INTERNATIONAL SCIENTIFIC AND PROFESSIONAL CONFERENCE
POLITEHNIKA 2023
Belgrade, 15th December 2023

ENVIRONMENT AND SUSTAINABLE DEVELOPMENT. MECHATRONICS. OCCUPATIONAL SAFETY AND HEALTH AND FIRE SAFETY. SMART MANAGEMENT SYSTEMS. GRAPHIC ENGINEERING. DESIGN. TRAFFIC ENGINEERING. BIOTECHNOLOGY AND HEALTHCARE. MECHANICAL ENGINEERING. ECOTOURISM AND RURAL DEVELOPMENT.

ANALYSIS OF HEAVY METAL(LOID)S IN COAL FLY ASH LEACHATE BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

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Abstract: *Fly ash is a by-product of coal combustion in thermal power plants. Heavy metal(loid)s (HMs) are the most recognized among the many dangerous compounds in fly ash. These substances may contaminate the environment and can pose a threat to human health. Various analytical techniques are used to analyze HMs in leachate. To investigate the possibility of contamination of the environment, heavy metals and metalloids (Pb, Zn, Mn, Fe, As, Ba, Be, Cu, Cr, Co, Cd, Sb, Se, and V) were leached from fly ash using a toxicity characteristic leaching procedure (TCLP). The fly ash samples used in this work were obtained from four thermal power plants (Kostolac, Kolubara, Tent B, and Morava). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique was used to determine the concentration of these elements in the leachate. Accurate elemental analysis was achieved with this technique. Among all analyzed metal(loid)s, Fe, Mn, Zn, and As were the most abundant.*
Keywords: ICP-OES, TCLP, trace elements, power plant, coal combustion

1. INTRODUCTION

Coal combustion in coal-fired boilers produces several different types of ashes, including fly ash, bottom ash, boiler slag, flue gas desulfurization materials, and other fluidized bed combustion ash, cenospheres, and scrubber residues, amongst other things [1]. Coal fly ash and bottom ash are the two main industrial by-products generated during the combustion of coal [2]. Due to the enrichment of heavy metals and metalloids (heavy metal(loid)s, HMs) in the ash particles, the disposal of these solid residues is considered a potential source of soil and groundwater pollution. The concentration of HMs in the ashes depends on several factors, including the type of coal feed, coal source, the occurrence of significant elements and their association with the organic and inorganic components of the coal, combustion conditions, volatilization-condensation mechanisms, and the particle size of the ash [3],[4]. During the transport and disposal of the residues from coal combustion, they are exposed to the leaching effects of rain. It is imperative to predict the leaching behavior of residues to prevent the environmental effects [5],[6].
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a powerful analytical technique widely employed in environmental and materials analysis to determine HMs in various matrices. It has several characteristics, such as the ability to simultaneously analyze multiple HMs, wide dynamic range, high sensitivity, and low interference from matrix effects, which make it an indispensable tool in environmental monitoring, where HMs play a critical role.

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The aim of this study was to develop an ICP-OES method for analyzing HMs in the coal ash leachate and to investigate coal ash leaching behavior in order to analyze the potential for their reuse.

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Coal fly ash and bottom ash samples were collected from four thermal power plants in Serbia that combust coal. Leaching of various HMs was carried out by applying batch Extraction Procedure (EP) and toxicity characteristic leaching procedure (TCLP). The TCLP extraction fluid (pH = 2.88) was prepared by diluting glacial acetic acid, while the EP extraction solution was deionized water (18.2 MΩ·cm). Deionized water was prepared using a Simplicity ultrapure water system (Millipore, Bedford, MA, USA). Acetic acid was supplied from Sigma Aldrich (Buchs, Switzerland). Standard solutions were purchased from AccuStandard (New Haven, USA).

2.2 Sample preparation

In a polyethylene bottle, 50 mL of EP or TCLP leaching fluid was mixed with 1.0 g of sample (20÷1 solid-to-liquid ratio), and the mixture was stirred at room temperature for 24 hours. The leachate was centrifuged at 6000 rpm for 10 minutes. The obtained supernatants were used for the analysis of HMs. Triplicate leaching tests were performed using the same weight of the sample and the same volume of the leaching solvent.

2.3 ICP-OES Measurements

The concentrations of HMS were determined by the ICP-OES instruments (Thermo Scientific model iCAP 6500 duo). To control the ICP-OES system, Thermo Scientific™ Qtegra™ software was employed.

3. RESULTS AND DISCUSSION

The first step was to optimize the ICP-OES parameters to enhance the analytical performance and achieve better results in HM analysis in coal fly ash leachate. The simplex method [7] was used to get optimal conditions for this analysis (Table 1).

Table 1. ICP-OES instrumental operating conditions

Parameter	Setting
RF Power	1150 W
Nebulizer gas flow	0.6 L/min
Auxiliary gas flow	0.5 L/min
Cooling gas flow	12 L/min
Exposure time	Axial/Radial
Low (UV)	15 secs
High (Visible)	5 secs
Peristaltic pump speed	50 rpm

Next, the linearity, detection limits (LOD), recoveries, and precision of the method have been investigated. To determine the linearity of the method, a calibration curve was constructed by analyzing a series of standard solutions with known concentrations of the HMs. The response of the instrument is plotted against the concentration of each HM, and the linearity is evaluated by calculating the correlation coefficient (R^2) of the calibration curve. The LOD was estimated by analyzing a series of blank samples and calculating the standard deviation of the blank measurements and then calculated as three times the standard deviation of the blank measurements. A known amount of HM is spiked into a sample matrix, and the recovery is calculated as the ratio of the measured concentration to the spiked concentration. Finally, the precision of the method was determined by analyzing a series of replicate samples and calculating the relative standard deviation (RSD) of the ICP-OES measurements. Table 2 shows the wavelengths (λ) of the analyzed elements as well as the interferants, LODs, RSDs, and recoveries.

Table 2. Analytical parameters for ICP-OES determination of HMs in fly ash leachate

No.	HM	λ (nm)	Interferant	LOD (ppb)	Spiked conc. (ppm)	Recovery (EP) (%)	Recovery (TCLP) (%)	RSD (%)
1	As	189.042	Al, Co, Fe, V, Ni	2.91	0.3528	103	105	4.1
2	Ba	493.409	None	1.23	0.2601	101	103	3.4
3	Be	313.042	Ce, V	0.97	0.0025	102	102	2.7
4	Cd	228.082 214.438	Ce, Ni, Fe, Ti	0.42	0.0035	98	94	1.9
5	Co	228.616	Ba, Ce, Cd, Cr, Ni, Ti, Mo	0.97	0.0270	104	99	1.8
6	Cr	283.563 267.716	Ni, Mo, Be	1.72	0.0728	103	104	2.0
7	Cu	324.754	Mo, Ti	0.94	0.0447	101	98	1.6
8	Fe	259.940 239.562	None	4.28	3.7163	93	96	4.8
9	Mn	257.610 279.482	Ce	0.87	1.2607	94	97	4.5
10	Sb	206.833	Al, Ce, Cr, Co, Fe, Ni, Ti,	0.54	0.0204	105	96	4.3
11	Se	196.090	Fe	2.33	0.0552	104	98	4.1
12	V	282.402	Ce, Cr, Fe, Ti, Mo	0.91	0.0480	95	92	3.2
13	Zn	202.548	Cu, Fe, Ni	0.18	0.1964	102	97	2.1

The lowest value of the detection limit is 0.18 ppb for Zn, while the highest LOD is 4.28 ppb for Fe. The recovery ranges from 93 to 105%. A good linearity was observed for all HMs (R^2>0.999), and RSD is within ±5%. There are no notable differences between TCLP and EP recoveries.

The chemical constituents of fly ash and bottom ash are very similar, with the main difference being particle shape and size. Bottom ash is larger in size and very irregular, containing pores and cavities [8]. Ground to a suitable fineness, bottom ash can have a similar purpose as fly ash (e.g., production of building materials).

3.1 Leaching of heavy metal(loid)s from fly ash with EP leaching solution

The HM concentrations in the EP leachate are shown in Figure 1. Arsenic is the most prevalent (1.49 ppm) HM in the fly ash sample originating from the Kolubara thermal power plant. Arsenic (As) is markedly toxic and carcinogenic, and it is one of the most important HMs that cause both ecological and human health problems [9]. Concentrations of other HMs do not exceed 0.6 ppm.

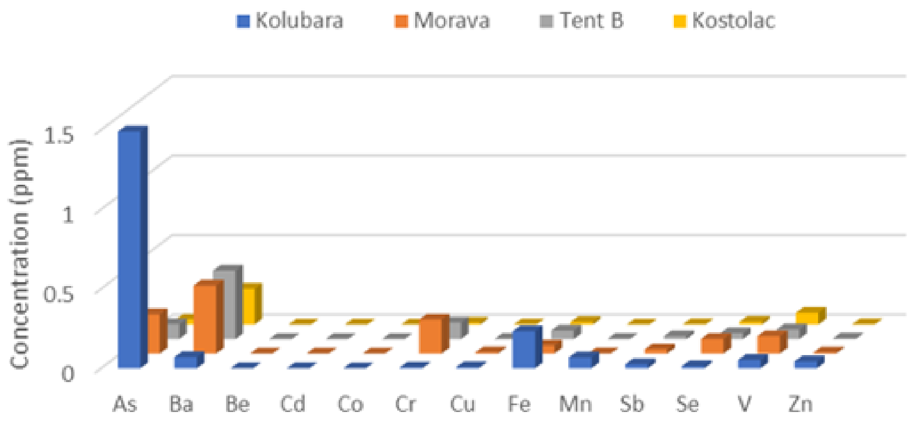

Figure 1. Concentrations of heavy metal(loid)s in fly ash leachate (EP leachate)

3.2 Leaching of heavy metal(loid)s from fly ash with TCLP leaching solution.

Figure 2 shows the results of fly ash leaching using the TCLP leaching solution. Concentrations of HMs are significantly higher in TCLP leachate compared to EP leachate. This is because metal solubility generally decreases with increasing pH. The most abundant HMs in fly ash leachate were As, Fe, and Mn, which were found in the range of 0.03–1.49 ppm, 0.02–0.23 ppm, 0.0005–0.07 ppm and 0.05–1.41 ppm, 1.28–24.38 ppm, 2.24–3.04 ppm, for EP and TCLP leachate, respectively. The ash sample from the Tent B thermal power plant contained the highest concentration of these elements.

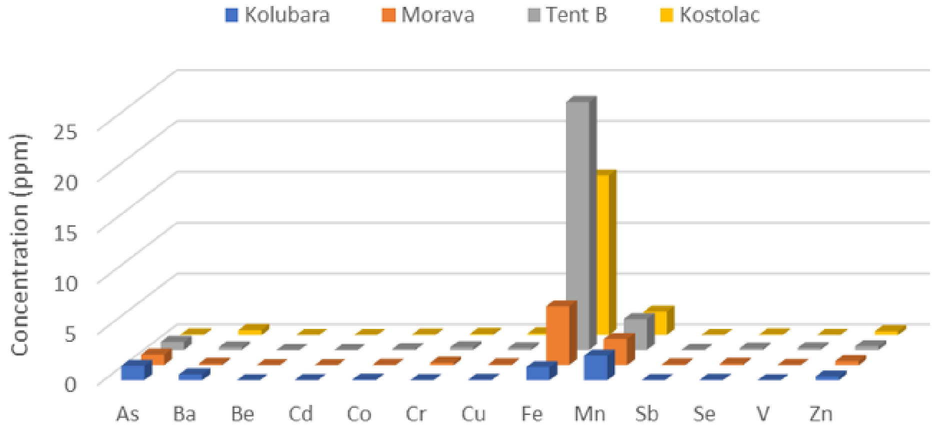

Figure 2. Concentrations of heavy metal(loid)s in fly ash leachate (TCLP leachate)

3.3 Leaching of heavy metal(loids)s from bottom ash with EP leaching solution.

The levels of HMs in the bottom ash leachate are shown in Figure 3. Compared to fly ash samples, less arsenic was leached into deionized water in this instance. Similar to fly ash, the most prevalent metals in this leachate were Fe, Mn, Zn, As, and Ba, though in smaller quantities.

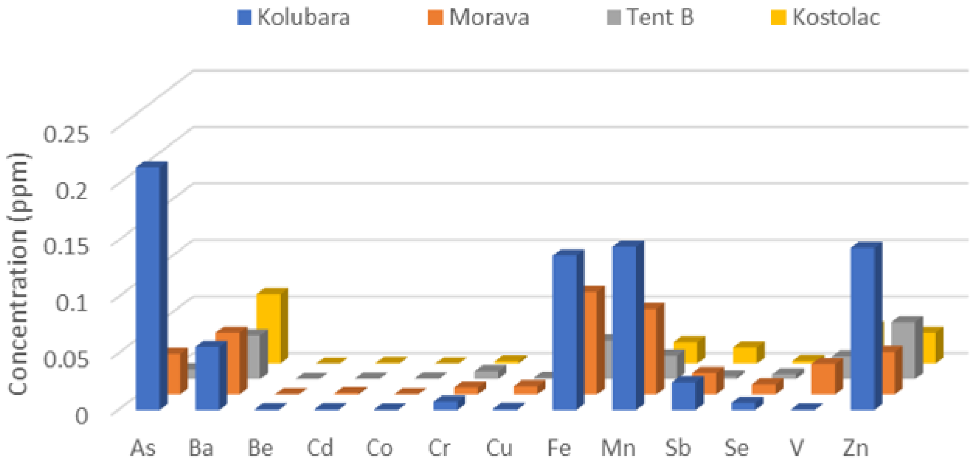

Figure 3. Concentrations of heavy metal(loid)s in bottom ash leachate (EP leachate)

These results can be explained by the similar composition of these two ashes but the different sizes of the particles, which is one of the important factors affecting the amount of leached HMs.

3.4 Leaching of heavy metal(loids)s from bottom ash with EP leaching solution.

The concentrations of the heavy metals(loids) that were leached out with TCLP solvent are shown in Figure 4. Similar to the fly ash samples (Figure 2), the most abundant HMs in the bottom ash TCLP leachate were Fe, Mn, As, and Ba.

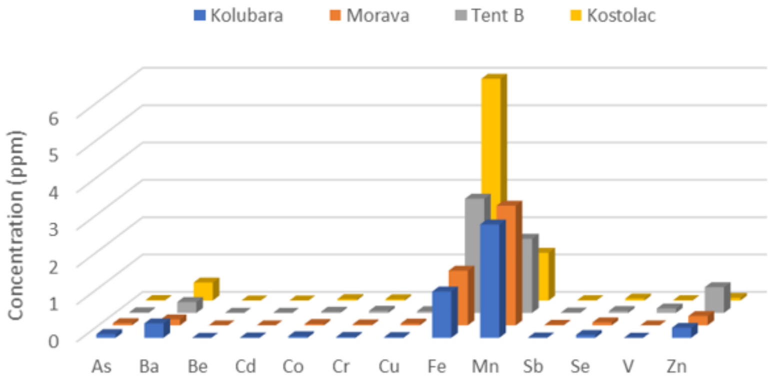

Figure 4. Concentrations of heavy metal(loid)s in bottom ash leachate (TCLP leachate)

4. CONCLUSION

In general, ICP-OES is a reliable and robust technique, offering good linearity, recovery, and precision, making it suitable for analyzing HMs in coal ash leachate. According to the leaching tests, coal fly ash and bottom ash from various locations have similar leaching characteristics. Higher concentrations of heavy metals (loids) were leached during the TCLP leaching test, which can be explained by the lower pH value affecting the mobility of heavy metals. Among all analyzed metal(loid)s, Fe, Mn, Zn, and As were the most abundant in the ash samples.

This research was supported by the Science Fund of the Republic of Serbia, GRANT No 7743343, Serbian Industrial Waste towards Sustainable Environment: Resource of Strategic Elements and Removal Agent for Pollutants - SIW4SE, Program IDEAS.

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