Rapid and Simultaneous Detection of Hazardous Heavy Metals Contamination in Agricultural Soil Using Infrared Reflectance Spectroscopy

Devianti1, Sufardi2, Zulfahrizal1, Agus Arip Munawar1*
1Department of Agricultural Engineering, Syiah Kuala University, Banda Aceh - Indonesia.
2Department of Soil Science, Syiah Kuala University, Banda Aceh - Indonesia.
*Corresponding author: aamunawar@unsyiah.ac.id

Abstract. Soil function can be disrupted by highly accumulated contaminations in soils, due to several human activities such as building construction, mining, sewage disposal, transportation, and fertilizing. These activities may cause contaminations especially by heavy metals accumulated in soil and surely will affects growing plants on it. A real time, quick, robust and simultaneous method is therefore required to rapidly detect heavy metal contamination in agricultural soil. Infrared technology has been widely employed and applied in many field areas including in agriculture and soil science. The main aim of this research is to study the feasibility of infrared spectroscopy as a fast and robust method in detecting hazardous contaminations caused by accumulated heavy metals namely Zn and Pb in agricultural soil. Diffuse reflectance spectral data were acquired for a total of 8 soil samples from four different site locations in Aceh province. Spectra data, in wavelength range of 1000-2500 nm, were enhanced using multiplicative scatter correction (MSC). Hazardous detection was performed using principal component analysis (PCA) and accumulated heavy metals were predicted using partial least square regression (PLSR) method. The results showed that IR spectroscopy can clearly distinguish contaminated soil and un-contaminated ones, with total explained variance derived from PCA was 97%. Both accumulated heavy metals (Zn and Pb) can be predicted simultaneously with coefficient correlation (r) were 0.98 for Zn and 0.98 for Pb, whereas residual predictive deviation (RPD) indexed were 3.85 for Zn and 3.91 for Pb. It may conclude that infrared spectroscopy can be used as a fast, robust and accurate method in detecting and predicting heavy metal contaminations in agricultural soil.

Keyword : infrared reflectance spectroscopy, principle component analysis, partial least square regression

1. Introduction
Soil is the main media for growing plants, whether it is food crops or plantations. In fact, plants can grow ideally on healthy soil, if the soil has physical and chemical properties that are suitable with plant growth. Healthy soil conditions can be seen visually by looking its texture, structure and humidity. Soil chemical properties are related to the amount of nutrients needed by plants, with the amount needed will be different for each growing phase [1]. Soil fertility is largely determined by the presence of nutrients in the soil, both macro nutrients, secondary, and micro nutrients. Nutrients that are lacking in the soil will obviously affect plant growth. Growth rate will be very disturbed and susceptible to disease because
soil nutrients do not meet the minimum requirements needed. Conversely, the amount of excessive nutrients in the soil will also affect plant growth and the surrounding environment [2].

Human activities, such as mining, transportation, sewage disposal and fertilizing, have been posing an ongoing threat to the soil health [3]. Moreover, the consumption of metal-polluted crops (e.g., rice, corn and soybean) grown in agricultural soils greatly raises the potential risks of food security and human health [2, 4]. In precision agriculture practice, fertilization and excessive use of fertilizer will cause pollution to the environment because it can cause artificial nutrient deposits that are not utilized by plants. This of course will accumulate and make new problems especially pollution due to the use of pesticides, fertilizers and fertilizers that are above the normal amount [3].

The chemical, biological, and physical unbalance caused by soil contamination by hazardous materials may be detrimental to plant, animal, and human health. For example, the symptoms of reduced root growth, reduced seed sprouting, and seedling stunting, necrosis, and chlorosis appear susceptible plants growing in soils contaminated with heavy metals [5]. Agricultural crops (fruits, grains, and vegetables) for livestock human consumption, growing on contaminated soil, can potentially uptake and accumulate hazardous materials in their edible plant parts, and may be harmful to animal and human health through the food chains [6].

From this point of view, the determination of hazardous contamination on agricultural soils is necessary to monitor the health of agricultural soils and further to take preventative measures to avoid soil contamination. A reliable and environmentally friendly method is therefore needed to rapidly detect and survey the spatial distribution soil contaminations, to diagnose suspected contaminated areas as well as control the rehabilitation processes [2, 3, 7].

During the last few decades, infrared technology has been widely used and become most promising methods of analysis in many field areas including in soil science and agriculture due to its advantage; simple sample preparation, rapid, and environmental-friendly since no chemicals are used. More importantly, it has the potential ability to determine multiple parameters simultaneously [3, 6, 8, 9].

The overall research findings of numerous studies [9, 10, 11] on the application of near infrared spectroscopy (NIRS), shows that NIRS was feasible to be applied as a rapid and non-destructive tool for quality attributes prediction in agricultural sectors. The prediction model performance was sufficiently robust and accurate with correlation coefficient (r) range of 0.93 – 0.99 and residual predictive deviation (RPD) index was 1.53 – 4.68 which is categorized as coarse, sufficient and excellent prediction models respectively.

Therefore, based on advantages and excellence of NIRS, we attempted to apply the NIRS method in predicting soil contaminations by heavy metals (Pb, Zn and Cu). We hope that we will achieve satisfactory results from which NIRS can detect and classify soil condition. This study will describe the feasibility of NIRS technology in detecting hazardous contaminations on agricultural soil rapidly and develop the prediction model to quantify the amount of accumulated heavy metals on agricultural soil. The prediction model was established based on IR spectroscopic data after scatter correction using principal component analysis (PCA) and partial least square regression (PLSR).

2. Materials and Methods
2.1. Samples
A bulk of soil samples from four different site locations in Banda Aceh and Aceh Besar area were taken and stored for two days to equilibrate before spectra acquisition and further chemical analysis. Soil contaminations were made manually by injecting 250, 500, 750 and 1000 ppm heavy metals liquid namely Zn and Pb.

2.2. Spectra data acquisition
Infrared spectral data in form of diffuse reflectance spectrum were taken of all soil samples using infrared instrument (FTIR, Thermo Nicolet Antaris II MDS). The basic measurement with probe detector was chosen as a basic measurement in high resolution format. The infrared spectrum was collected and recorded in wavenumbers range from 4000 to 10 000 cm$^{-1}$ with co-added 32 scans and averaged. Spectra data were stored in local computer with three different file formats (*.SPA, *.JDX and *.CSV) [5].
2.3. Spectra data correction
In order to obtain accurate and robust prediction results, infrared spectra data were enhanced and corrected using multiplicative scatter correction (MSC) [6].

2.4. Soil contaminant detection
Once spectra correction was completed, soil contamination was detected rapidly using corrected spectra data. These data were projected onto principal component analysis (PCA) in order to classify and distinguish soil samples between contaminated and un-contaminated [5]. On the other hand, soil contamination prediction models were developed using partial least square regression (PLSR) and validated using leverage validation method [5].

2.5. Prediction model performance
Soil organic prediction performances were judged for their accuracies and robustness using several statistical indicators: coefficient of determination ($R^2$), correlation coefficient ($r$), root mean square error (RMSE) and the residual predictive deviation (RPD) defined as the ratio between the standard deviation and the root mean square error. The higher the RPD, the greater and robust the model to predict heavy metal contamination on soil samples [5, 6]. It is obvious that the good model should have high $R^2$ and $r$ coefficient, low value of RMSE and few number latent variables of PLSR [5].

3. Result and discussion
3.1. Typical spectra of soil sample
Typical diffuse reflectance spectra for soil samples was presented in Figure 1. The result shows several peaks represent the vibration of molecular bonds of C-C, O-H, N-H, C-H-O and C-H. Original spectra data before correction were still interference due to noise resulted from light scattering. These noises were corrected using several pre-treatment methods namely multiplicative scatter correction (MSC). As shown in Figure 2, these spectra correction methods clearly enhance spectra appearance and remove some noises due to light scattering.

![Figure 1. Typical diffuse reflectance spectra data of soil samples before correction.](image-url)

Spectral data acquired from the near infrared instrument generally contain background information and noises which are interfered and affected desired relevant soil quality information such as C-organic or even soil contaminations. Interfering spectral parameters, such as light scattering, path length variations and random noise resulted from variable physical sample properties or instrumental effects need to be removed or minimized in order to obtain accurate, robust and stable calibration models. Thus, it is necessary to enhance and correct spectral data before further analysis. Spectra enhancement was conducted using multiplicative scatter correction (MSC) as presented in Figure 2.
Figure 2. Diffuse reflectance spectra after correction using MSC.

As shown in Figure 2, spectra data were obviously enhanced and corrected compared to un-corrected one. In this study, NIR spectra data were enhanced using MSC, de-trending (DT) and combination of DT+MSC. The de-trending pre-treatment method tends to remove nonlinear trends in spectroscopic data, while MSC method used to reduce amplification due to light scattering and offset due to additive chemical effects in near infrared spectra.

3.2. Soil classification based on spectra data

The PCA result as for soil contamination detection was shown in Figure 3. It shows a significantly cluster based on soil characteristics. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. PCA is used as a tool for screening, extracting, compressing and discriminating samples based on their similarities or dissimilarities of multivariate data. The first PC (PC1) accounted 91% of all spectra data while remaining 7% was explained by the second component (PC2).

Figure 3. PCA based on infrared spectra for soil contamination detection

The differentiation of showed PCA classification is probably due to nutrient content and heavy metals contamination of related soil. Based on principal component analysis (PCA) results, it was obvious that NIRS method was able to distinguish and classify soil based on heavy metal contaminations. Soil spectral features in the infrared wavebands are highly correlated to the vibration modes of functional groups like the chemical bond of H and C, N, and O.

Moreover, the NIR technology applied in this study, was able to predict soil contaminations caused by heavy metals namely Zn and Pb. The best and most accurate prediction results for both heavy metals contaminants can be predicted by using MSC spectra data.
Figure 4. Pb and Zn prediction of soil samples

As shown in Figure 4, for Zn prediction, the NIR technique achieved excellent prediction result with correlation coefficient (r) was 0.98 and residual predictive deviation (RPD) index was 4.57. Furthermore, for Pb prediction, the SNV spectra correction method gave also excellent prediction result with r coefficient was 0.98 and RPD index was 4.25.

4. Conclusion
Based on obtained results, we may conclude that near infrared spectroscopy can be used and employed as a rapid and environmental-friendly method used to predict soil contaminations. Achieved present study shows that infrared technology was feasible to use as a rapid, innovative and non-destructive method in soils quality properties classification and evaluation based on their contamination. Moreover, this technology can also predict heavy metals contamination with excellent satisfactory result: r = 0.98 and RPD = 4.57 for Zn prediction, and r = 0.98 with RPD = 4.25 for Pb prediction.

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