide about 100 g sub-samples after removing large objects (including stones, pieces of brick, concrete and cinders). The sub-samples were air-dried at $<30^\circ\text{C}$ under local exhaust ventilation and then sieved through a 1 mm nylon mesh.

2.2. Composting material

In this study, an initial sludge compost was prepared as a mixture of shrimp sludge, plants materials and animal manure at the ratio of 1 (sludge): 4 (crushed bark and husk): 0.5 animal manure (w/w). This mixture was composted in the open air and matured in about 6 months as compost 1. Compost 2 consisted of the compost shrimp sludge co-composted with coco peat waste which previously used as a growing medium for chilli plant in fertigation system. The air-dried compost samples (20 g) were then coned and quartered again and 0.5 g of each sub-sample was employed for both methods of digestion in triplicate.

2.3. Reagents

All reagents used hydrochloric acid (36% HCl), nitric acid (69% HNO_3) and hydrofluoric acid (48% HF) were of analytical grade (Problab, VWR International, France). These reagents are commonly used in digestion methods of environmental samples. A combination of different volume ratio of mineral acids (HCl and HNO_3 and HF) as a reagent mixture was used to ensure a complete digestion of the samples. HCl and HNO_3 dissolve carbonates [20], HNO_3 oxidises organic matters [20], and HF breaks down the aluminosilicate phase [14,41,42]. The chosen acids were in accordance with previously used methods [11,20,43,44] and the microwave manufacturer (Multiwave 3000, Anton Paar, Austria) recommendation. Ultrapure water of an $18\text{ M}\Omega/\text{cm}$ resistivity (Milli-Q water purification system, Millipore, USA) was used throughout this work for preparation the solutions and rinsing the vessels. All the polypropylene bottles were used for storing the solutions. All glassware and plastic containers used throughout this experiment were immersed in a dilute HNO_3 solution overnight and rinsed with ultrapure water, and finally dried in a clean bench.

Standards solutions were prepared from a 1000 mg/l standard for atomic absorption spectroscopy (BDH Chemical, Poole, England) by dilution with acidified ultrapure water (5% (w/w) HNO_3).

2.4. Certified reference material

A certified reference material, BCR 146-R (sewage sludge) was obtained from the Community Bureau of References, Belgium. The triplicate samples of CRM were dried according to the BCR suggestions and thoroughly mixed prior to analysis.

2.5. Apparatus

A flame atomic absorption spectrometer (PerkinElmer AAnalyst 400 with WinLab 32 Software Version 6.5) was used in this study. All measurements were carried out in an air/acetylene flame. The operating parameters for working elements were set as recommended by the manufacturer.

A pressurised closed-vessel Microwave Digestion system (Multiwave 3000, Anton Paar, Austria) was used to perform microwave assisted digestion procedures for the compost samples. It is equipped with an 8-position rotor (Rotor 8S). The HF vessel consisted of the fluoropolymer liner and the ceramic vessel jacket.

2.6. microwave assisted digestion procedures (MAD)

Microwave PTFE vessels were cleaned using 10 ml of concentrated HNO_3 , heated for 15 min at 180°C (800 W) and then rinsed with ultrapure water heated for 15 min at 180°C before each digestion. PTFE evaporation vials were soaked overnight with diluted HNO_3 and then rinsed with ultrapure water. All samples were accurately weighted to approximately 0.5 g directly in microwave vessels. Relative volumes of each mineral acid were derived from

Table 1
Reagents, volumes and operating condition for microwave digestion (MWD) methods.

Step	Procedure	Reagents (ml)	Power (W)	Hold time (min)	Pressure (Pa)	Temperature (°C)
1	A	HNO ₃ (6 ml), HCl (1 ml), HF (1 ml)	1000	15	10 ⁶	200
2	B	HNO ₃ (6 ml), HCl (2 ml), HF (2 ml)	1000	15	10 ⁶	200
3	C	HNO ₃ (1 ml), HCl (6 ml), HF (1 ml)	1000	15	10 ⁶	200
4	D	HNO ₃ (2 ml), HCl (6 ml), HF (2 ml)	1000	15	10 ⁶	200
Vent				50		

the aqua regia digestion procedure with small changes as summarized in Table 1. The same amount of HNO₃ (6 ml) with different volumes of HF and HCl were used for the digestion in procedures A and B. In procedure A, the same amount of HCl and HF (1 ml each) was added to HNO₃, giving a total of 8 ml of an acid mixture. The volume of both acids (HCl and HF) was increased twice with the amount of HNO₃ (6 ml) as procedure B. In procedures C and D, 6 ml of HCl was mixed with different volumes of HNO₃ and HF. However, the same ratio of HNO₃ and HF was employed in these procedures. The only different between procedures C and D was that procedure C used less amount of HNO₃ and HF compared to procedure D. The digestion program itself consisted of a 10-min gradual increase in temperature to 200 °C, a 15-min step at 200 °C (1000 W; 10⁶ Pa) and then a ventilated cooling stage. This program was chosen in agreement with manufacturer recommendations and earlier studies on microwave assisted digestion optimisation [11,14,45,46].

After cooling to room temperature, all the digests from the each procedure (Table 1) were filtered through a 0.45 μm PTFE filter and then evaporated on a hot plate at 60 °C. Evaporation was a necessary step since acid concentrations would have been too high for the AAS (atomic absorption spectrometry) and would have required dilutions to take place to such an extent that trace element could not have been detected. Care was taken to avoid burning of the evaporation residues. All solutions were diluted to 50 ml with ultrapure water and stored in polyethylene vials at 4 °C until analysis using AAS. Blanks were treated in the same way without sample for all procedures. This procedure completed in 75 min.

2.7. Open (conventional) wet acid digestion procedure (OD)

A mixture of mineral acids as tabulated in Table 1 was employed in an open system digestion method. The trace elements content followed the procedure recommended the International Organization for Standardization (ISO 11466) [47]. 0.5 g of each triplicate compost sample with a total volume of 8 ml or 10 ml of an acid mixture (HNO₃ + HF + HCl) were added into a digestion flask covered with a watch glass and heated in a sand bath heater for 16 h. After cooling at room temperature, the digests was filtered through a 0.45 μm PTFE filter paper into a 50-ml volumetric flask and diluted with ultrapure water containing 5% HNO₃ to the mark. Finally, all solutions were kept in refrigerator at 4 °C until analysis using AAS.

3. Results and discussion

3.1. Method validation

Microwave digestion programs (Table 1) and open system digestion technique were compared to determine the capability of the methods to be used in sample preparation of compost samples herein, taking into account the information obtained when comparing the recovery, the total time taken for analysis, the operational difficulties, the amount of acid used and the safety requirements during the process.

Tables 2 and 3 show the results obtained for Zn, Cu, Cr, Ni, Pb and Cd in the analysis of the certified reference material BCR 146-R. Triplicate measurements were performed using both MAD

and OD methods. During the AAS analysis, a procedure blank and spike samples involving all reagents were run to check cross contamination and interferences for each set of every ten samples. The accuracy assessment revealed that the recoveries of MAD method ranging from 88.7% to 95.5%, 95.7% to 98.8%, 82.1% to 95.6% and 87.7% to 97.2% for procedures A–D, respectively. The recovery of each metal was calculated based on the mean value for CRMs [(measured concentration (μg g⁻¹)/mean CRM certified value (μg g⁻¹)) × 100]. Our results indicate that the lowest recoveries of MAD were found in C for Cr (82%). The best recoveries were found in B for all metals.

For OD method, the best recoveries were found in B. Nevertheless, when compared between MAD and OD methods the highest recoveries were found in MAD except for Zn. The obtained result in procedure B for both digestion systems was in good agreement with the certified values. Comparison between procedures A and B in MAD for determination of metals in the analysis of the certified reference material (BCR 146-R) showed that the addition of 1 ml HCl and 1 ml HF more, the recoveries of all metals were increased intensively. Our results revealed that an aqua regia with the ratio of 3 (HNO₃):1 (HCl) is the best combinations of acid used in microwave digestion. More concentrated HNO₃ was required for the digestion as the sludge samples contained more organic materials. The sludge samples should be treated with HF, assuming that some heavy metals might have deposited on silicate compounds. Furthermore, the metals might be released into an aquatic phase in the environment. The ratio of 1 (HNO₃):3 (HCl) (in method D showed that) the recoveries of all metals were significantly decreased except for Pb. These results showed that trace elements in the CRM 146 sludge samples could be released easily with HNO₃ as the matrix consisted of organic materials.

The results of the open digestion system are found to be similar to that of microwave assisted digestion. Nevertheless, the recoveries obtained from microwave assisted digestion are better than that of open system digestion. Perhaps, this is due to lost and oxidation of some elements in open system digestion. More HF required in these samples since silicate base as a matrix of these samples.

With comparison between these two digestion systems it could be deduced that in most cases microwave assisted digestion extraction was sufficient to quantify the level of concentrations of these trace elements in the soil and also seemed to be a more attractive procedure from the point of low acid consumption, shorter digestion time, and safety coupled to a good accuracy. Consequently, this investigation was done to evaluate the best acid combinations for digestion of compost shrimp samples for use in further experiments.

Fig. 1 shows the comparison of concentration of trace elements between open system digestions; microwave assisted digestion and certified values.

3.2. Detection and quantitation limits

Limits of detection (LOD) and limits of quantitation (LOQ) were calculated, over 10 measurements of the blank for each procedure, as 3σ and 10σ, respectively [48]. Values are presented in Table 4. LODs ranged from 0.3 μg l⁻¹ to 14 μg l⁻¹ and LOQ values from 1 μg l⁻¹ to 33 μg l⁻¹ for microwave assisted digestion and LODs

Table 2
Concentration of metals in CRM 146-R using microwave assisted system digestion (MWD) ($\mu\text{g g}^{-1}$).

	Method	Zn	Cu	Cr	Ni	Pb	Cd
CRM (certified)		3060 ± 60	838 ± 16	196 ± 7	70 ± 5	609 ± 14	18.8 ± 0.5
CRM (found)	A	2923 ± 39	796 ± 21	174 ± 9	63 ± 8	571 ± 14	17.9 ± 0.7
Recovery (%)		95.5	95.0	88.7	90.0	93.7	95.2
CRM (found)	B	3025 ± 64	824 ± 17	190 ± 16	67 ± 8	596 ± 13	18.3 ± 0.8
Recovery (%)		98.8	98.3	96.9	95.7	97.9	97.3
CRM (found)	C	2888 ± 49	777 ± 11	161 ± 12	61 ± 9	582 ± 17	16.9 ± 1.2
Recovery (%)		94.3	92.7	82.1	87.2	95.6	89.9
CRM (found)	D	2902 ± 59	782 ± 18	172 ± 15	63 ± 9	592 ± 22	17.2 ± 1.4
Recovery (%)		94.8	93.3	87.7	90.0	97.2	91.5

Table 3
Concentration of metals in CRM 146-R using open system digestion (OD) ($\mu\text{g g}^{-1}$).

	Method	Zn	Cu	Cr	Ni	Pb	Cd
CRM (certified)		3060 ± 60	838 ± 16	196 ± 7	70 ± 5	609 ± 14	18.8 ± 0.5
CRM (found)	A	2906 ± 48	777 ± 28	168 ± 9	59 ± 8	573 ± 22	17.0 ± 1.3
Recovery (%)		94.6	92.7	85.7	84.2	94.1	90.4
CRM (found)	B	3031 ± 52	818 ± 21	188 ± 13	66 ± 7	590 ± 12	18.1 ± 0.8
Recovery (%)		99.0	97.6	95.9	95.1	96.9	96.2
CRM (found)	C	2791 ± 55	713 ± 26	165 ± 22	56 ± 9	561 ± 24	16.6 ± 1.6
Recovery (%)		91.2	85.1	84.2	80.0	92.1	88.3
CRM (found)	D	2803 ± 43	702 ± 16	159 ± 19	58 ± 8	549 ± 20	16.9 ± 2.1
Recovery (%)		91.6	83.7	81.1	82.8	90.1	89.9

ranged from $0.3 \mu\text{g l}^{-1}$ to $17 \mu\text{g l}^{-1}$ and LOQ values from $1 \mu\text{g l}^{-1}$ to $37 \mu\text{g l}^{-1}$ for open system digestion.

3.3. Analysis of real samples

The development method for both microwave assisted digestion and open system digestion were applied for analysis of two

different composts (Sample 1 and 2) as shrimp aquaculture sludge compost by atomic absorption spectrometry. The mean concentration of each element studied have is shown in Tables 5 and 6.

3.3.1. Microwave assisted digestion method

The elemental concentration of six metals measured in shrimp aquaculture sludge compost using microwave assisted digestion

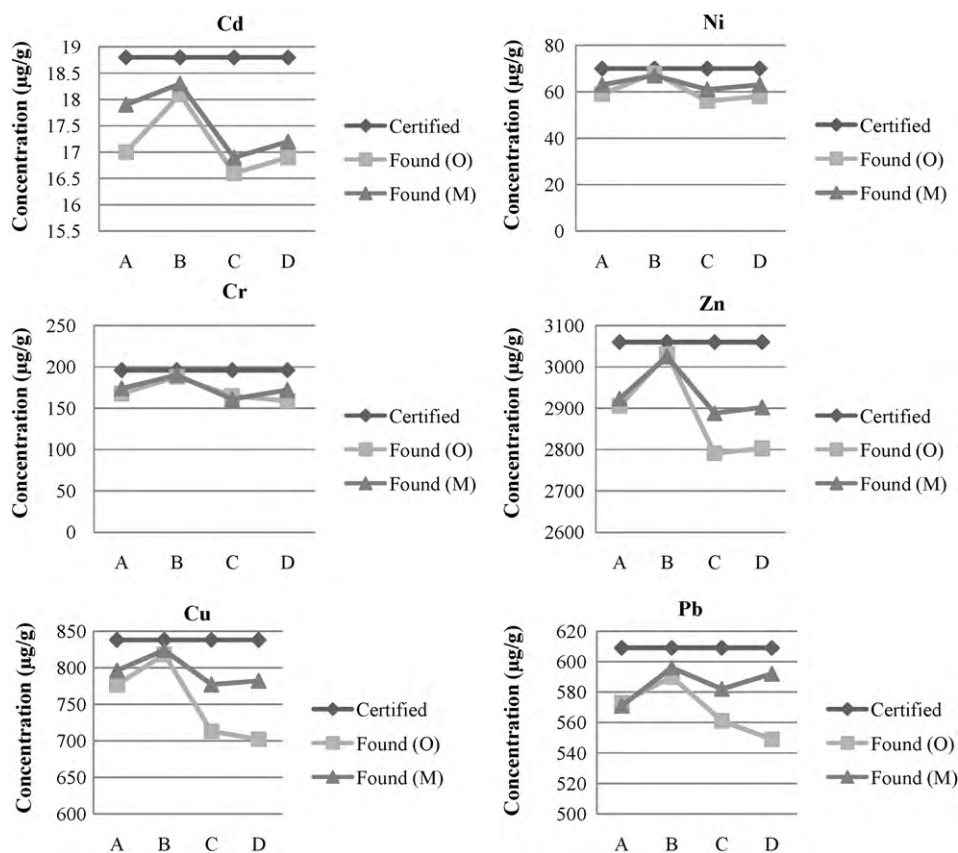


Fig. 1. Comparison between microwave assisted digestion and open system digestion methods for the mean concentration of metals (Cd, Ni, Cr, Zn, Cu and Pb) in CRM BCR 146.

Table 4
Limits of detection and quantitation (LOD/LOQ; $\mu\text{g l}^{-1}$) for HNO_3 – HCl – HF mixture using microwave assisted digestion and open system digestion methods.

HNO_3 – HCl – HF	Zn	Cu	Cr	Ni	Pb	Cd
Microwave assisted digestion	14/33	2/7	11/26	4/13	9/21	0.3/1
Open system digestion	17/37	2/6	10/29	6/15	11/24	0.3/1

with different volumes of reagents were found in the range of 271–373 $\mu\text{g g}^{-1}$ for sample 1 and 267–352 $\mu\text{g g}^{-1}$ for sample 2 (Zn), 13–17 $\mu\text{g g}^{-1}$ for sample 1 and 13–20 $\mu\text{g g}^{-1}$ for sample 2 (Cu), 60–89 $\mu\text{g g}^{-1}$ for sample 1 and 52–82 $\mu\text{g g}^{-1}$ for sample 2 (Cr), 20–37 $\mu\text{g g}^{-1}$ for sample 1 and 16–32 $\mu\text{g g}^{-1}$ for sample 2 (Ni), 166–216 $\mu\text{g g}^{-1}$ for sample 1 and 155–202 $\mu\text{g g}^{-1}$ for sample 2 (Pb), 7.1–9.3 $\mu\text{g g}^{-1}$ for sample 1 and 6.7–8.8 $\mu\text{g g}^{-1}$ for sample 2 (Cd), respectively (refer Table 6).

3.3.2. Open system digestion

In this digestion system, the concentrations of trace elements by using different solvents were analyzed (refer Table 6). Although, the recoveries obtained for all trace elements in method B of open system digestion were similar to microwave assisted digestion, however the percentage recoveries in the microwave were better. The concentration of trace elements were in the range of 281–335 $\mu\text{g g}^{-1}$ for sample 1 and 263–302 $\mu\text{g g}^{-1}$ for sample 2 (Zn), 13–19 $\mu\text{g g}^{-1}$ for sample 1 and 11–16 $\mu\text{g g}^{-1}$ for sample 2 (Cu), 56–78 $\mu\text{g g}^{-1}$ for sample 1 and 51–67 $\mu\text{g g}^{-1}$ for sample 2 (Cr), 21–33 $\mu\text{g g}^{-1}$ for sample 1 and 17–31 $\mu\text{g g}^{-1}$ for sample 2 (Ni), 153–197 $\mu\text{g g}^{-1}$ for sample 1 and 155–182 $\mu\text{g g}^{-1}$ for sample 2 (Pb), 6.8–8.2 $\mu\text{g g}^{-1}$ for sample 1 and 6.0–7.9 $\mu\text{g g}^{-1}$ for sample 2 (Cd), respectively. The concentration of Cd, Pb and Zn are found higher than the world soil mean values [48] but in comparison with allowable concentrations of trace metals considered in agriculture soil by the European Community [18], except Cd. A remediation should be taken to remove such metal for sustainable practices in agriculture. The results obtained in this work revealed that the concentration of trace elements in sample 1 is mostly higher than sample 2 in both method digestions, suggesting the sources of the metals were mostly obtained from the sludge itself and not from other materials (crushed bark, husk, coco peat and animal manure) used for the composting.

Table 5
Mean concentration of metals with different solvent using microwave assisted system digestion ($\mu\text{g g}^{-1}$).

	Method	Zn	Cu	Cr	Ni	Pb	Cd
Sample 1	A	343 ± 26	17 ± 1.0	86 ± 15	32 ± 8	207 ± 15	7.2 ± 1.3
Sample 1	B	373 ± 14	21 ± 2.6	89 ± 9	37 ± 12	216 ± 21	9.3 ± 1.1
Sample 1	C	277 ± 12	13 ± 1.1	62 ± 15	20 ± 5	171 ± 26	7.1 ± 0.5
Sample 1	D	271 ± 22	14 ± 1.3	60 ± 15	23 ± 8	166 ± 18	7.3 ± 0.7
Sample 2	A	330 ± 19	16 ± 1.2	80 ± 14	28 ± 6	191 ± 21	6.8 ± 0.6
Sample 2	B	352 ± 23	20 ± 2.5	82 ± 14	32 ± 9	202 ± 19	8.8 ± 0.2
Sample 2	C	270 ± 17	13 ± 2.2	52 ± 10	18 ± 6	159 ± 16	6.7 ± 0.5
Sample 2	D	267 ± 14	13 ± 1.5	54 ± 11	16 ± 5	155 ± 25	6.9 ± 0.3

Table 6
Mean concentration of metals with different solvent ratio used in open system digestion method ($\mu\text{g g}^{-1}$).

	Method	Zn	Cu	Cr	Ni	Pb	Cd
Sample 1	A	333 ± 17	17 ± 1	69 ± 11	30 ± 6	178 ± 26	7.4 ± 0.6
Sample 1	B	335 ± 18	19 ± 2	78 ± 13	33 ± 9	197 ± 22	8.2 ± 1.1
Sample 1	C	281 ± 17	13 ± 2	56 ± 13	21 ± 4	159 ± 28	6.8 ± 0.3
Sample 1	D	285 ± 22	13 ± 1	58 ± 17	24 ± 7	153 ± 20	7.1 ± 0.5
Sample 2	A	301 ± 21	16 ± 2	63 ± 10	31 ± 5	162 ± 20	7.5 ± 0.8
Sample 2	B	322 ± 16	16 ± 2	67 ± 7	29 ± 6	182 ± 14	7.9 ± 0.9
Sample 2	C	266 ± 18	11 ± 1	51 ± 8	18 ± 4	155 ± 17	6.1 ± 0.6
Sample 2	D	263 ± 22	11 ± 1	53 ± 10	17 ± 6	159 ± 15	6.0 ± 0.9

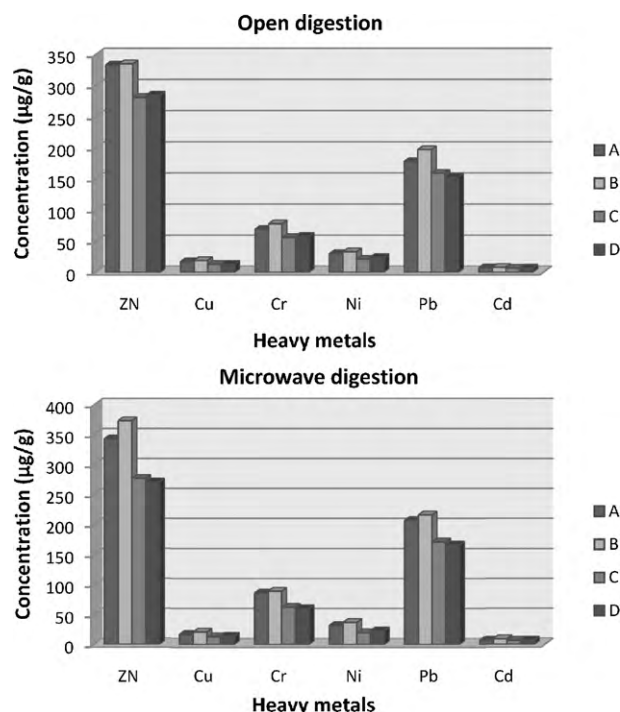


Fig. 2. Effects of different solvent volume and systems digestion on elements concentration in sample 1. (A) 6 ml HNO_3 + 1 ml HCl + 1 ml HF ; (B) 6 ml HNO_3 + 2 ml HCl + 2 ml HF ; (C) 1 ml HNO_3 + 6 ml HCl + 1 ml HF ; (D) 2 ml HNO_3 + 6 ml HCl + 2 ml HF . Sample 1: the ratio of 1 (shrimp sludge): 4 (crushed bark and husk): 0.5 animal manure (w/w).

The source of water used for the shrimp aquaculture should be monitored and treated at the early stage of breeding process (from irrigated or storage pond) in order to decrease the level of heavy metals in sludge during the harvest period [6]. The texture of the soil used (sandy of peat) for the aquaculture activities also will contribute to the high level of the heavy metals in the shrimp sludge [6].

Our previous studies showed that shrimp sludge contained significantly high level of zinc, calcium, nitrate and phosphate, indi-

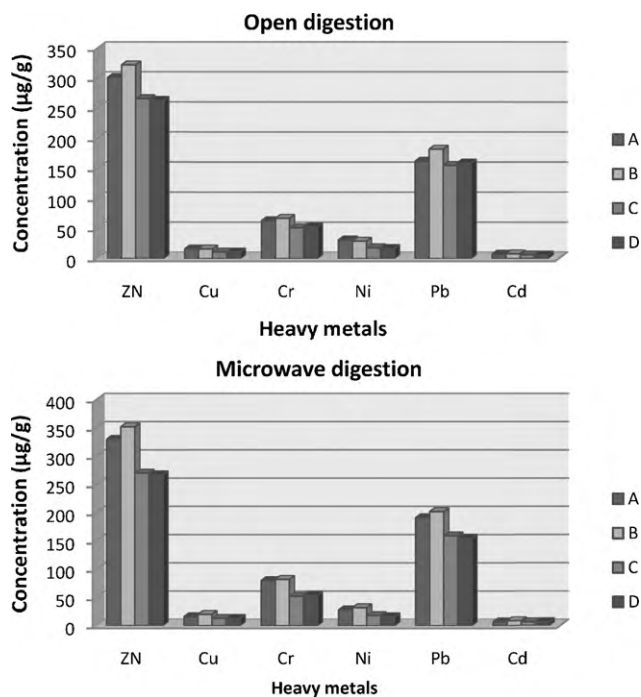


Fig. 3. Effects of different solvent volume and systems digestion on elements concentration in sample 2. (A) 6 ml HNO_3 + 1 ml HCl + 1 ml HF ; (B) 6 ml HNO_3 + 2 ml HCl + 2 ml HF ; (C) 1 ml HNO_3 + 6 ml HCl + 1 ml HF (D) 2 ml HNO_3 + 6 ml HCl + 2 ml HF . Sample 2: the ratio of 1 (compost shrimp sludge): 1 (coco peat waste).

cating that the remediation sludge waste has a potential to be used as an organic medium for growing crop especially for rubber plantation or other fruitless crop [6]. At the same time, it will solve the problem related to disposal of shrimp sludge from aquaculture pond.

Effects of different solvent volume and systems digestion on elements concentration for both samples have been shown in Figs. 2 and 3.

Comparison between two digestion methods with different volumes of acid mixture (HCl – HNO_3 – HF) revealed that method B included of 6 ml HNO_3 , 2 ml of HCl and 2 ml of HF was the best acid mixture used in both microwave and open system digestions methods for the compost samples analyzed by AAS in this work. Also open system digestion takes 16 h for complete reflex digestion whereas, microwave assisted system takes less than 75 min.

4. Conclusion

Total trace (Zn, Cu, Cr, Ni, Pb and Cd) element concentrations in two different composts containing shrimp aquaculture were determined using microwave assisted digestion and open system digestion procedures with AAS analysis. Four different digestion procedures using various HCl , HNO_3 and HF combinations and volumes were tested for both samples.

The results obtained for trace elements recoveries (Zn, Cu, Cr, Ni, Pb and Cd) of the certified material (BCR 146-R) using microwave acid digestion yield a recovery of 88.7–95.5%, 95.7–98.8%, 82.1–95.65% and 87.7–97.2% for procedures A–D, respectively. Good results were observed in both systems digestion. Nevertheless, the recoveries obtained for all elements in microwave assisted digestion were better compared to open system digestion with HNO_3 – HCl – HF ratios of 6:2:2 for both systems digestion. This was further confirmed by derived from shrimp sludge compost samples.

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