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Research article

A comparison of two digestion methods for assessing heavy metals level in urban soils influenced by mining and industrial activities

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ABSTRACT

A comparison between two digestion methods of hot plate Hossner (total-total) and USEPA method 3051 (total-recoverable) was carried out to suggest a proper method for determining nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) content of three urban soils affected by mining (Mahd AD'Dahab) or industrial activities (Riyadh and Jubail) at Saudi Arabia. The results showed no significant differences between two digestion methods for Cd, Cu, Pb and Zn in soils affected by mining and for Cr, Cu, Pb and Zn in soils affected by industrial activities. Additionally, lower biases were obtained between two methods for metals Cd, Cu, Zn and Pb in the urban soil samples from mining area with the percent biases of −16.5%, +6.24%, −12.4% and +24.1%, respectively. The results also revealed that only Cu and Zn in the soil samples from Riyadh were extracted satisfactorily using USEPA 3051 with low biases of +5.69% and −9.61%, respectively. Meanwhile, only Pb in soil samples from Jubail showed lower baise between two methods with satisfactory biase of −8.07%. The correlation coefficients were significant between total-recoverable and total-total concentrations for Cu ($r = 0.66$), Pb ($r = 0.72$) and Cd ($r = 0.65$) in soil samples from mining area. Overall, concentrations of Co, Cr, Fe, Mn, and Ni that may show soil background concentrations were found higher by Hossner method than by USEPA 3051; thus, this suggests the addition of hydrofluoric acid (HF) is necessary for the determination of lithogenic metal concentrations. It could be concluded that the USEPA 3051 may be recommended and applied for total Cd, Cu, Pb and Zn originated from anthropogenic source in mining and industrial areas.

1. Introduction

Heavy metals are considered as the main inorganic contaminants in the environment due to their negative impact on living organisms and their disordering of the environmental balance (Al-Bakheet et al., 2013). Heavy metals occur naturally in the environment with differences in their concentrations. However, the ecosystem has been influenced and polluted by heavy metals generated from anthropogenic sources such as the disposal of residues from fossil fuel combustion processes and from different branches of the metallurgical, mining, and chemical industries (Alloway, 2013). The concentration of heavy metals in topsoil may be generated by the processes of soil formation; however, it has been decisively established that heavy metal concentration derives from agricultural and human activities (Meuser, 2010). Currently, an accurate estimating for heavy metal concentrations in different compartments of the ecosystem poses a great challenge.

Recent studies have suggested that a simple, clean and efficient process can be used as an alternative to the conventional complex process to extract heavy metals from metal containing materials (Elsentriecy et al., 2015). Digestion procedures, including conventional acid digestion and microwave-assisted acid digestion, have been widely applied to prepare samples for spectral analysis. The conventional procedures involve use of an open vessel, where the solids must be extracted after heating the sample in the presence of a mixture of acids. The conventional procedures have many advantages, such as relatively low-cost devices and instruments, and reduce the need for advanced treatment of samples. However, the

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conventional digestion procedures often take a long time and many stages for analysis, and they are labor intensive, arduous and tedious and often have a high contamination potential (Sastre et al., 2002). Because the conventional methods are conducted in an open system under heating, there are risk of atmospheric contamination and a significant threat to the health of the laboratory technicians due to releasing toxic gases (Chen and Ma, 2001). By contrast, the microwave-assisted digestion method is reportedly very fast (one half hour) and safer than the previous method because the system is closed. This closed procedure permits use of higher temperature and pressure and leads to an efficient dissolution of metals; moreover, it reduces the loss of volatile components, consumption of acids, and risk of contamination (da Silva et al., 2014; Lo and Sakamoto, 2005). Because of the need for fast and accurate estimates of heavy metal content in solid components of soil, sediment or other sources, different methods of microwave-assisted digestion have been developed to provide an effective decomposition of metals (Lo and Sakamoto, 2005). These methods are numerous and dependent on the choice of reagents and specific heating programs. In most studies, high pressure has been applied to the samples using advanced technology digestion devices (Sastre et al., 2002; Sandroni et al., 2003; Ramanathan and Ting, 2015). It has been shown that the method of acidic digestion by microwave is the most appropriate method for the digestion of complex materials such as soil and sediment containing oxides, silicates and organic material (Kingston and Haswell, 1997). Most data show that digestion methods using acids, whether Aqua regia or HNO_3, yield results close to 100% of the total elemental composition depending on the studied component, with the exception of the metals associated with silicates (Andersen and Kisser, 2003; Santoro et al., 2017). Therefore, the partial digestion methods using acids are considered appropriate for pseudo-total analysis, but they do not completely dissolve silicates.

It is not clear whether these results can be applied to soils that are considerably influenced by anthropogenic contamination due to dust deposition in urban areas affected by mining and industrial activities. Thus, the objective of this study was to compare two digestion methods, the total digestion (total-total) method by Hossner (1996), and the partial digestion (total-recovery) method by USEPA 3051 (HNO_3), for determining the heavy metals level in soils collected from three different sites affected by mining and industrial activities.

2. Materials and method

2.1. Areas of study

Mahd AD'Dahab and the industrial areas of Jubail and Riyadh represent a special model in terms of the type and intensity of industrial activity in Saudi Arabia, so the studied samples were collected from the affected areas in these three cities. Riyadh is the capital and inhabited by approximately 18% of the population of Saudi Arabia. Near Riyadh, there are two industrial cities containing more than 2150 factories. The studied area in Riyadh received liquid waste derived from pulp, textile, plating, or leather tanning industries (Usman et al., 2017). It is located east of the second industrial city in Riyadh, and covers approximately 73 hectares. This area is located between longitude (E) 46° 55′, and latitude (N) 24° 32'. The industrial area of Jubail (101,600 ha) is considered the primary industrial area, which specializing in petrochemicals and oil refining. Jubail city is located on the Arabian Gulf Coast, and approximately 80 km to the north of Dammam city. It is located at longitude (E) 48° 54′, and latitude (N) 26° 89'. Mahd AD'Dahab also contains the oldest and largest gold mine in the Kingdom of Saudi Arabia. The studied area represents the area of Mahd AD'Dahab, which falls within the province of Mahd AD'Dahab southeast of Medina and covers almost 966 ha. It is located between longitude (E) 40° 87′, and latitude (N) 23° 48′ (see Fig. 1).

2.2. Soil sampling and analysis

Ten soil samples from a depth of 0–5 cm were collected randomly from each location (Mahd AD'Dahab, Riyadh industrial area, and Jubail industrial area) in the Kingdom of Saudi Arabia. The soil samples were air-dried at room temperature and sieved through a 2-mm screen.

The particle size distribution was determined by the hydrometer method (Gee and Bauder, 2002). Soil pH was measured using a glass electrode in a water suspension at 1:5 ratio, and electric conductivity (EC) in its extractants was measured by EC meter. The concentrations of soluble Na and K were measured using a flame photometer. The concentrations of soluble Ca and Mg were determined by titration with ethylene-diamine-tetra-acetic acid (EDTA) 0.01 N, and an appropriate indicator. The concentrations of CO_3^{-2} and HCO_3^{-1} were estimated by titration with sulfuric acid (0.005N), while Cl^{-1} was titrated with $AgNO_3$ (0.02N) according to Gupta (2007). Sulfate (SO_4^{2-}) was determined using the turbid metric method, and the resulting turbidity was measured by a spectrometer (Gupta, 2007). Calcium carbonate content was determined using a calcimeter (Loeppert and Suarez, 1996). The content of soil organic carbon was determined by the method of Nelson and Sommers (1996) with a back titration method. Cation Exchange Capacity (CEC) was estimated by the sodium acetate method (Loeppert and Suarez, 1996). Gypsum was determined by the acetone method (Loeppert and Suarez, 1996).

The total metal content in soils was determined by the (total-recoverable) USEPA 3051 method (USEPA, 1994) and the (total–total) digestion method according to the Hossner method (HF-H_2SO_4-$HClO_4$) (Hossner, 1996). For the 3051 method, a representative sample (0.5 g of ground dried soil) was transferred into a Teflon microwave digestion vessel, and 10 ml of concentrated HNO_3 was added. The sample vessels were placed into a microwave digestion unit (MARS), and appropriate software was used to heat the sample to 180 °C for 10 min. After digestion, the supernatant was collected and passed through Whatman No. 42 filter paper. The filtered solutions were then diluted to 25 ml and analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). For the Hossner (HF-H_2SO_4-$HClO_4$) method, a ground soil sample (0.5 g) was placed in a crucible (50 ml) and was moistened with few drops of H_2SO_4 18 M (98%). Then, 5 ml of HF 29 M (48%) and 0.5 ml of $HClO_4$ 12 M (70%) were added. The mixture was then heated on a hot plate until the $HClO_4$ fumes were exhausted, and then the mixture was removed from the hot plate and cooled. Approximately 5 ml of HF was added to the crucible, and the mixture was then heated at 250 °C until dry. When the mixture was not clear upon cooling and still had organic matter, the addition of acids was repeated until the solution was clear. After cooling, 5 ml of HCl 6 M (98%) and 5 ml of distilled water were added to the crucible and heated until boiling. Thereafter, the solution was removed from the hot plate to cool and was filtered through Whatman No. 42 filter paper, was then transferred quantitatively to a 25-ml volumetric flask by adding distilled water, and was finally stored in 50-ml polyethylene bottles at 4 °C until analysis.

2.3. Geo-accumulation index

The geo-accumulation index (I_{geo}) has been applied to quantify heavy metal pollution levels in soil samples. The I_{geo} can be calculated by the following equation (Eq. (1)) according to Muller (1979):