



The evaluation of sequentially extracted mercury fractions in Thar coal samples by using different extraction schemes



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ABSTRACT

In the present study, various sequential extraction methods were applied to assess the mercury (Hg) contents bounded with different chemical fractions of coal samples, collected from four different seams of the blocks III and V in Thar coalfield, Pakistan. The BCR sequential extraction (BCR-SE) method and two alternative modified schemes (conventional and ultrasonic assisted single step extractions) were designed and applied on the same operating conditions for each individual BCR fraction. Proximate and elemental analyses of coal samples were also performed to point out the physicochemical characteristics of the Thar coal samples. Validation of the desired methodologies was checked by the standard addition method to the real coal samples. The Hg concentration in extractable fractions was determined by cold vapor atomic absorption spectrometer (CV-AAS). The proposed conventional (CSE) and ultrasonic assisted single step (USE) extraction methods were non-tedious and time saving, as the extraction time was reduced from 51 h to 36 h and 2 h, respectively. The extraction efficiency of CSE and USE was comparable with those data obtained with the conventional BCR protocol. The relative mobility of Hg in coal samples obtained from different depths was found in the following increasing order: oxidizable fraction < reducible fraction < acid soluble fraction.

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1. Introduction

Emissions of Hg from coal-fired power plants and other anthropogenic activities induce health risks (Luo et al., 2013). Coal is one of the most important energy sources in developing countries, due to its lower cost than other power generation sources (Liu et al., 2007). Coal combustion for power and heat generation may result in significant atmospheric emissions of volatile organic and inorganic toxicants (Matschullat, 2000). Worldwide, fossil fuel combustion accounts for 45% of the total Hg emissions (Yudovich and Ketris, 2005a, 2005b). Many studies have been carried out to quantify Hg and how to control its emissions from coal (Finkelman, 2003; Iwashita et al., 2004; Hower et al., 2000, 2005; Geng et al., 2008; Ohki et al., 2008; López-Antón et al., 2012). Recently, the nature of Hg in coal became a 'hot' issue in environmental prospective (Goodarzi et al., 2008; Tian et al., 2012). All Hg forms in coal are vaporized and converted to elemental form, which can

persist in the atmosphere for a period of 6–24 months (Dastoor and Larocque, 2004; Luo et al., 2013).

The release of Hg into the environment during coal combustion can be reduced by air pollution-control devices such as electrostatic precipitators or fabric filters, while Hg²⁺ is water soluble and can be captured by wet scrubbers (Chang and Ghorishi, 2003; Lee et al., 2006; Lei et al., 2007; Luo et al., 2009; Park et al., 2008). The distribution and mode of Hg occurrence in coal and how to improve its reduction have been extensively focused (Liu et al., 2007; Swaine, 2013; Zheng et al., 2008). The Hg contents in coal were largely diffused into other phases, due to its association with sulfides, pyrite, and organic fractions at various coal ranks (Hower et al., 2010; Wilcox et al., 2012).

The identification and quantification of various Hg forms in coal are important but a difficult task is the redistribution of Hg species during the separation process. Quevauviller (2002) has been noted that the determination of chemical forms or the nature of binding is more important than the total Hg content. The toxic effects and the geochemical pathways of elements are mainly depended on their mobile forms or bound with different fractions (Finkelman et al., 1990; Dai et al., 2004). The sequential extraction procedures have an important role in the assessment of different physicochemical behaviors of Hg in different environmental samples, but limited literature is available for coal samples (Hall et al., 2005; He et al., 2006; Noel et al., 2007). The BCR sequential extraction (BCR-SE) scheme is relatively complicated, time-

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consuming and not used frequently for routine analysis. A new modification in BCR-SE scheme has been put forward by using ultrasound energy to increase efficiency and reduce extraction time (Davidson and Delevoe, 2001; Ipolyi et al., 2002). The use of ultrasound power has been investigated to speed up sequential extraction methods because it has long been recognized that the cavitation effect created by ultrasound waves can break down the particle size, exposing a fresh surface and aggressively agitating the solution system (Mason, 1990). Thus, the USE is a more efficient scheme than CSE and BCR-SE (Greenway and Song, 2002; Kazi et al., 2006). Another attractive approach consists of replacing the sequential, stepwise extractions by single-step extractions with the same reagents and operating conditions as the sequential procedure, but a different sub-sample is employed for each fraction (Arain et al., 2008; Jamali et al., 2007). This option has been applied for the extraction scheme of Tessier's (Cid et al., 2001) and modified BCR as a single-step method on environmental solid samples, sediment, soil and sewage sludge (Canepari et al., 2005; Filgueiras et al., 2002; Arain et al., 2008). A variety of analytical techniques has been used for the determination of Hg content (Dai et al., 2015; Dai et al., 2006; Yudovich and Ketris, 2005b). The cold vapor-atomic absorption spectrometry (CV-AAS) is used for accurate and precise Hg results in various environmental and biological samples (Nguyen et al., 1998; Shah et al., 2010).

The total Hg content in environmental samples is a poor indicator of its bioavailability, mobility or toxicity, while analyses of different chemical forms are mandatory as it provides more useful information related to the distribution of Hg forms, potential toxicity and health risk. Mercury toxicity in the environment depends on total and chemical forms bound with different phases of coal (Nguyen et al., 1998). The objective of this study was to evaluate the Hg bound with various fractions of coal (exchangeable, reducible, and oxidizable), applying BCR-SE and the obtained resulted data compared with values of Hg from single-step extraction schemes (conventional and ultrasonic assisted) under the same operating conditions.

2. Geological setting

The Thar coalfield is situated in Thar Desert, south-eastern part of the Sindh Province of Pakistan (Fig. 1a). Major coal deposits are confined in north-east of Islamkot Town and positioned between 24°40'–25°00' N and 70°10'–70°30' E (Fig. 1b). The coalfield is spread over an area of more than 9100 km² with dimensions of 140 km north–south, 65 km east–west and 175 Gt estimated reserves. The coal rank is lignite (Ali et al., 2015) and for mining purpose, Thar coalfield is divided into 12 blocks.

The study area is covered by thick sand dunes; outcrops are lacking. Varieties of igneous and metamorphic rocks of Proterozoic to Late Proterozoic age are exposed in Karunjhar Hill, near Nagarparkar Town, south-east of Islamkot (Fig. 1b). The stratigraphic structure (Fig. 2) mainly relays on 39 boreholes drilled for coal mining purposes. The basement consists of granitic rocks of Precambrian age. The core cuttings of these rocks show resemblance with the igneous and metamorphic of Proterozoic to Late Proterozoic age exposed at Nagarparkar. The igneous and metamorphic rocks can be correlated with the Late Proterozoic Malani magmatic ones of western Rajasthan, India (Ahmad and Chaudhry, 2007, 2008). The granites show affinity for plate A-type per-alkaline to per-aluminous granites with some acid–basic dykes and rhyolite plugs (Ahmad and Chaudhry, 2007; Ahmed et al., 2012). The upper part of granites is weathered and altered into kaolin (Baig and Ahmad, 2007; Choudry et al., 2010; Malkani, 2012). The kaolin deposits are generally covered by 30-m-thick sand dunes and alluvial sediments. The dune sands are mainly composed of quartz and feldspar, with a number of minerals. The sizes of the sand grains are in the range of \varnothing 2.30–2.74 mm (Kar et al., 2001). The thickness of the kaolin pockets is estimated to be 2–8 m (Naseem et al., 2010).

Sedimentary rocks of Bara Formation (Middle Paleocene–Early Eocene) overlay unconformably the granite (Kazmi and Jan, 1997). The Bara Formation consists of claystone, carbonaceous sandstone, siltstone, and interlaminated coal beds (Fig. 2). At a depth around 150 m beneath the current surface, several coal layers of variable thickness (8–36 m) is intercalating. Maceral analysis indicates that huminite ranges from 85 to 95%; Liptinite and Inertinite group macerals constitute 1.0 to 8.1% and 1.1–8.1%, respectively (Ahmed et al., 2012). The coal contains significant amounts of trace elements, notably As, B, Cd, Pb, Hg, Mo and Se. The topmost horizon comprises sand dunes formed through desertification, approximately 150 ka ago (Dhir et al., 2004; Singhvi and Kar, 2004).

3. Material and methods

3.1. Sampling

Coal samples were collected from four seams at different depths (125–255 m beneath surface), from blocks III and V of Thar coalfield. Five coal samples were collected from each seam by using core sampling, so the twenty samples were collected from each block. Blocks III and V were being drilled at the time of sampling in 2014. The collected coal samples were subsequently transferred to clean polypropylene bags, to avoid contamination.

3.2. Reagents and glassware

Ultrapure water (resistance 0.05 μ S/cm) obtained from an ELGA laboratory water system (Bucks, UK), was used throughout the experimental work. The extracting solutions were prepared from reagents of analytical grade and were checked for possible trace metal contamination. HCl (purity 37%, Sp.gr: 1.19), HNO₃ (purity 65%, Sp.gr: 1.41), and H₂O₂ (purity 30%, Sp.gr: 1.11) were obtained from Merck (Darmstadt, Germany). A working standard solution of Hg was prepared for calibration from stock standard solution (1000 mg/L), Fluka Kamica (Bushs, Switzerland). Ammonium acetate was purchased from Sigma-Aldrich (Milwaukee, WI, USA). Analytical reagent grade, acetic acid and hydroxylammonium chloride (HONH₂·HCl), were obtained from Merck. All glassware and polyethylene bottles were thoroughly washed then soaked overnight (5.0 mol/L, HNO₃) and were rinsed in ultrapure water before use. In the laboratory, each coal sample was spread on the plastic trays in fume hoods separately and allowed to dry at ambient temperature for eight days. The samples were prepared by grinding and screening through 100-mesh sieve and stored in plastic bags to avoid contamination.

3.3. Apparatus

An end-over-end mechanical shaker (Gallankamp, Germany) was used for shaking. The phase separation was assisted with a centrifuge ROWKA Laboratory type WE-1, nr-6933 (Mechanika Preczyzjna, Poland). A pH meter (Ecoscan Ion 6, Kuala Lumpur, Malaysia) was employed for pH adjustments as well as for measuring the pH values of water extractable solutions. The Hg content in all samples was determined by a double-beam Perkin Elmer model A Analyst 700 (Norwalk, CT, USA) atomic absorption spectrophotometer, coupled with MHS-15 chemical vapor generation system (Perkin-Elmer). A single element hollow cathode lamp of Hg operated at 5 mA was used as energy source. The Hg signal was isolated at 253.7 nm with a spectral bandwidth of 2.6 nm. The WinLab 32 software was used to process and calculate analytical data.

3.4. Proximate analysis

Proximate analysis of coal samples was conducted according to a standard test method (ASTM Standard D7582, 2013). Moisture was

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