

A Comparison of ICP-OES and UV-Vis Spectrophotometer for Heavy Metals Determination in Soil Irrigated with Secondary Treated Wastewater

Ali, M.F and Shakrani, S. A.

Faculty of Civil Engineering, Universiti Teknologi MARA (UiTM), Malaysia
mohdfozi@salam.uitm.edu.my, shahrulazwan.shakrani@gmail.com

Abstract— The concentrations of selected heavy metals such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in soil irrigated with secondary treated wastewater were determined by means of ICP-OES and UV-Vis Spectrophotometer after combined acid wet digestion. The results revealed that heavy metals concentrations of secondary treated wastewater were significantly higher in the FSTW as compared to the BSTW suggested that seasonal variations and efficiency of the treatment system affected the wastewater quality. Besides, the heavy metals characteristics of soil irrigated with secondary treated wastewater were found to be relatively higher in the SPS as compared to the SEPS suggesting that cross sectional area of soil affected the accumulation of macronutrients and trace elements. Meanwhile, the comparative study between ICP-OES and UV-Vis spectrophotometer for detection of heavy metals in soil irrigated with secondary treated wastewater demonstrated the higher trends of heavy metals levels obtained in UV-Vis spectrophotometer as compared to ICP-OES suggesting that lots of interferences with other elements during analysis under UV-Vis spectrophotometer. Thus, ICP-OES is recommended for analysis of soil irrigated with secondary treated wastewater as the ICP-OES was found suitable for analysis of elements in soils with good accuracy due to high sample throughput capacity, rapid multielement characteristics, varies detection limits makes it suitable for this kind of application while HACH DR5000 UV-Vis Spectrophotometer was suggested to have better functionality towards water than soil analysis.

Index Term— ICP-OES, heavy metals, secondary treated wastewater, soil, UV-Vis spectrophotometer.

I. INTRODUCTION

THE reuse of secondary treated wastewater for irrigation is believed to provide the water resources optional as freshwater has no guarantee sufficient. However, the secondary treated wastewater is always contaminated and possible present of trace elements, particularly heavy metals, although after have

been through the treatment process. Heavy metals are detrimental and often associated with

environmental issues and health problems to the plants, animals and humans. Generally, there are two major sources of heavy metals, namely natural and anthropogenic. Heavy metals occur naturally in soils, but human activities lead to greater levels of heavy metals contamination in soils and to the environment. Kabata-Pendias [1] revealed that Ag, Au, Cd, Cr, Hg, Mn, Pb, Sb, Sn, Te, W, and Zn are among potentially most hazardous trace metals to the biosphere while Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn are considered to be of great risk to environmental health. Thus, proper assessment of the environmental status of heavy metals is very important in order to minimize contamination, though proper sampling and analysis as well as appropriate analytical methods [2].

The process of determination of heavy metals in soils requires matrix destruction which depends on the dissolution processes and digestion technique was performed through decomposition of complex substance into simple salts and volatile gases under soluble acid solution [3, 4]. There are many techniques introduced for digestion procedures such as dry, wet and microwave. Both dry and wet digestions, are slow and time consuming, whereas microwave digestion is much more rapid and low consumption of time and reagents [5]. In recent years, combined wet digestion has been introduced to enhance the dissolution process for a short period of time, which provides the greater recovery as compared to single wet digestion technique [6].

In combined analytical methods, the decomposition of solid samples is an important stage whereby the sample is measured in an aqueous solution and by means of highly sensitive techniques such as Flame Atomic Absorption Spectrophotometer (FAAS), Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Optical Mass Spectrometry (ICP-

M. F. Ali is with the Division of Water Resources and Environmental Systems, Faculty of Civil Engineering, Universiti Teknologi MARA (UiTM), 40450, Shah Alam, Selangor, Malaysia. (e-mail: mohdfozi@salam.uitm.edu.my).

S. A. Shakrani is with the Faculty of Civil Engineering, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia. (e-mail: shahrulazwan.shakrani@gmail.com).

MS) [7, 4]. These combined analytical methods are favoured for multi element analysis of samples at very short period. Previously, the calorimetric method was introduced for the analysis of samples along with UV-Vis spectrophotometer measurement which is considered as a low tech instrument. Yet, there is little comparative information available between combined analytical methods, particularly between ICP-OES and calorimetric method assisted by UV-Vis spectrophotometer. In this study, the levels of selected heavy metals concentrations in soil samples irrigated with secondary treated wastewater were determined by both ICP-OES and UV-Vis spectrophotometer after combined acid wet digestion.

II. MATERIALS AND METHODS

A. Wastewater and Soil Sampling

The final secondary treated wastewater (FSTW) and biological secondary treated wastewater (BSTW) used for irrigation was collected six times from Mawar Wastewater Treatment Plant located at Universiti Teknologi MARA (UiTM) Shah Alam, Malaysia. This wastewater treatment plant consists of screening, grit removal, primary sedimentation and conventional activated sludge treatment process with a population equivalent of 11 000. The wastewater sampling was conducted in accordance with APHA *et al.* [8], BS EN ISO 5667:1 [9], BS EN ISO 5667:3 [10] and BS 6068:6.10 [11]. For both types of wastewater, about 1 litre of samples was taken into polypropylene sampling bottles and later transferred to the laboratory for analysis. The wastewater was preserved with concentrated nitric acid (pH<2) to prevent any microbial degradation of heavy metals and stored in a refrigerator at about 4 °C in order to prevent any possible change in volume due to evaporation.

The mustard greens (*Brassica campestris Sp. parachinensis*) were planted on the experimental plot (SEPS) located at the Faculty of Plantation and Agrotechnology, UiTM as well as polybag soil (SPS) located at Mawar Wastewater Treatment Plant, UiTM. Both experimental plot and polybags soil were watered seven days per week with FSTW and BSTW. The soil sampling was conducted in accordance with BS ISO 10381:1 [12], BS ISO 10381:2 [13] and ASTM D5633 [14]. Six samples of top soil at 15 cm depth were manually collected from centre of experimental plot and polybag soil with clean stainless steel trowel of 8 cm diameter. At least 500 g of soil were collected and transported into polyethylene containers. Samples were later transferred to the laboratory together with label and sealed. The details of the experiments were adopted from Ali and Shakrani [15].

B. Instrumentation Details and Calibration

A Thermo Scientific iCAP 6000 Series ICP-OES (Thermo Fisher Scientific, Cambridge, UK) was used in this study to determine of selected heavy metals such as Cd, Cr, Co, Cu, Fe,

Pb, Mn, Ni and Zn in soil irrigated with secondary treated wastewater. Details of the instrument and operating conditions for ICP-OES were described in Table I.

TABLE I
Instrumental Details and Operating Conditions for ICP-OES Thermo Scientific iCAP 6000 Series

Subject	Descriptions
Pump tubing	Orange/white tygon sample White/white tygon drain
Pump rate	50 rpm
Nebulizer	Standard concentric
Nebulizer argon flow rate	0.6L/min or 0.22MPa
Spray chamber	Standard cyclonic
Centre tube	2.0mm
Torch orientation	Duo
RF forward power	1150 W
Auxiliary flow	0.5 L/min
Integration times	
High wavelengths	5 seconds
Low wave lengths	15 seconds
Replicates	3

The digested samples of soil and plant as well as wastewater samples were simultaneously prepared with a blank sample contains of distilled water through the complete procedure, analyzed and then used for correction of the analytical signals. Working standard solutions were prepared by suitable dilution (0.25, 0.5, 1, 3, and 5 ppm) of the ICP multi-element standard solution supplied by Merck Millipore (Darmstadt, Germany). In this stage, calibration was performed with a blank and standard solution samples and detection limits (LOD) were determined with a standard deviation of blank solutions. The ranges of the calibration curves were selected to match the expected concentrations of all the elements of the sample studied. The analytical characteristics of heavy metals by ICP-OES were listed in Table II with demonstrated the detection limits and wavelengths.

TABLE II
The Analytical Characteristics of Heavy Metals by ICP-OES

Element	Detection Limit (µg/L)	Wavelength (nm)	References
Cd	>0.01 and ≤0.1	214.438	[8]
Cr	>0.01 and ≤0.1	205.552	[8]
Co	>0.1 and ≤1	230.786	[8]
Cu	>0.1 and ≤1	324.754	[8]
Fe	>0.1 and ≤1	271.441	[8]
Pb	>0.1 and ≤1	220.353	[8]
Mn	>0.01 and ≤0.1	257.610	[8]
Ni	>0.1 and ≤1	231.604	[8]
Zn	>0.01 and ≤0.1	213.856	[8]

As a comparison, the HACH DR5000 UV-Vis Spectrophotometer [16] (Hach, Colorado, USA) was also used for detection of heavy metals such as Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn in wastewater and soil samples. The specifications of HACH DR5000 UV-Vis Spectrophotometer instrument were described in Table III.

TABLE III
The Instrumental Specifications for HACH DR 5000 UV-Vis Spectrophotometer

Subject	Descriptions
Operating Mode	Transmittance (%), Absorbance and Concentration
Source Lamp	Tungsten (VIS) and Deuterium (UV)
Wavelength Range	190 to 1100 nm
Wavelength Accuracy	± 1 nm in wavelength range 200 to 900 nm
Wavelength Resolution	0.1 nm
Wavelength Calibration	Automatic
Wavelength Selection	Automatic, based on selected program method
Scanning Speed	900 nm/min in 1 nm steps; 1 complete scan/1 min
Spectral bandwidth	2 nm
Photometric Measuring Range	± 3 Abs in the wavelength range 200 to 900 nm
Photometric Accuracy	5 mAbs at 0.0-0.5 Abs, 1 % at 0.50-2.0 Abs
Photometric Linearity:	< 0.5 % up to 2 Abs, ≤ 1 % at > 2 Abs
Stray Light	KI-solution at 220 nm > 3.3 Abs or < 0.05%
Sample Cell Compatibility	1-in. square; 1-in. round; 1x1, 2x1, 5x1, 10x1 cm; 13 mm round; 16 mm round; 1 cm, 5 cm, and 1-in. Pour-Thru Cells; AccuVac Ampules
Operating Temperature Range	10 to 40 °C at 95% Relative Humidity (non-condensing)
Storage Conditions	-40 °C to 60 °C ; 80% Relative Humidity
Power Requirements	100 V - 120 V, 50 - 60 Hz, 100 - 240 V AC
Optical System	Split Beam

For calibration, the standard additional (sample spike) and standard solution samples were prepared and measured by HACH DR5000 UV-Vis Spectrophotometer. The brief procedures for calibration can be referred in HACH Company [16]. The analytical descriptions such as detection limits and wavelengths were presented in Table IV while the precision and sensitivity analysis were presented in Table V.

TABLE IV
The Analytical Characteristics of Heavy Metals by HACH DR 5000 UV-Vis Spectrophotometer

Element	Method	Detection Limit (mg/L)	Wave length (nm)	References
Cd	Dithizone	0 to 80.0 µg/L	515	[8]
Cr	1, 5-Diphenylcarbohydrazide	0.010 to 0.700	540	[8]
Co	1-(2-Pyridylazo)-2-Naphthol (PAN)	0.01 to 2.00	620	[17]
Cu	Bicinchoninate	0.04 to 5.00	560	[18]
Fe	FerroVer®	0.02 to 3.00	510	[8]
Pb	Dithizone	3 to 300 µg/L	515	[8]
Mn	1-(2-Pyridylazo)-2-Naphthol (PAN)	0.006 to 0.700	560	[20]
Ni	1-(2-Pyridylazo)-2-Naphthol (PAN)	0.006 to 1.000	620	[17]
Zn	Zincon	0.01 to 3.00	620	[8]

TABLE V
The Precision and Sensitivity Analysis of Heavy Metals Characteristics by HACH DR 5000 UV-Vis Spectrophotometer

Element	Precision		Sensitivity
	Standard Solution	95% Confidence Limits of Distribution	ΔConcentration
Cd	40.0 µg/L Cd	39.3–40.7 µg/L Cd	0.73 µg/L Cd
Cr	0.500 mg/L Cr ⁶⁺	0.497–0.503 mg/L Cr ⁶⁺	0.005 mg/L Cr ⁶⁺
Co	1.00 mg/L Co	0.99–1.01 mg/L Co	0.01 mg/L Co
Cu	1.00 mg/L Cu	0.97–1.03 mg/L Cu	0.04 mg/L Cu
Fe	2.00 mg/L Fe	1.99–2.01 mg/L Fe	0.021 mg/L Fe
Pb	150 µg/L Pb	140–160 µg/L Pb	2.3 µg/L Pb
Mn	0.500 mg/L Mn	0.491–0.509 mg/L Mn	0.006 mg/L Mn
Ni	0.500 mg/L Ni	0.492–0.508 mg/L Ni	0.006 mg/L Ni
Zn	1.00 mg/L Zn	0.97–1.03 mg/L Zn	0.013 mg/L Zn

Note: Portion of Curve=Entire range, ΔAbs=0.010

C. Reagents and Glassware

All reagents were prepared using water previously deionized with PURELAB Option-Q (ELGA Labwater, UK). Analytical reagents-grade chemicals were used in the preparation of all solution. The sulphuric acid (65%) was purchased from Mallinckordt Chemicals Inc. (St. Louis, MO, USA) while chloroform (65%), nitric acid (65%) and hydrogen peroxide (50%) were obtained from Merck Schuchardt OHG (Hohenbrunn, Germany). The ICP multi elements standard solution was supplied by Merck Millipore (Darmstadt, Germany). All reagents used to perform the calometric method and by means of Hach DR 5000 UV-Vis Spectrophotometer was obtained from Hach Company (Colorado, USA). All glassware and plastic materials used were soaked into 10% of nitric acid for 24 hours and rinsed with double distilled water and then with deionized water.

D. Acid Wet Digestion

The wet digestion of soil samples was conducted using HACH Digesdahl Digestion Apparatus [21]. This method was introduced by Jones and Case [22] and later prescribed by Brayton [3] as Piranha Clean Method (also known as Vigreux Method) where a mixture of sulphuric acid and hydrogen peroxide were initiated [4, 23]. This procedure was performed after preparation of samples. After oven-dried at 70 °C for 48 h to remove all moisture, soil samples were ground became the fine powder by using a mortar and pestle. The samples were later sieved and passed through 2 mm mesh sieve.

Then, 0.25 to 0.5 g of each soil samples were accurately weighted by analytical weighing balance (A & D Company Limited, Tokyo Japan) into 100 mL digesdahl digestion flask. Then, 4 to 6 mL of concentrated sulphuric acid was added to the digestion flask. The sample was then heated and boiled at 440 °C (825 °F) for 4 minutes. Afterwards, 10 to 20 mL of 50 % hydrogen peroxide was added to the flask via the funnel. The sample was then continued heated for one more minute. After that, the digested sample was diluted to approximately 70 mL with 18 Ω demonized water. After cooling, the sample was filtered through a Whatman No.41 filter paper into a 100 mL volumetric flask pre-washed with 10 % concentrated

HNO₃. Later, samples were further filtered through a 0.5 µm polytetrafluoroethylene (PTFE) membrane (Whatman Ltd, UK).

E. Statistical Analysis

The data were statistically analyzed using the SPSS version 17 software with a significance level of $P < 0.05$. All collected data carried out were subjected to one way analysis of variance (1 Way - ANOVA).

III. RESULTS AND DISCUSSION

A. A Comparison of Heavy Metals Characteristics of Secondary Treated Wastewater by Using ICP-OES and HACH DR5000 UV-Vis Spectrophotometer

The heavy metals characteristics of FSTW and BSTW studied with ICP-OES and UV-Vis spectrophotometer are presented in Table VI. In general, the heavy metals concentrations of secondary treated wastewater were significantly higher in FSTW as compared to BSTW suggested that seasonal variations and efficiency of the treatment system affected the wastewater quality. Al-Absi *et al.* [24] explained that treated wastewater contained lower levels of the mineral during rainfall due to dilution effect. The failure to properly treat and manage wastewater for irrigation purposes may generate adverse health effects [25].

TABLE VI
Heavy Metals Characteristics of FSTW and BSTW by Means of ICP-OES and UV-Vis Spectrophotometer

Element (mg/L)	ICP-OES		UV-Vis Spectrophotometer	
	FSTW	BSTW	FSTW	BSTW
Cd	ND	ND	0.005±0.001	0.006±0.001
Co	ND	ND	0.040±0.013	0.100±0.013
Cr	0.011±0.004	0.010±0.001	0.042±0.001	0.039±0.002
Cu	0.103±0.007	0.027±0.008	0.855±0.049	0.565±0.012
Fe	0.260±0.047	0.465±0.031	1.026±0.012	1.197±0.091
Mn	0.078±0.002	0.069±0.008	0.073±0.002	0.064±0.001
Ni	0.007±0.001	0.006±0.001	0.024±0.001	0.013±0.002
Pb	0.019±0.005	0.011±0.003	0.023±0.002	0.016±0.001
Zn	1.029±0.134	1.122±0.058	0.197±0.010	0.230±0.026

Note: Each data represents the mean of 6 values ± the standard deviation. ND= none detected

The lowest and highest of Cd concentrations were found at 0.005 mg/L for FSTW and 0.006 mg/L for BSTW. Meanwhile, the lowest and highest levels of Co were found at 0.04 mg/L for FSTW and 0.1 mg/L for BSTW. The lowest of Cr contents was found at 0.01 mg/L for BSTW whereas the highest content of Cr was found at 0.042 mg/L for FSTW. The concentrations of Cu were found at 0.027 mg/L for FSTW and 1.197 mg/L for BSTW as lowest and highest values. Besides, the lowest and highest values of Fe were recognized at 0.26 mg/L for FSTW and 1.197 mg/L for BSTW. The concentrations of Mn were found at 0.064 mg/L for BSTW as the lowest and 0.078 mg/L for FSTW as the highest. Both Ni and Pb concentrations were found lowest in BSTW at 0.006 mg/L and 0.011 mg/L while

highest in FSTW at 0.024 mg/L and 0.023 mg/L. The contents of Zn were detected at 0.197 mg/L in FSTW and 1.122 mg/L in BSTW as lowest and highest. In general, most of characteristics of FSTW and BSTW were found within the allowable limit regulated by Malaysia Environmental Quality Act 2009 [26], World Health Organization [27], Food and Agriculture Organization of the United Nations [28] and United States Environmental Protection Agency [29].

The concentrations of heavy metals in both FSTW and BSTW were resulted from the used of cleaning products together with personal and body care products as well as pipes and fittings [30, 31, 32]. The low range of Cd in secondary treated wastewater resulted from an impurity in galvanized pipes and fitting along with contaminant used of phosphate in detergent and washing powder. Besides, shampoos and cosmetics product along with hand wash also contributed to the sources of Cd in wastewater. The low concentrations of Co in wastewater were caused from the availability of Co in sewage sludge (biosolids) as well as food products. Meanwhile, the low concentrations of Cr found in wastewater were due to corrosion of welded metals and stainless steel in piping systems, fittings and taps. The Cu concentrations availability in secondary treated wastewater was determined from the corrosion of copper pipes and leaching of plumbing. Moreover, cosmetics and shampoo products had also added the Cu concentrations in secondary treated wastewater. Iron pipes contributed to the high sources of Fe in wastewater. Besides, cleaning and personal products, including toothpaste had also contributed to high level of Fe in wastewater. The sources of Mn in wastewater are usually derived from sewage sludge as well as cast iron and steel objects such storage tanks, piping and pumps. Low concentrations of Ni were resulted from rechargeable batteries, metal coated and galvanized pipes and fittings. Besides, Ni concentrations found in wastewater were due to the used of deodorants, toothpaste, conditioners, hand wash, body wash and shampoo. The lower level of Pb in secondary treated wastewater was resulted from toilet paper, toilet refreshers, dishwashing tablets, personal care products for instance mouthwash, hair conditioner and toothpaste, detergent as well as laundry. High concentrations of Zn in wastewater were resulted from galvanized iron pipe and fitting, personal and body care product such as deodorant, shampoo as well as cosmetic.

The analysis of variance (ANOVA) performed at 95% confidence intervals indicated all of the F-value and P-value to determine if there was any significant difference between means of heavy metals concentrations for both secondary treated wastewater effluents studied. Most of the parameters demonstrated the p-value was less than 0.05 which rejected the null hypothesis of the study as shown in Table 7. Thus, the quality of both secondary treated wastewater effluents was found to be relatively significant in most of heavy metals studied.

TABLE VII
Analysis of Variance at 95% Confidence Intervals for Secondary Treated Wastewater

Element	Analysis of Variances (ANOVA)		
	F Value	P Value	Significance Level ns= P _{value} >0.05 * = P _{value} <0.05
Cd	260.862	0.000	*
Co	111.667	0.000	*
Cr	382.160	0.000	*
Cu	1374.486	0.000	*
Fe	414.458	0.000	*
Mn	11.892	0.000	*
Ni	255.611	0.000	*
Pb	14.744	0.000	*
Zn	270.304	0.000	*

Note: *=statistically significance, ns= statistically not significance

Meanwhile, the heavy metals characteristics for both secondary treated wastewater effluents were found to be higher in the analysis of sampling by means of HACH method as compared to ICP-OES. The percentage difference between results obtained from HACH method and ICP-OES analysis for Cr 73.809% to 74.359 %, Cu 87.953% to 95.221%, Fe 61.153% to 74.659%, Mn 6.410% to 7.246%, Ni 53.846% to 70.833%, Pb 17.391% to 31.250%, and Zn 79.501% to 80.855%. However, there was no percentage difference between results obtained from HACH method and ICP-OES for Cd and Co since these elements were not detected in samples by ICP-OES.

In general, HACH method is based on the reaction of gases with some chemical agents to form a coloured complex, the intensity of the colour is measured electronically to calculate the concentrations of macronutrients and trace elements in wastewater samples [33]. Meanwhile, the ICP technique uses the plasma to ionise components, whereby the sample is acidified and sprayed into the plasma, then the high temperature of the plasma atomises and ionises all forms of element so that the response does not vary within species, and mostly used in conjunction with other analytical techniques such OES, AES and MS [34].

Previously, Wellborn [35] conducted the study on the comparison between HACH and ICP-MS for detection of As levels in water samples and discovered that higher trends of As concentrations obtained with the HACH method as compared to ICP-MS. Most ions and elements in HACH method were believed to interfere with S²⁻, Se, antimony (Sb), tellurium (Te), CaCO₃ and Fe and resulted in inconsistency values by HACH method as compared to ICP-MS.

Besides, Geen *et al.* [36] compared the characteristics of AS obtained from groundwater with HACH method and ICP-MS and discovered the inconsistencies of HACH method as compared to ICP-MS. The inconsistencies in the HACH method mainly underestimate in the range of 50 to 100µg/L [36, 37]. In addition, Tyrell *et al.* [38] examined the concentrations of Pb in paint by means of X-Ray Diffraction

(XRD), ICP and HACH colorimetric analysis and discovered the concentration of Pb ranges from 0.004 to 10.8 weight percent by HACH colorimetric analysis while varies between 1.05 to 2.67 weight percent by means of XRD. It was suggested that Pb paint weathers it hydrates and transformed from Pb oxides and carbonates to hydrated Pb compounds. However, Pearson's correlation coefficient performed for the data indicates good correlation ($r^2=0.97$) between analysis by HACH colorimetric and ICP and suggested that HACH colorimetric provides a rapid digestion method for Pb analysis of the field-test study.

Thus, multielement analytical capabilities of ICP-OES make it ideal tools for processing multiple analysis of large numbers of samples quickly and efficiently. The combination of low detection limits and wide analytical concentrations make it well suitable to analyze of the low to moderate concentrations of many elements, particularly for water sample analysis [39]. Therefore, it was suggested that the uses of ICP-OES for analysis of wastewater samples particularly for analysis of heavy metals characteristics while HACH DR5000 Uv-Vis Spectrophotometer could be used for analysis of macronutrients characteristics such N, P and K.

B. A Comparison of Heavy Metals Characteristics of Different Sample of Soil Irrigated with Secondary Treated Wastewater by Using ICP-OES and HACH DR5000 UV-Vis Spectrophotometer

The heavy metals characteristics of the soil before and after irrigated with FSTW and BSTW are presented in Table 8. In most cases, the heavy metals levels in soil irrigated with FSTW and BSTW were found to be relatively higher in SPS as compared to SEPS suggesting that cross sectional area of soil affected the accumulation of macronutrients and trace elements. SPS was likely to accumulate a greater level of heavy metals in soils due to the smaller cross sectional area as compared to the SEPS. Besides, the accumulation of heavy metals was slightly higher on the top and reduced as it went deeper. However, the concentrations of Cr, Fe, Mn, Ni, Pb and Zn in soils were decreased after irrigated with FSTW and BSTW. Only Cd, Co and Cu levels were increased in soils after irrigated with FSTW and BSTW.

The lowest and highest concentrations of heavy metals in soil irrigated with FSTW and BSTW were found at 0.002 mg/L and 0.03 mg/L for Cd; 0.03 mg/L and 0.04 mg/L for Co; 0.03 mg/L and 0.18 mg/L for Cr; 0.05 mg/L and 2.21 mg/L for Cu; 0.55 mg/L and 105.84 mg/L for Fe; 0.04 mg/L and 0.24 mg/L for Mn ; 0.01 mg/L and 0.03 mg/L for Ni; 0.01 mg/L and 0.08 mg/L for Pb ; and 0.09 mg/L and 0.58 mg/L for Zn. However, most of the parameters were recognized to meet the maximum permissible limits as reported in Pedrero and Alarcon [25].

TABLE VIII
Heavy metals characteristics of soil before and after irrigated with FSTW and BSTW

Element (mg/L)	ICP-OES					UV-Vis Spectrophotometer				
	Before	FSTW		BSTW		Before	FSTW		BSTW	
		SEPS	SPS	SEPS	SPS		SEPS	SPS	SEPS	SPS
Cd	0.003 ±0.002	0.02±0.00	0.03±0.002	0.03±0.00	0.03±0.00	0.002±0.0	0.02±0.00	0.03±0.00	0.03±0.00	0.03±0.00
Co	ND	ND	ND	ND	ND	0.03±0.01	0.04±0.01	0.04±0.01	0.04±0.01	0.04±0.01
Cr	0.18±0.03	ND	0.04±0.04	ND	ND	0.18±0.02	0.03±0.00	0.06±0.01	0.03±0.00	0.08±0.00
Cu	0.05±0.02	1.46±0.02	2.01±0.63	1.45±0.01	2.21±0.42	0.08±0.01	1.10±0.05	1.83±0.41	1.07±0.03	1.79±0.52
Fe	105.84±14.35	0.55±0.02	44.82±16.34	0.56±0.01	1.88±0.82	6.85±0.26	3.70±0.02	6.18±0.07	3.49±0.03	5.83±0.08
Mn	0.21±0.06	ND	0.04±0.05	ND	ND	0.24±0.01	0.09±0.01	0.12±0.01	0.09±0.01	0.09±0.01
Ni	0.03±0.01	0.01±0.00	0.02±0.00	0.01±0.00	0.01±0.00	0.03±0.00	0.01±0.00	0.03±0.00	0.02±0.00	0.03±0.00
Pb	0.08±0.01	ND	0.01±0.01	ND	ND	0.08±0.01	0.02±0.00	0.03±0.00	0.02±0.00	0.02±0.00
Zn	0.58±0.31	0.15±0.00	0.26±0.11	0.09±0.00	0.06±0.02	0.31±0.05	0.13±0.02	0.28±0.07	0.13±0.02	0.13±0.04

Note: Each data represents the mean of 6 values ± the standard deviation. ND= none detected

In general, Co, Cr, Cu, Fe, Mn, Ni and Zn are considered as micronutrients required for plants growth and development. Thus, most of micronutrients in soil absorbed instantly for plant growth and metabolism and decreased in soils [40, 41]. The concentrations of Cd in soils were increased after irrigation with FSTW and BSTW as Cd is not required during growth and development of plants. The concentration of Co in soil is not numerous and absorbed by plants from the soil solution through passive transport [41]. Meanwhile, McLean and Bledsoe [42] discovered that Cr tends to oxidize in soils and resulted in lower levels in soil while Pb reacted with clays, phosphates, sulphates, carbonates, hydroxides and organic matters in soils. The augmentation of Cu concentration in soil is believed to be due to the excessive level of Cu in secondary treated wastewater. Besides, the soil obviously retained Cu though the exchanges and the adsorption mechanism processes as documented earlier by McLean and Bledsoe [42]. High level of Fe in the soil was due to the oxidation process in soil. Previously, Briat and Lobreau [43] together with Schmidt [44] discovered that Fe that appeared in oxidation form in soil with higher pH which is copious elements on earth. The lower concentrations of Mn proved by Marschner [41] as Mn only formed in soil solution with lower pH. Meanwhile, the lower level of Ni was due to the absorption by clays, iron, manganese oxides and organic matter, while Zn is absorbed by clay minerals, carbonates and hydrous oxides [42].

The analysis of variance (ANOVA) performed at 95% confidence intervals indicated all of the F-value and P-value to determine if there was any significant difference between means of heavy metals concentrations in soils before and after irrigated with FSTW and BSTW. Most of the parameters demonstrated the p-value was less than 0.05 which rejected the null hypothesis of the study as shown in Table 9. Thus, the concentrations of heavy metals were found to be relatively significant in soils after irrigated with FSTW and BSTW.

TABLE IX
Analysis of Variance at 95% Confidence Interval of Soil Before and After Irrigated with Secondary Treated Wastewater

Parameter	Analysis of Variances (ANOVA)		
	F Value	P Value	Significance Level ns=P _{value} >0.05 *=P _{value} <0.05
Cd	343.318	0.000	*
Co	52.388	0.000	*
Cr	106.681	0.000	*
Cu	32.802	0.000	*
Fe	142.522	0.000	*
Mn	69.454	0.000	*
Ni	96.473	0.000	*
Pb	243.547	0.000	*
Zn	12.519	0.000	*

Note: *=statistically significance, ns= statistically not significance

Similarly to the secondary treated wastewater, the values of heavy metals characteristics in soil, which was obtained by HACH method was slightly higher as compared to those acquired by ICP-OES method. The percentage difference between results obtained from HACH method and ICP-OES analysis for Cd 3.030% to 33.333%, Cr 3.804% to 37.931 %, Cu 9.037% to 28.947%, Fe 67.788% to 93.528%, Mn 12.605% to 64.655%, Ni 8.824% to 61.290%, Pb 0.000% to 68.000%, and Zn 5.495% to 55.639%. However, there was no percentage difference between results obtained from HACH method and ICP-OES for Co since this element was not detected in samples by ICP-OES.

The ICP technique uses the plasma to ionise components, whereby the sample is acidified and sprayed into the plasma, then the high temperature of the plasma atomises and ionises all forms of element so that the response does not vary within species, and mostly used in conjunction with other analytical techniques such OES, AES and MS [34]. In general, ICP-OES is useful for measuring higher concentrations, especially nutritional and high concentration elements [45]. The ICP-OES is normally applied for a comparison and more accurate for a multi-element sample analysis and Hung *et al.* [34]

discovered that determination of low concentrations of As in real samples suffers from low sensitivity due to the poor ionization efficiency in ICP. Besides, the determination of all the elements by ICP-OES was not possible because of the limits of detection limitations [46]. In addition, selected parameters for determination by ICP-OES can influence the signal intensities and the sensitivity of the method [47]. However, Aydin [48] recognized ICP-OES with ability to analyze a larger number of elements simultaneously with low detection limits of the investigated trace elements. Similarly, Rodushkin *et al.* [49] proved that ICP-OES is a convenient technique, capacity for simultaneous, rapid, precise determination with wide analytical range and low detection limits. Besides, Grosser *et al.* [50] revealed that interferences and analytes interact differently with the gas, resulting in reduction of the interfering species and usually low levels of analytes were detected and measured even with the presence of interfering species.

In contrast, HACH method is based on the reaction of gases with some chemical agents to form a coloured complex, the intensity of the colour is measured electronically to calculate the concentrations of macronutrients and trace elements in wastewater samples [33]. As in secondary treated wastewater samples, the characteristics of soil samples by HACH analysis was affected by interferences between ions and elements during HACH calorimetric analysis.

However, similar trends were observed in both HACH and ICP-OES methods. The results showed good agreement with Subki *et al.* [51] which demonstrated the analysis of heavy metals in batik industry wastewater, plant and soil samples by using HACH calorimeter analytical and flame atomic absorption spectrometry (FAAS) capabilities. The results showed differences among the concentrations of Fe, Cu and Zn from samples measured by both instruments and suggested that HACH calorimeter showed better optimal functionality towards water than compared to soil and plant sample analysis. The use of ICP-OES is suitable for analysis of nutrients such as P, K, Ca, Mg, Fe, Mn, B, Cu, Zn, S, and Na in soils with good accuracy since its high sample throughput capacity, rapid multielement characteristics, and parts per billion detection limits make it well suitable for this kind of application [52].

IV. CONCLUSION AND RECOMMENDATIONS

By using ICP-OES and UV-Vis spectrophotometer, the concentrations of heavy metals in secondary treated wastewater and soil were found to be relatively significant. However, the secondary treated wastewater samples were believed to interfere with other elements during analysis with HACH DR5000 UV-Vis Spectrophotometer and suggested that ICP-OES is an ideal tool for processing multiple analytes analysis of large numbers of samples quickly and efficiently, suitable for wide analytical concentrations while HACH DR5000 UV-Vis Spectrophotometer is suitable for field test

study. Besides, the use of ICP-OES was found suitable for analysis of elements in soils with good accuracy due to high sample throughput capacity, rapid multielement characteristics, varies detection limits makes it suitable for this kind of application while HACH DR5000 UV-Vis Spectrophotometer was suggested to have better functionality towards water than soil and plant analysis.

ACKNOWLEDGMENT

A special thanks to the Faculty of Civil Engineering, Research Management Institute (RMI) of UiTM, FRGS funding, the Faculty of Plantation and Agrotechnology, the Faculty of Chemical Engineering and the Facility Management Office, UiTM Shah Alam for providing facilities.

REFERENCES

- [1] A. Kabata-Pendias, "The anthroposphere," in *Trace Elements in Soils and Plants*, 3rd ed. Florida: CRC Press, 2000, pp.3-26.
- [2] D. J. Swaine, "Why trace elements are important," *Fuel Processing Technology*, vol. 65-66, pp. 21-33, 2000.
- [3] S.V. Brayton, "Acid digestions using the Hach Digesdahl Apparatus : Sample preparation for protein and elemental analysis," HACH Company, Loveland, CO, Technical information series-booklet no.14, 1992.
- [4] M. Tuzen, "Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry," *Microchemical Journal*, vol. 74, pp. 289-297, 2003.
- [5] C. Esen and A. Balci, "Application of microwave-assisted digestion to trace heavy metal determination in sea sediment sample," *Hacettepe Journal of Biology and Chemistry*, vol. 36, no. 2, pp. 123-128, 2008.
- [6] D. Bakircioglu, Y. B. Kurtulus and G. Ucar, "Determination of some traces metal levels in cheese samples packaged in plastic and tin containers by ICP-OES after dry, wet and microwave digestion," *Food and Chemical Toxicology*, vol. 49, pp. 202-207, 2011.
- [7] G. Knapp, "Mechanized techniques for sample decomposition and element preconcentration," *Mikrochimica Acta*, vol. 2, pp.445-455, 1991.
- [8] American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), *Standard methods for the examination of water and wastewater*, 21th ed. Washington, DC: American Public Health Associated, 2005.
- [9] British Standards Institution (BS EN ISO 5667:1), *Water quality-Sampling-Part 1: Guidance on the design of sampling programmes and sampling techniques*, Milton Keynes: BSI, 2006.
- [10] British Standards Institution (BS EN ISO 5667:3), *Water quality-Sampling-Part 3: Guidance on the preservation and handling of water samples*, Milton Keynes: BSI, 2003.
- [11] British Standards Institution (BS 6068:6.10), *Water quality-Part 6: Sampling-Section 6.10 Guidance on sampling of waste waters*, Milton Keynes: BSI, 1993.
- [12] British Standards Institution (BS ISO 10381:1), *Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes*, Milton Keynes: BSI, 2002.
- [13] British Standards Institution (BS ISO 10381:2), *Soil quality – Sampling – Part 2: Guidance on sampling techniques*, Milton Keynes: BSI, 2002.
- [14] American Society for Testing and Materials (ASTM D5633), *Standard practice for sampling with a scoop*, West Conshohocken, PA: ASTM International, 2008.
- [15] Ali, M. F. and S. A. Shakrani, "Risk associated with secondary treated wastewater on mustard greens growth under soil and soilless culture," *International Journal of Civil & Environmental Engineering*, vol. 12, no.6, pp.18-27, 2012.
- [16] HACH Company, *DR 5000 UV-Vis Spectrophotometer Procedures Manual*, Loveland, CO: HACH Company, 2005.
- [17] H. Watanabe, "Spectrophotometric determination of cobalt with 1-(2-pyridylazo)-2-naphthol and surfactants," *Talanta*, vol. 21, no.4, pp.295-302, 1974.

- [18] S. Nakano, "Studies on 2,2'-biquinoline derives. vi. copper (I) chelates of 4,4'-substituted 2,2'-biquinoline derivatives and the determination of copper by 2,2'-bicinchoninic acid," *Yakugaku Zasshi*, vol.82, pp.486-491, 1962.
- [19] L. J. Snyder, "Improved dithizone method for determination of lead," *Analytical Chemistry*, vol. 19, pp. 684, 1947.
- [20] K. Goto, S. Taguchi, Y. Fukue, K. Ohta and H. Watanabe, "Spectrophotometric determination of manganese with 1-(2-pyridylazo)-2-naphthol and a non-ionic surfactant," *Talanta*, vol. 24, no. 12, pp. 752-753, 1977.
- [21] HACH Company, Models 23130-20 Digesdahl® Digestion Apparatus Instruction Manual, Loveland, CO: HACH Company, 1999.
- [22] J. B. Jones and V. W. Case, "Sampling, handling and analyzing plant tissue samples," in *Soil Testing and Plant Analysis*, 3th ed., R. L. Westerman, Ed. Madison, Wisconsin: Soil Science Society of America, 1990, pp. 389-427.
- [23] Z. Y. Hseu, "Evaluating heavy metal contents in nine composts using four digestion methods," *Bioresource Technology*, vol. 95, pp. 53-59, 2004.
- [24] K. M. Al-Absi, F. M. Al-Nasir and A. Y. Mahadeen, "Mineral content of three olive cultivars irrigated with treated industrial wastewater," *Agricultural Water Management*, vol. 96, pp. 616-626, 2009.
- [25] F. Pedrero and J. J. Alarcón, "Effects of treated wastewater irrigation on lemon trees," *Desalination*, vol. 246, pp. 631-639, 2009.
- [26] Department of Environment Malaysia (DOE), "Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders: As at 10th February 2012," Petaling Jaya: International Law Books Services, 2012.
- [27] World Health Organization (WHO), "WHO guidelines for the safe use of wastewater, excreta and greywater - Volume 2 Wastewater use in agriculture," Geneva: World Health Organization, 2006.
- [28] Food and Agriculture Organization of the United Nations (FAO), "Water quality for agriculture," Rome : Food and Agriculture Organization of the United Nations, FAO Irrigation and Drainage Paper 29, 1985.
- [29] United States Environmental Protection Agency (USEPA), "Guidelines for Water Reuse," Washington, DC: United States Environmental Protection Agency, EPA 645-R-04-108, 2004.
- [30] G. Tjandraatmadja and C. Diaper, "Sources of critical contaminants in domestic wastewater – a literature review," CSIRO: Water for a Healthy Country National Research Flagship, 2006.
- [31] G. Tjandraatmadja, C. Diaper, Y. Gozukara, L. Burch, C. Sheedy and G. Price, "Sources of priority contaminants in domestic wastewater: Contaminant contribution from household products," CSIRO: Water for a Healthy Country National Research Flagship, 2008.
- [32] G. Tjandraatmadja, C. Pollard, C. Sheedy and Y. Gozukara, "Sources of contaminants in domestic wastewater: nutrients and additional elements from household products," CSIRO: Water for a Healthy Country National Research Flagship, 2010.
- [33] M. Arora, M. Megharaj and R. Naidu, "Arsenic testing field kits: some considerations and recommendations," *Environmental Geochemistry and Health*, vol. 31, pp. 45-48, 2009.
- [34] D. Q. Hung, O. Nekrassova and R. G. Compton, "Analytical methods for inorganic arsenic in water: a review," *Talanta*, vol. 64, pp. 269-277, 2004.
- [35] C. F. Wellborn, "Naturally occurring arsenic levels: A method comparison," *Geological Society of America Abstracts with Programs*, vol. 44, no. 4, pp 3, 2012.
- [36] A. V. Geen, Z. Cheng, A. A. Seddique, M. A. Hoque, A. Gelman, J. H. Graziano, H. Ahsan, F. Parvez and K. M. Ahmed, "Reliability of a commercial kit to test groundwater for arsenic in Bangladesh," *Environmental Science & Technology*, vol. 39, no. 1, pp. 299-303, 2005.
- [37] A. Mukherjee, M. K. Sengupta, S. Ahamed, M. A. Hossain, B. Das, B. Nayak and D. Chakraborti, "Comment on "reliability of a commercial kit to test groundwater for arsenic in bangladesh," *Environmental Science & Technology*, vol. 39, no. 14, pp.5501-5502, 2005.
- [38] K. M. Tyrell, T. J. Boyles, C. L. Hollabaugh and C. A. Crews, "Lead in paint in West Georgia: X-Ray Diffraction, ICP and HACH colorimeter analysis," *Georgia Journal of Science*, vol. 58, no.2, pp.113-122, 2000.
- [39] B. Spence, K. Harper, J. Wills and F. Keenan, "ICP source spectrometry techniques in regulated water analysis," *Spectroscopy*, vol. 10, 2007.
- [40] D. I. Arnon and P. R. Stout, "The essentially of certain elements in minute quantity for plants with special reference to copper," *Plant Physiology*, vol. 14, no. 2, pp. 371-375, 1939.
- [41] M. Marschner, *Mineral Nutrition in Higher Plants*, 3rd ed., London: Academic Press, 2012.
- [42] J. E McLean and B. E. Bledsoe, "Behavior of metals in soils," Washington, DC: Technology Innovation Office, Office of Solid Waste and Emergency Response, 1992.
- [43] J. F. Briat and S. Lobréaux, "Iron transport and storage in plants," *Trends in Plant Science*, vol. 2, no. 5, pp. 187-193, 1997.
- [44] W. Schmidt, "Iron solutions: acquisition strategies and signaling pathways in plants," *Trends in Plant Science*, vol. 8, no. 4, pp. 188-193, 2003.
- [45] I. J. Cindrić, M. Zeiner, M. Kröppel and G. Stingeder, "Comparison of sample preparation methods for the ICP-AES determination of minor and major elements in clarified apple juices," *Microchemical Journal*, vol. 99, pp. 364-369, 2011.
- [46] F. C. Bressy, G. B. Brito, I. S. Barbosa, L. S. G. Teixeira and M. G. A. Korn, "Determination of trace element concentrations in tomato samples at different stages of maturation by ICP OES and ICP-MS following microwave-assisted digestion," *Microchemical Journal*, vol. 109, pp. 145-149, 2013.
- [47] L. C. Trevizan and J. A. Nóbrega, "Inductively coupled plasma optical emission spectrometry with axially viewed configuration: an overview of applications," *Journal of the Brazilian Chemical Society*, vol. 18, pp. 678-690, 2007.
- [48] I. Aydin, "Comparison of dry, wet and microwave digestion procedures for the determination of chemical elements in wool samples in Turkey using ICP-OES technique," *Microchemical Journal*, vol. 90, pp. 82-87, 2008.
- [49] I. Rodushkin, T. Ruth and A. Huhtasaari, "Comparison of two digestion methods for elemental determinations in plant material by ICP techniques," *Analytica Chimica Acta*, vol. 378, pp.191-200, 1999.
- [50] Z. A. Grosser, K. Neubauer, L. Thompson and L. Davidowski, "A comparison of ICP-OES and ICP-MS for the determination of metals in food," *Spectroscopy*, vol. 5, 2008.
- [51] N. S. Subki, R. Hashim and N. Z. M. Muslim, "Heavy metal analysis of batik industry wastewater, plant and soil samples: a comparison study of FAAS and HACH calorimeter analytical capabilities," *From Sources to Solution*, vol. 52, pp. 285-289, 2014.
- [52] C. P. Bonsak, D. Yates and R. Thomas, "Optimization of a high sample throughput method for the determination of trace nutrients in agricultural soil samples using ICP-OES," *Spectroscopy*, vol. 10, 2006.