



Comparative study of the sequential extraction methodologies for fractionation analysis of mercury in coal of Thar coalfield

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Abstract

The primary objective of this study was to evaluate the bound fractions of mercury (Hg), physicochemical parameters, and mineral composition of coal. Coal samples were collected from various depths within Block-VII of the Thar coalfield in Pakistan. The Hg associated with different chemical fractions of coal was extracted using a sequential extraction scheme as per the community bureau of reference (BCR) protocol. This study utilized both the BCR-sequential extraction method (BCR-SEM) and a single-step sequential extraction based on an ultrasonic-assisted method (SSE-UAM) for the fractionation analysis of Hg in coal. The extraction methodologies, BCR-SEM and SSE-UAM, were specifically designed for analyzing Hg fractionation in coal samples. The SSE-UAM offers an operational advantage, requiring only 2 h compared to the 51 h needed for BCR-SEM. The analyses were validated using standard reference material (SRM-1635a) and the spiking addition method, achieving a recovery percentage of 97.1% for total Hg concentrations using the pseudo-extraction method in SRM-1635A. Total Hg content in the coal samples ranged from 0.60 to 2.34 $\mu\text{g g}^{-1}$ across four different coal seams from Block-VII of the Thar coalfield. Additionally, Hg concentration was observed to decrease with increasing depth, attributed to changes in mineralogical composition. The highest concentration of Hg was detected at a depth of 200–203 m, while the lowest concentration was at a depth of 152–154 m. The concentration of Hg in various fractions was 32–60% in the acid-soluble fraction, 1.72–4.92% in the reducible fraction, and 9.58–50.8% in the oxidizable fractions. The coal sample characteristics were analyzed using an elemental analyzer and scanning electron microscopy with energy-dispersive spectroscopy. Cold vapor atomic absorption spectrometry (CV-AAS) was used to measure the extracted fractional concentration of Hg in coal.

Keywords Sequential methods · Fractionation analysis · Hg · Coal · Thar coalfield

Introduction

In Pakistan, many energy resources are used for generation of electricity; among them is coal which is the main source for electricity generation due to its low cost and easy availability. Environmental pollution due to Hg emissions from coal burning and other anthropogenic activities are the main factors to induce health risks (Charvat et al. 2020). The volatile toxicants

such as inorganic and organic toxic species were produced during coal combustion for electricity generation. Total Hg emissions account for more than 45% due to fossil fuel combustion using coal for power generation (Xie et al. 2021). Studies dealing with the presence of Hg in coal and how to control its emissions have been reported in the literatures. In the environmental pollution, Hg become a main issue due to its nature and toxicity. The elemental form of Hg can remain 6 to 24 months in the environment (Luo et al. 2013; Tian et al. 2012). Electrostatic precipitators are used for the collection of fine particulate matter in various industrial applications, including the reduction of Hg emissions from combustion processes. Electrostatic precipitators and fabric filters were used for controlling Hg in air pollution. Meanwhile, wet bushes were used to trap oxidized Hg from water contamination because oxidized Hg is easily soluble in water (Krzyzyska et al. 2020, Li et al. 2022). The studies have been extensively focusing on how to improve the reduction of Hg from a different mode of occurrence and

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distribution in coal. The high concentration of Hg in coal is due to its bounding with organic materials and pyrite phase in different coal types (Manceau et al. 2018). It is an important task to the identification and quantification of Hg fractions, but it is a very difficult and sensitive task due to the redistribution nature of Hg in coal. Fractionation analysis of Hg in coal samples allows for a more comprehensive understanding of its environmental and health impacts. By identifying the specific Hg species, it is possible to better predict their behavior during coal combustion, their environmental fate, and their toxicity. This detailed information is crucial for developing effective pollution control strategies, complying with regulations and protecting public health and the environment (Diao et al. 2018). Environmental contamination of Hg has been dependent on its various phases, leachable forms, and geochemical pathways. Fractionation analysis of Hg by BCR-SEM play an essential role to evaluated the Hg behaviors in various phases bound with coal.

In the literature, there are so many modified BCR-SEMs which are available for fractionation analysis of Hg in coal (Connor et al. 2019; Waris et al. 2022). The original BCR-SEM is time consuming and not frequently used for routine analysis. Therefore, several efficient and time-saving approaches have been developed. In the literature, extraction efficiency was increased using ultrasound energy and decreasing extraction time in the modified SSE-UAM. However, ultrasound jet and associated shock waves eliminate solids, causing particles to disperse locally. Thus, SSE-UAM proved to be a more efficient and reliable method as compared to BCR-SEM. It is a favorable extraction technique as compared to BCR-SEM with the same operational requirements. The SSE-UAM was applicable for largely available coal samples by using different analytical techniques. In literature, large data is available for the determination of total and chemical fraction of Hg contents in coal samples by CV-AAS (Mostafavi and Ebrahimi 2019). Fractionation analysis of Hg is necessary to get useful information about its distribution behaviors, chemical toxicity, and health risk assessment. The Hg toxicity depends on its total concentration as well as on bound forms of Hg with coal phases.

The aim of this study was to assess the Hg associated with different coal fractions (acid-soluble, reducible, and oxidizable) using BCR-SEM and to compare the findings with Hg values obtained from SSE-UAM under identical operating conditions. Additionally, the study investigates the physical and elemental composition of coal from Block-VII of the Thar coalfield.

Materials and methods

Study area description

The Thar coalfield is located in the Tharparkar district of Sindh, Pakistan. Extensive coal deposits were discovered near

Islamkot city in the Tharparkar district. The coordinates of the Thar coalfield are 24°7'7"-24°9'8" N and 70°1'6"-70°4'5" E (Fig. 1). The coalfield spans an area of over 9100 km² with reserves extending 140 km north–south and 65 km east–west, totaling 175.5 billion tonnes (Ali et al. 2015c). The Thar coalfield is divided into 12 blocks for drilling and mining purposes and has been identified as lignite coal (Ali et al. 2015a).

The study area is covered by thick dunes; lacking outcrops, Proterozoic to late Proterozoic igneous and metamorphic rock varieties were found in overall Nagarparkar, southeast of Islamkot. Sub-surface stratigraphy operates primarily on 39 wells dug for mining and drilling of coal. Pre-cambrian granite rock was observed in the basement. The basic parts of these rocks bear a resemblance to the Agni and metamorphic eras that are exposed in Nagarparkar from Proterozoic to upper Proterozoic. Agnes and metamorphic rocks can be combined with magmatic rocks from the upper protrusions of western Rajasthan, India (Rafique et al. 2015). Granite is related to plate type A parasailing granite and peraluminous granite which contains some acid-based dioxide and revoluted buffer (Munir et al. 2018). The upper part of the granite has a season and they turn into kaolin (Malkani 2012). Coraline deposits are usually covered with thick dunes and sediments that extend to an average depth of 30 m. The sand of the dunes consists mainly of quartz and field spar, which contains a series of minerals. The grain size of the sand ranges 2.30–2.74 mm. The thickness of kaolin bags is estimated at 2–8 m (Naseem et al. 2010). The middle Bara formation (Pelosin-Early Eocene) overlaps impregnable granite rock (Ali et al. 2015c). The Bara formation consists of coal, clay stone, sandstone, earthen rock, and carbonaceous underlayment beds. At a depth of 150 m from the earth's surface, different coal layers in various thicknesses of 8–36 m are interconnected. Mackerel analysis shows that the range of 85–95% is 1.0–8.1 and 1.1–8.1, respectively. Coal contains a large number of trace elements, especially arsenic, lead, cadmium, Hg, molybdenum, and selenium which are bound with different phases. Twelve formations are invincible through the Bara formation of the late Pleistocene. The highest horizon consists of dunes formed by the desert, about 150 km behind.

Collection of coal samples

For the present study, 0.5 kg coal samples were collected from four seams (152–154, 158–160, 200–203, and 209–210) of Block-VII of the Thar coalfield. The core sampling approach was used to the collection of coal samples from four seams in Block-VII of Thar coalfield. The number of coal samples ($n = 25/\text{depth}$) was collected from four depths, so the total of 100 coal samples were collected from Block-VII of Thar coalfield. The coal samples were collected in plastic bags marked with identification numbers of the different depths. At the time of sampling in June 2019,

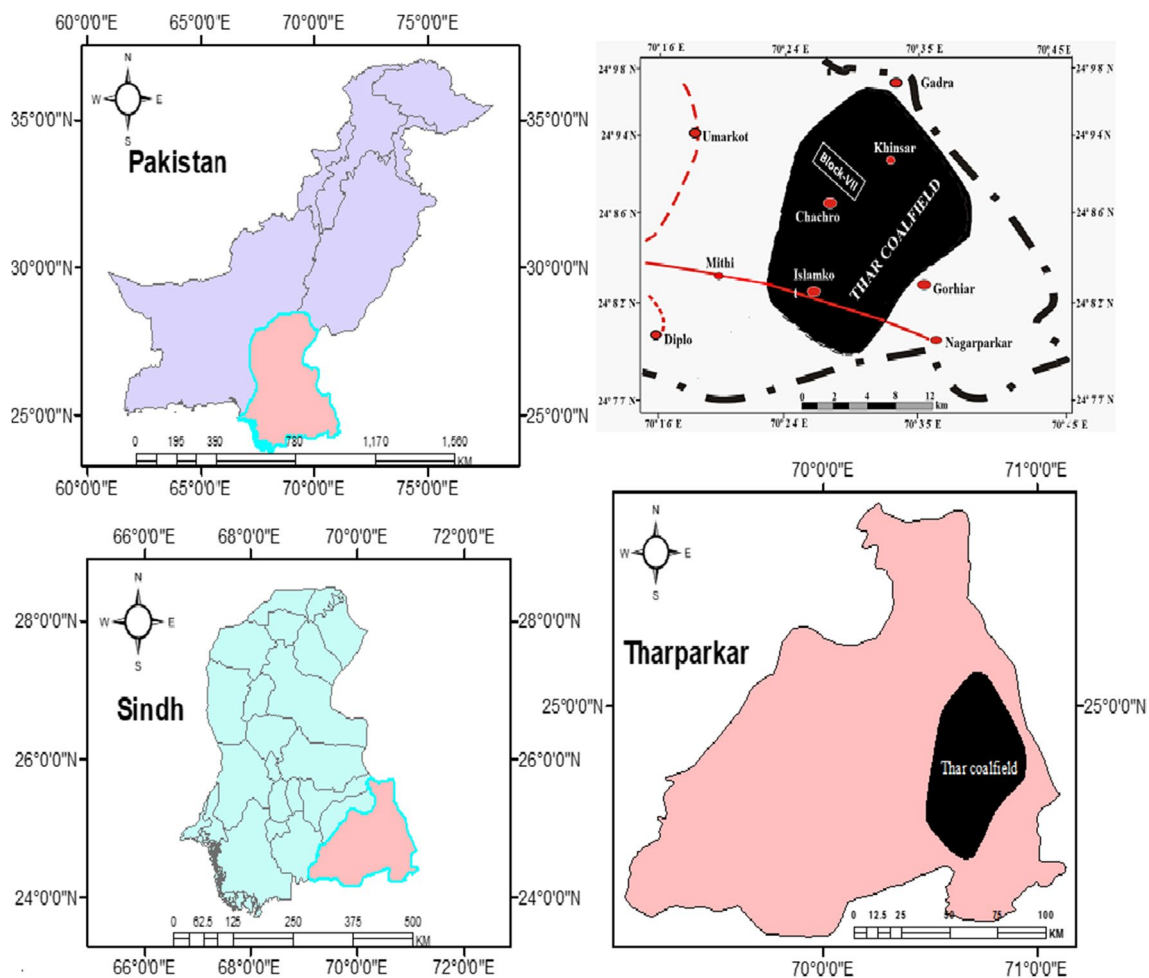


Fig. 1 The study area of Block-VII of the Thar coalfield in province of Sindh, Pakistan

coal was being mined in Block-VII of Thar coalfield. All collected coal samples were stored in polypropylene bags to avoid contamination and transferred to the laboratory as soon as possible.

Reagents and glassware

In practical performance, double distilled water (resistance $0.05 \mu\text{S cm}^{-1}$) was obtained from an ELGA laboratory water system (Box, UK). Analytical reagent-grade chemicals were used to prepare standard and real solutions to avoid contamination. Stock and working standard solutions were prepared using a 1000 mg kg^{-1} Hg standard from Falaka Kameka (Bush, Switzerland). Analytical grade reagents, acetic acid, and hydroxylammonium hydrochloride were purchased from Merck (Darmstadt, Germany). Vials and sampling bags were gently washed, soaked in concentrated nitric acid for more than 12 h and then rinsed with double distilled water. All collected coal samples were dried at room temperature on different hood trays in the laboratory for 1 week. Laboratory

pre-treatments involved separating powdered coal using a 100-mesh sieve to remove unwanted materials.

Instrumentations

Uniform shaking of each coal fraction was achieved using an end-to-end mechanical shaker from Gelankamp, Germany. The centrifuge machine used for separating the supernatant solution from the residue was purchased from ROWKA Laboratory, Poland. A pH meter was obtained from Ecoscan Ion 6, Kuala Lumpur, Malaysia. Physicochemical analysis was performed using a microwave oven and an electric furnace with programmable time/temperature control, purchased from MDS-2003F, SMCT Co. Ltd., Shanghai, China, and Thermolyne 79300, Germany, respectively. Coal characteristics analysis was carried out using an EA and SEM-EDS from PE2400-II, Elementar Vario, Germany, and Agilent 7700x, Agilent Technologies Inc., California, USA, respectively. The concentration of Hg in the extracted solution was

measured by CV-AAS using Model-III from Brooks Rand Laboratories, USA.

Characteristics of coal

Characteristic analysis of coal samples was performed according to the American standard for testing materials (ASTM)-D7582. The ASTM-D3173 method was used to determine the percentage humidity in coal samples. Moisture contents were measured by heating coal samples at 100 ± 5 °C in a microwave oven until constant weight was reported (Ali et al. 2015b). Volatile matters in coal are determined by the ASTM D-3175 method. Volatile matter can be estimated by heating the coal at 950 ± 20 °C for 7 min in a programmable electric furnace. The percentage of ash content in each coal sample was determined using the standard ASTM D 3174 method. After estimating the volatile matter, the residual coal was heated in a programmable electric furnace at 700 ± 20 °C for 30 min. The percentage of fixed carbon was estimated by the ASTM D-3172 method. It can be determined by subtracting the sum of the percentage moisture, percentage volatile matters, and percentage ash from 100. The ultimate parameters and elemental composition of coal were performed by using EA and SEM-EDS.

Water-soluble fraction and total Hg contents

Triplicate 5.0 g of air-dry coal from each seam of Block-VII was weighed in polytetrafluoroethylene (PTFE) tube for extraction of water-soluble Hg fraction in coal. The water-soluble Hg fraction in coal was determined by the Deutsches Institut für Normung (DIN) method. DIN test provides information about the behavior of Hg when it comes in contact with water (Nuic et al. 2022). Pseudo extraction method was used to determine the total Hg contents in coal by microwave-assisted acid digestion process (Krishna et al. 2012). In Pseudo extraction method, 200 mg of triplicate air-dried coal samples was taken in PTFE flasks. The mixture of analytical grade concentrated 2.0 mL nitric acid and 6.0 mL hydrochloride acid was added into PTFE flasks and kept for 10 min at ambient temperature. Then, PTFE bottles were heated to 80% full power (900 W) in the microwave oven. After microwave digestion, the sample vials were kept at room temperature for cooling and evaporation of the excess acid (Ali et al. 2015c). Approximately 10.0 mL of 0.2 N nitric acid was used to mark up the volume. The revised BCR-SEM was accurately validated for total Hg determination in coal samples by the standard spiking addition method. The same process was used for the preparation of the analytical blanks, without using samples or standards.

BCR-sequential extraction method

The BCR-SEM was used to determine the concentration of Hg in different fractions in air-dry triplicate coal samples from Block-VII of the Thar coalfield. The experimental conditions and chemical reagents for fractionation analysis of Hg in coal are given in Table 1. 25.0 mL volume of acetic acid 0.11 mol L^{-1} is added to 0.80 g of coal samples on the air-dry basis and then mixed in a mechanical stirrer for 16 h. The extract was separated from the mixture by centrifugation at 3000 rpm for 10 min (Ali et al. 2015c). Superintending solution was saved in a clean vial for Hg determined in acid-soluble fraction, and the remaining residue is also used for further extraction type. The volume of 25.0 mL of freshly prepared 0.5 mol L^{-1} hydroxylamine hydrochloride was added into the remaining residue adjusted pH 1.5 by using (2.0 mol L^{-1}) nitric acid in a centrifuge tube, and then stirred. The volume of 8.0 mL of hydrogen peroxide was added into the remaining residual from reducible Hg fraction in the test tube. The stopper was used to cover the sampling container and then placed on a hot plate for digestion with manual stirring at 75 °C; another 8.0 mL of hydrogen peroxide was added again (Ali et al. 2015c). Continue digestion, then the stopper is removed, and the volume of the sample is reduced to 1.0–2.0 mL, then 30.0 mL of ammonium acetate is added, adjusted to pH 2.0, and is extracted as above shown in Table 1.

Single-step sequential extraction based on ultrasonic-assisted method

The SSE-UAM was performed in an ultrasonic bath capable of processing multiple samples simultaneously. The main advantage of the proposed SSE-UAM was less extraction time as compared to BCR-SEM. Time is an important factor in every extraction approach. All of these conditions were designed to achieve high efficiency in the shortest possible time. Avoid temperature increase, which could alter the chemical balance of the extracted solution. Experimental parameters are changed to the extraction of Hg in the setup procedures. In the SSE-UAM, extraction parameters were selected based on Hg values compared to the BCR-SEM. The total time for every fraction in SSE-UAM was taken 15–30 min, and the frequency was 35 kHz at 30–35 °C as shown in Table 1.

Results and discussion

Characteristics of coal samples

The two types of moisture observed in coal are as follows: one is surface moisture the and second one is inherent

Table 1 The BCR-SEM and SSE-UAM procedure for extraction of Hg fractions in coal

Steps	Fractions	Extractants	Extraction conditions
BCR-SEM, procedure			
01	Acid-soluble fraction	25 mL acetic acid (0.11 mol L ⁻¹)	Mixing by mechanical shaker for 16 h then centrifugation, Save the supernatant solution and residue
02	Reducible fraction	25 mL hydroxylamine hydrochloride (0.5 mol L ⁻¹), pH=1.5	Mixing by mechanical shaker for 16 h then centrifugations, save extracted solution and residue for next step
03	Oxidizable fraction	8 mL hydrogen peroxide (30%) 30 mL ammonium acetate (1.0 mol L ⁻¹), pH=2.0	Residue of step 2 was digested by hot plate and extractants twice. Shaking for 16 h then centrifugation and save the supernatant solution
04	Residual fraction	10.0 mL aqua regia 25 mL 0.2 mol L ⁻¹ nitric acid	Residue of step 3 was digested by aqua regia at 85 °C. After filtration save supernatant solution
SSE-UAM, procedure			
01	Acid-soluble fraction	25 mL acetic acid (0.11 mol L ⁻¹)	Sonication time for 15–30 min then centrifugation, save the supernatant solution for analysis
02	Reducible fraction	25 mL hydroxylamine hydrochloride (0.5 mol L ⁻¹), pH=1.5	Sonication time for 15–30 min then centrifugation, save the supernatant solution and residue for next step
03	Oxidizable fraction	8.0 mL hydrogen peroxide (30%), 30 mL ammonium acetate (1.0 mol L ⁻¹), pH=2.0	Step 2 residue was digested on hot plate twice. Sonication time for 15–30 min then centrifugation save the supernatant solution for fractionation analysis

moisture. Surface moisture can be removed easily to spread out in the laboratory at ambient temperature, while inherent moisture can be measured by an electric oven at 105 °C according to ASTM method. The moisture contents were observed in increasing order with increased depth except for 209–210 m. The percentage moisture was observed in the range of 36.8–40.4% in the Block-VII of Thar coalfield (Table 2). The high percentage moisture contents in coal have some disadvantages such as decrease calorific value, large amount of coal used for heating, and more time is required to get the desired temperature. Hence, a high percentage moisture in coal is not suitable for the generation of electricity. Volatile organic matters produce various gases due to burning at specific temperature. In power plants, coal pyrolysis produces volatile matters, and it is an indication of low quality of coal. The burning of coal produced volatile matters in the form of methane, hydrogen, hydrocarbons, carbon monoxide, carbon dioxide, ammonia, water gas, hydrogen sulfate gas nitrogen, etc. Volatile matters in coal of the Block-VII were observed in the range of 29.2–34.0%. The high percentage volatile matters in coal proportionately increase the flame length and help in easier ignition of coal. Ash is a non-combustible substance which reduces the calorific value of coal. Ash is an impurity that will not burn, and its typical range is 5–40% in coal (Peiravi et al. 2017). Therefore, the lower the quantity of ash contents, the better the quality of coal. The percentage ash on air-dry weight basis was observed in the range of 7.24–9.10% in coal of Block-VII of the Thar coalfield. It was also observed that percentage ash contents were increasing order with depth increases. These values are similar to previous ones reported in the literature (Ali et al. 2015b). Fixed carbon is the solid

Table 2 Results of physical and elemental composition of coal from Block-VII of the Thar coalfield

Depth (m)	152–154	158–160	200–203	209–210
Moisture (%)	36.8	39.6	40.4	38.9
Volatile matters (%)	29.2	31.5	32.4	34.0
Ash contents (%)	7.28	7.24	9.06	9.10
Fixed carbon (%)	26.1	22.2	18.4	19.6
Carbon (%)	56.62	57.6	55.8	49.8
Hydrogen (%)	3.65	3.37	3.42	3.88
Nitrogen (%)	0.70	0.72	0.53	0.94
Oxygen (%)	41.6	36.6	39.7	41.4
Sulfur (%)	2.10	1.20	1.25	2.48
Sodium (%)	1.17	1.00	0.78	0.69
Magnesium (%)	0.42	0.37	0.36	0.34
Aluminum (%)	3.28	1.28	1.33	1.00
Silicon (%)	2.66	1.36	1.12	0.58
Calcium (%)	0.88	1.13	0.78	1.05
Iron (%)	1.56	1.15	1.38	0.77

fuel left in the furnace after volatile matter is distilled off. It consists mostly of carbon but also contains some hydrogen, oxygen, sulfur, and nitrogen not driven off with the gases. Fixed carbon in coal of the Block-VII was obtained in the range of 18.4–26.1% (Table 2). For power generation, the amount of fixed carbon is more essential to produce high electricity by using less amount of coal.

The elemental composition of coal such as carbon, oxygen, hydrogen, nitrogen, and sulfur was determined. It is useful in determining the quantity of air required for combustion and composition of the combustion gases. It is

required for the calculation of flame temperature and the flue duct design, etc. The EA was used to determine the composition of coal from four seams of Thar coalfield. The resulted data of carbon, hydrogen, nitrogen, and oxygen are represented in Table 2. The percentage of carbon in coal from four different depths of Block-VII was observed in the range of 49.8–57.6%, which is one of the major constituents of coal. The highest percentage of carbon was found in the 158–160 m coal seam of Block-VII of the Thar coalfield. It was reported that a high percentage of carbon is characteristic of the best quality of coal and enhances the coal rank (Cai et al. 2011). Hydrogen increases the calorific value of the coal, while the presence of nitrogen decreases the calorific value of coal. These are associated with the volatile matter of the coal. The percentage of hydrogen and nitrogen in coal samples was observed in the range of 3.37–3.88% and 0.53–0.94% respectively. Hydrogen is also the main constituent of coal, and we have found hydrogen percentage in increasing order as depth increases of Block-VII. Oxygen is the second most important constituent of coal; probable values of oxygen are indicated rank of coal. The percentage of oxygen was obtained in the range of 36.6–41.6% in the coal from Block-VII, and it indicates a lower quality of coal represented in Table 2. Sulfur increases the calorific value of the coal, yet it has the following undesirable effect. The oxidation products of sulfur such as sulfur dioxide and sulfur trioxides especially in the presence of moisture form sulfuric acid which corrodes the equipment and pollutes the atmosphere. Resulted data show the percentage of sulfur in the range of 1.2–2.48% (Table 2). In literature reported low content of sulfur in coal of Thar coalfield (Ali et al. 2015c). The sulfur content is also an important factor in coal quality, mainly because of corrosion and environmental impacts.

Elemental analysis is very important to find out the composition of coal and the application of coal in energy-producing activities (Yi et al. 2017). In the present study, the percentage of sodium, magnesium, aluminum, silicon, calcium, and iron in coal from four coal seams was estimated by EA and SEM–EDS. The percentage of elemental composition was determined based on air-dry weight of coal from four different depths of Block-VII of the Thar coalfield. The validity and accuracy of the elemental analysis in coal were measured by using SRM-1635A. The percentage composition of the studied elements sodium, magnesium, aluminum, silicon, calcium, and iron in coal samples was found in the range of 0.69–1.17, 0.34–0.42, 1.00–3.28, 0.58–2.66, 0.88–1.13, and 0.77–1.56%, respectively (Table 2). All studied elements were observed in decreased order with increased depth except calcium. Calcium was observed in the highest percentage at 158–160 m of coal seam and the lowest percentage at 152–154 m of Block-VII. The elemental composition of coal might depend on its affinity with different chemical fractions, physical changes, contents, and

chemically bound to trace elements or sulfur (Kazi et al. 2019).

Methods validation

Validation of analytical measurement

Validation of total Hg and other trace elements (sulfur, aluminum, calcium, hydrogen, iron, magnesium, and sodium) was checked by using SRM-1635a in sub-bituminous coal. Total Hg was determined by Pseudo extraction methods in SRM-1635a. It is a good agreement to the certified values as obtained percentage recovery > 97.1% given in Table 3. It proved that the Pseudo method favorably works for the extraction of total Hg in SRM as well as in coal. This SRM-1635a is also suitable for the validation and determination of sulfur, aluminum, calcium, hydrogen, iron, magnesium, and sodium by using EA and SEM–EDS. Resulted data of all the above-mentioned elements in coal has been carried out to find out the validity by SRM-1635a. The percentage recovery for SRM-1635a was calculated by using the given formula:

$$\text{Recovery}(\%) = \left\{ \frac{\text{experimental value}}{\text{certified value}} \right\} \times 100$$

Standard spiking addition method is used to check the accuracy and precision of the analytical measurement for total Hg in coal samples. Accuracy of total Hg was performed by spiking the three concentrations (2.0, 4.0, and 6.0 $\mu\text{g g}^{-1}$) into the extracted solution (Table 3). The percentage recovery of the total Hg determined by using Pseudo extraction method was observed in the range of 96.5–1001% shown in Table 3. After extraction of total Hg by Pseudo extraction method, the CV-AAS was used to determine the Hg concentration in coal of Block-VII. The percentage recovery in the standard spiking addition method was calculated by using the following formula:

$$\text{Recovery}(\%) = \left\{ \frac{\text{spiked Hg} - \text{unspiked Hg}}{\text{added Hg standard}} \right\} \times 100$$

where Spiked Hg means concentration of Hg in coal samples with spiking Hg standard solution; Unspiked Hg means concentration of Hg in coal samples without spiking Hg, standard solution; Added Hg standard (2.0, 4.0 and 6.0 $\mu\text{g g}^{-1}$), solution for each fraction.

DIN test for water-soluble fraction of Hg

Water-soluble Hg was extracted from coal by using a reported method named as DIN test (Ali et al. 2017). DIN test is applicable for mobility assessment of metals of high

Table 3 Method validation for total Hg determination by SRM and standard addition method

SRM-1635A				
Total Hg	Certified value		Experimental value	Recovery (%) ^a
Hg ($\mu\text{g g}^{-1}$)	0.0836		0.0812 ± 0.004^b	97.1
Standard Addition Method				
Added Hg	0.0 ($\mu\text{g g}^{-1}$)	2.0 ($\mu\text{g g}^{-1}$)	4.0 ($\mu\text{g g}^{-1}$)	6.0 ($\mu\text{g g}^{-1}$)
Pseudo Hg ($\mu\text{g g}^{-1}$)	1.65 ^c	3.58	5.71	7.60
Recovery (%) ^d	–	96.5	101	99.2

Key: ^bSample mean \pm standard deviation^cTotal Hg concentration at 152–154 m

$$^a\text{Recovery (\%)} = \left\{ \frac{\text{experimental value}}{\text{certified value}} \right\} \times 100$$

$$^d\text{Recovery (\%)} = \left\{ \frac{\text{spiked Hg} - \text{unspiked Hg}}{\text{added Hg standard}} \right\} \times 100$$

environmental concern. The Hg leaching process depends on environmental conditions and physicochemical parameters like pH, salinity, total dissolved salt, and electrical conductivity. Therefore, its external influence increases mobility under natural conditions. It is easily leached into the environment to participate in biogeochemical cycling (Zak et al. 2021). Water-soluble fraction of Hg in all studied coal samples was obtained in the range of $0.022\text{--}0.036 \mu\text{g g}^{-1}$ given in Table 4. DIN testing approach recommended assessing and determining the possible environmental hazards by easily leaching. The Hg in the water-soluble fraction was comparatively lower than as obtained Hg in the acid-soluble fraction. The results showed that it was easy to extract Hg by using DIN test from coal of the Thar coalfield.

Pseudo extraction method for total Hg

Pseudo extraction method is used to the determination of total Hg in solid samples. The resulted values of total Hg in coal from four coal seams of Block-VII were obtained in the range of $1.65\text{--}2.15 \mu\text{g g}^{-1}$. Resulted data indicated that the highest concentration of Hg in 200–203 m, while the lowest in 209–210 m is represented in Table 4. The concentration level of Hg was decreased with depths; it may be due to different mineralogical composition. Pseudo-total Hg and the sum of (acid-soluble + reducible + oxidizable) fractional concentration of Hg were obtained almost the same. The pattern of Hg occurrence in coal of the Block-VII was observed that the Hg concentration decreased with depth increased. Meanwhile, the pattern in decreasing order

Table 4 Results of total and fractions of Hg concentration in coal by using both extraction methods

Depth (m)	152–154	158–160	200–203	209–210
Water soluble ($\mu\text{g g}^{-1}$)	0.022 ± 0.001	0.036 ± 0.002	0.032 ± 0.001	0.034 ± 0.002
Pseudo Hg ($\mu\text{g g}^{-1}$)	1.65 ± 0.08	1.86 ± 0.10	2.15 ± 0.11	1.73 ± 0.08
BCR-SEM				
Fractions/depth (m)	152–154	158–160	200–203	209–210
Acid-soluble ($\mu\text{g g}^{-1}$)	0.14 ± 0.006	0.15 ± 0.008	0.24 ± 0.011	0.19 ± 0.01
Reducible ($\mu\text{g g}^{-1}$)	0.12 ± 0.005	0.16 ± 0.009	0.14 ± 0.005	0.13 ± 0.003
Oxidizable ($\mu\text{g g}^{-1}$)	1.18 ± 0.06	1.24 ± 0.07	1.21 ± 0.05	1.17 ± 0.058
Residual ($\mu\text{g g}^{-1}$)	0.29 ± 0.02	0.27 ± 0.02	0.24 ± 0.01	0.21 ± 0.01
Sum ^a ($\mu\text{g g}^{-1}$)	1.34 ± 0.08	1.55 ± 0.06	1.59 ± 0.09	1.49 ± 0.08
C_f^b	4.62	5.74	6.62	7.10
SSE-UAM				
Acid-soluble ($\mu\text{g g}^{-1}$)	0.16 ± 0.008	0.23 ± 0.002	0.19 ± 0.007	0.15 ± 0.004
Reducible ($\mu\text{g g}^{-1}$)	0.14 ± 0.006	0.19 ± 0.01	0.15 ± 0.008	0.15 ± 0.01
Oxidizable ($\mu\text{g g}^{-1}$)	1.25 ± 0.07	1.26 ± 0.04	1.40 ± 0.06	1.24 ± 0.05
Sum ^a ($\mu\text{g g}^{-1}$)	1.55 ± 0.09	1.68 ± 0.10	1.74 ± 0.11	1.54 ± 0.08
C_f^b	5.34	6.22	7.25	7.33

Key: ^aSummation of acid-soluble + reducible + oxidizable fraction

$$^b\text{The formula of } C_f = \frac{\Sigma(\text{Acid} + \text{Red} + \text{Oxid})}{\text{Residual}}$$

is as follows: 200–203 > 152–154 > 158–160 > 209–210 m of four depth of coal seams in Block-VII. Variation in Hg levels of the studied coal samples might be due to many factors, such as the different percentage composition of sulfur in coal from different depths (Ali et al. 2016). The concentration of Hg is high due to organic materials being dominant when the percentage of sulfur > 0.5%, while sulfur contents in coal can be captured in Hg. It was reported that Hg can be contained in pyrites coal; a higher percentage of organic sulfur is an indication that coal has a high level of Hg (Dai et al. 2017; Manceau et al. 2018). A high concentration of Hg was observed in the presence of pyrite coal and sulfide coal. Literature-reported data indicated that Hg also occurs in other minerals such as calcite, chlorite, clausenthalite, getchellite, and kleinite (Dziok et al. 2019b; Zhao et al. 2019). Total Hg concentrations were obtained in the range of 1.65–2.15 $\mu\text{g g}^{-1}$ in Block-VII of Thar coalfield. The mean value of Hg concentration in Thar coal is 1.84 $\mu\text{g g}^{-1}$ which was significantly lower than Wulantuga coal 3.165 $\mu\text{g g}^{-1}$ in China. The Clarke level of Hg in lignite coal was reported in the range of 0.20–0.30 $\mu\text{g g}^{-1}$, while in bituminous coal, it was 0.30–0.16 $\mu\text{g g}^{-1}$ (Dziok et al. 2019a).

Fractionation analysis of Hg

Acid-soluble fraction of Hg

Resulted data of acid-soluble Hg fraction by using proposed extraction approaches are shown in Table 4. Acid-soluble fraction of Hg by BCR-SEM and SSE-UAM was obtained in the range of 0.14–0.24 and 0.15–0.23 $\mu\text{g g}^{-1}$, respectively. It is an easily leachable fraction from coal whenever environmental conditions change. Acid-soluble Hg fraction is always extracted directly by using acidic media. The resulted data of acid-soluble fraction of Hg by BCR-SEM and SSE-UAM is almost identical (Table 4). Acid-soluble fraction of Hg can contaminate the surface water and groundwater due to changes in physicochemical parameters (Reis et al. 2016).

Reducible fraction of Hg

Metals are bound with iron oxides/hydroxides and manganese oxides/hydroxides under reducing conditions (Jain and Maiti 2022). An acidic medium hydroxylammonium chloride is mostly used to extract a reducible fraction of Hg. Variability of the proposed methods BCR-SEM and SSE-UAM was used to extract a reducible fraction of Hg in coal of Block-VII. The concentration of reducible fraction of Hg in coal of four coal seams was obtained in the range of 0.12–0.16 and 0.14–0.19 by BCR-SEM and SSE-UAM respectively. The Hg content in the reducible fraction of all coal samples studied in the four depths of Block-VII was 1.72–4.92% of the total Hg concentration.

Oxidizable fraction of Hg

The oxidizable fractions of Hg cannot be considered mobile and bioavailable fraction due to their strong bound with coal matrix under normal conditions. But it can be released into the environment by burning, melting, and aiding digestion under oxidizing conditions (Mutwa 2020). The concentration of oxidizable fraction of Hg in coal of four coal seams was obtained in the range of 1.17–1.24 and 1.24–1.40 by BCR-SEM and SSE-UAM respectively, given in Table 4. The concentration of Hg in the oxidizable fraction is higher than the reducing fraction, while the acid-soluble fraction is the lowest. The resulting data show that the oxidizable fraction of Hg component consists of 9.58–50.8%, which is the total amount of Hg associated with organic matter. During the formation of coal beneath the earth's surface, Hg can react with organic matter to form stable compounds. The results indicated that a significant portion of Hg was present in organic matter (Padalkar et al. 2019).

Comparison of the sequential extraction methodologies

Fractionation analysis of Hg in coal was measured by BCR-SEM and SSE-UAM shown in Table 4. In the SSE-UAM, except for the first extraction fraction, the Hg concentration was estimated according to each fraction by subtracting the results obtained in two consecutive phases. For example, to estimate the decreasing Hg concentration in SSE-UAM, the concentration of Hg in acid-soluble fraction was observed in less than that obtained with reducible fractions (Ali et al. 2017). Extraction efficiency for the reducible fraction of Hg by SSE-UAM was higher recovery than the original BCR-SEM. It indicates that the hydroxylammonium chloride extraction efficiency was increased by the application of ultrasound energy. The shorter exposure time significantly increases the extraction efficiency by using ultrasound energy which cannot allow reabsorption process at this stage. Furthermore, the Hg content extracted by SSE-UAM in oxidizable fractions was relatively higher than that of BCR-SEM. The percentage recovery of Hg was calculated by using the following formula in all extracted fractions:

$$\text{Recovery (\%)} = \left\{ \frac{\sum \text{of Hg fractions by SSE - UAM}}{\sum \text{of Hg fractions by BCR - SEM}} \right\} \times 100$$

Contamination factors

The contamination factor (C_f) is a measure of the degree of contamination of a sample with a particular element. In the context of Hg contamination in coal, the C_f can be used to evaluate the degree of Hg contamination in the coal sample. The reported procedure for the calculation of contamination factor is applied to estimate the contamination status of the coal in this research

(Padalkar et al. 2019). Retention of Hg in coal was collected from four seams of the Block-VII. The C_f for individual coal sample was calculated by the following formula.

$$C_f = \left\{ \frac{\sum (\text{acid soluble} + \text{reducible} + \text{oxidisable})}{\text{residual Hg}} \right\}$$

The experimental results of BCR-SEM were used to calculate C_{Fs} , which were obtained in the range of 4.62–7.10 shown in Table 4. In the current research, the average concentration of Hg in residual fraction by BCR-SEM is considered the main concentration for the calculation of C_f . The C_f s of our study are observed within the considered limits. As reported in the literature $3 > C_f < 6$ are considered considerable limits, and $C_f > 6$ are very high limits (Banu et al. 2013).

Conclusions

The proposed sequential extraction methods BCR-SEM and SSE-UAM were developed for fractionation analysis of Hg in coal from four coal seams of the Block-VII of Thar coalfield. These sequential methods provide relevant information about possible Hg pollutions in the environment and may also help in reducing Hg pollution during coal mining. The current modified SSE-UAM reduced the longtime requirement for extraction in BCR-SEM. All fractions can be extracted simultaneously, and consequently, the total operational time for BCR-SEM and SSE-UAM could be reduced from 51 to 2 h. Variation are observed in each and every extraction step for fractionation analysis of Hg in coal by BCR-SEM and SS-UM. In contrast, the higher amount of sample is required, which might be difficult in some biological cases but does not have any problem in coal. Therefore, SSE-UAM is a useful extraction method for fractionation analysis of Hg in coal samples. In our study, the calculated C_f is very high which indicates the possible contamination ruts and Hg bioavailability in groundwater and aquifer water of the Thar coalfield. Water-soluble and acid-soluble fractions are mobile fractions. The resulted data indicates the concentration of Hg in water-soluble fraction is low as compared to acid-soluble fraction and all other fractions. Relatively, the higher concentration of Hg was observed in oxidizable fraction compared to all other fractions obtained by BCR-SEM, SSM, and SSE-UAM methods. Characteristics of coal and elemental analysis were performed by ASTM methods, EA, SEM–EDS, and CV–AAS respectively.

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Data availability Information used in this research article is available at any time from the corresponding author on reasonable request.

Declarations

Ethical approval This manuscript does not have any ethical issue related to human and animal subjects performed by any of the authors.

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