Rapid determination of mixed soil and biochar properties using a shortwave near infrared spectroscopy approach

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Abstract. Presented study aimed to apply the near infrared spectroscopy approach in determining some related properties of soil mixed by biochars. Spectra data of soil samples were acquired using a self-developed NIRS instrument (PSD NIRS i16) in shortwave near infrared (SW-NIRS) range from 1000 to 1750 nm with optical gain 4x and co-added of 32 scans per acquisitions. Spectra data were corrected and enhanced using mean centering and peak normalization. Multivariate analysis namely principal component regression (PCR) were employed to develop NIRS based models followed with leverage validation. The results showed that mixed soil samples with biochar properties (K and N) can be determined simultaneously with maximum correlation coefficient are 0.86 and 0.77 for K and N respectively. Based on this obtained performance, it may conclude that SW-NIRS approach can be applied to determine related properties of mixed soil biochar samples rapidly.

1. Introduction

The increase in population has caused the demand for land needs to continue to increase. Fulfilling land demands if not followed by an evaluation of land capability/suitability will cause land degradation (degradation). Then the uncontrolled clearing and land conversion triggers land degradation. This land damage can occur on mineral soils or organic soils such as peat [1], [2]. There are around 48.3 million ha or 25.1% of the total area of Indonesia which has been heavily degraded and become critical land. Degraded lands generally show a decrease in soil quality such as low soil carbon content, low porosity, unstable aggregates, low base saturation, cation exchange capacity, and ultimately decreased land productivity [3], [4].

Determination of soil quality parameters requires special instruments, expensive chemicals, takes a long time, and is not real time. Plant tissues such as biochar have complex, hygroscopic, porous, and heterogeneous characteristics. Because of the complex and heterogeneous nature of the sample analyzed, it must be truly representative, not exposed to free air for too long, and not destructive. This research was conducted to find alternative solutions [5]–[7].

Proximate and elemental analysis are two of several alternative analyzes used in determining nutrients for both plant tissue and mineral soils. Proximate analysis is a destructive analysis and has been widely used to determine substances present in plant tissue including their mineral stability. Proximate analysis still uses disturbed samples, so it is feared that the results obtained will also be disrupted if carefulness is not enough. The parameters analyzed by proximate are generally carbon content (carbon), volatile matter, water content, and ash content of plant tissue. Besides that, the proximate analysis method in the analysis process takes a long time, is expensive, uses chemicals and also requires more energy. Elemental analysis is a non-destructive analysis generally to determine the content of C, H, N, O and S plant tissue. Then for mineral soils, generally the determination is done destructively [8]–[10].
The problems of time, cost, real-time and accuracy have made experts try to use infrared light as a substitute for conventional methods, this is due to the fact that using infrared does not take a long time, is accurate, simple and real-time. One of the uses of infrared light is FTIR (Fourier Transform infrared) for characterization and monitoring of organic matter and biochar in the soil. FTIR provides the advantage of high sensitivity, resolution and data acquisition speed [11], [12]. However, FTIR requires higher costs because it requires a computer hardware device to process the resulting data. FTIR also has limitations or weaknesses, especially because this method cannot identify the type and content of a sample with certainty [13]–[15].

Realizing these limitations, experts became interested in using Near Infrared Spectroscopy as an alternative method to test and predict the content of an element. In 2018 the use of NIR was already used for soil and organic matter characterization [12], [16]. Then, this tool is proven not to damage the material (non-destructive), does not require chemicals so that it is pollution free, and can predict soil characteristics simultaneously. Based on the above description, this study aims to expand the ability of NIR to predict some nutrient content in soil and organic tissue (biochar), then serve as an alternative method to substitute proximate and conventional methods.

2. Materials and Methods
   2.1. Soil Samples and Biochar
   A total of 3 types of samples were used, namely the ex-excavation of the coal mine of PT Mifa Bersaudara, located in the western part of Aceh Province with coordinates 4°06’46.48”N and 96°11’11.86”BT, the soil that has been treated with biochar bamboo apus (Gigantochloa apus) 20 tons/ha for 50 days, 7 types of biochar whose feedstock is obtained from areas outside the campus of Syiah Kuala University, Banda Aceh as presented in Figure 1.

   ![Figure 1](image)

   Figure 1. The sample used. (a) Land ex excavated from a coal mine; (b) Biochar; (c) Mining land + Apus bamboo biochar.

   2.2. Actual soil properties measurements
   Soil samples, and mixed soil with bamboo biochar were put into a film bottle for actual properties measurements using these following methods namely Kjeldahl for nitrogen (N) and Walkey and Black or potassium (K) measurement [17].

   2.3. Spectra data acquisition
   Soil samples, soil applied with bamboo biochar, and biochar were put into a film bottle for spectrum taking by placing each sample in the light hole. The NIRS spectrum was obtained using a self-developed PSD NIRS i16 device with a workflow configuration that was built using the integrated software [11], [18], [19].

   2.4. Spectral data correction
   The near infrared spectra data were firstly corrected using the multiplicative scatter correction algorithm from which is suitable for bulk samples. The aims of spectral data correction are to eliminate various kinds of noise in the sample spectrum so that the prediction results are more accurate [20].
2.5. Prediction model
The nutrient contents of mixed soil and biochar were predicted by establishing models based on data from the acquisition of NIRS spectrum (variable X) and actual laboratory data as N and K using the proximate analysis method from the measurement results in the laboratory (variable Y). Evaluation of the model’s accuracy is evaluated by looking at statistical parameters which include; correlation coefficient (r), determination coefficient (R²), root mean square error (RMSE), ratio prediction to deviation (RPD), and the number of latent variables (LV). It is obvious that good model should have high r and R² values, low RMSEC, RPD > 2 and latent variable < 9 [21], [22],[23]–[26]: RMSEC and RPD is calculated by the equation [27]–[30]:

$$RMSEC = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\hat{y}_i - y_i)^2}$$

$$RPD = \frac{SD}{RMSEC}$$

Where: \( \hat{y}_i \): Parameters from the initial estimate of the \( i \)th sample model, \( y_i \): Parameter to the laboratory measured value for the \( i \)th sample, N: the number of samples in calibration or validation, SD: standard deviation for the actual data measured by means of standard laboratory methods.

3. Results and Discussion
Spectra features of mixed soil with biochar is presented in Figure 2. Spectral data corresponds to the vibration of molecular bonds in particular wave lengths in the near infrared region. The primary information obtained from the spectrum is related soil properties like macr and micro nutrient contents, minerals and other quality attributes.

![Figure 2](image-url)  
**Figure 2.** Spectra features of mixed soil and biochar samples in the SWNIR region.

Spectral data were then used to develop prediction models used to determine inner properties and chemical constituents of studied samples where in this case is mixed soil and biochar samples. This study uses several types of biochar with different types of feedstocks. Biochar was analyzed in the soil and plant research laboratory using the proximate analysis method. The descriptive statistics of mixed soil and biochar analysis is shown Table 1.
Table 1. Descriptive statistics of actual K and N measurement

| Statistical indicator | Soil properties |
|-----------------------|-----------------|
|                       | K              | N              |
| Mean                  | 0.88           | 0.15           |
| Max                   | 2.58           | 0.52           |
| Min                   | 0.26           | 0.02           |
| Range                 | 2.32           | 0.50           |
| Standard deviation    | 0.51           | 0.14           |
| Variance              | 0.26           | 0.02           |
| RMS                   | 1.02           | 0.21           |
| Skewness              | 1.44           | 1.25           |
| Kurtosis              | 2.14           | 0.47           |
| Median                | 0.69           | 0.09           |

First of all, prediction models were developed using raw original spectra data from which spectral data and actual soil properties are used to construct the models using the principal component regression approach. Prediction performance of K and N prediction is presented in Table 2.

Table 2. Prediction performance of K and N determination using raw spectra data

| Soil properties | Statistical parameters | R² | r      | RMSE | RPD | RER |
|-----------------|------------------------|----|--------|------|-----|-----|
| K               |                        | 0.73 | 0.86  | 0.26 | 1.96 | 8.92 |
| N               |                        | 0.59 | 0.77  | 0.09 | 1.60 | 5.58 |

K: potassium, N: nitrogen, R²: coefficient of determination, r: correlation coefficient, RMSE: the root mean square error, RPD: ratio prediction to deviation, RER: range to error ratio.

Scatter plot derived from actual measured K versus predicted K is presented in Figure 3, while for N prediction, is shown in Figure 4.

Figure 3. Scatter plot of actual and predicted K using raw spectra data

Based on obtained prediction performance, it can be seen that raw spectra data generated accurate and robust result for K prediction where the correlation coefficient reach 0.86 and the RPD index is 1.96. From the literature [27], [31]–[34], the prediction performance categorized as good model performance since the correlation coefficient is above 0.8 and RPD index is nearly 2. However, contradictory result is obtained when the model is constructed to determine N content of studied...
samples. The correlation coefficient reach is 0.77 and the RPD index is 1.60 where indicated as sufficient prediction performance and need improvement to increase prediction accuracy and robustness as presented in Figure 4.

![Figure 4](image)

Figure 4. Scatter plot of actual and predicted N using raw spectra data

In order to generate more robust and accurate prediction results, the models were then constructed using enhanced and corrected spectral data, where multiplicative scatter correction method is employed. The prediction performance of MSC models for K and N determination of mixed soil and biochar samples is shown in Table 3.

### Table 3. Prediction performance of K and N determination using MSC spectra data

| Soil properties | Statistical parameters |
|-----------------|------------------------|
|                 | $R^2$ | $r$ | RMSE | RPD | RER |
| K               | 0.79  | 0.89 | 0.23  | 2.21 | 10.08 |
| N               | 0.72  | 0.85 | 0.07  | 2.05 | 7.17  |

$K$: potassium, $N$: nitrogen, $R^2$: coefficient of determination, $r$: correlation coefficient, RMSE: the root mean square error, RPD: ratio prediction to deviation, RER: range to error ratio

Based on obtained results, it can be seen that enhanced spectra data using the MSC algorithm generated more accurate and robust results compared to raw original spectra data for K determination as presented on Figure 5.

![Figure 5](image)

Figure 5. Scatter plot of actual and predicted K using MSC spectra data.
It is obvious that the accuracy is improved when the model is constructed by mean of MSC spectra. The correlation coefficient is increased to 0.89, and consequently, the RMSE prediction error index is decrease to 0.23. Similar finds also found when the MSC based model is developed to determine the N content as sown in Figure 6.

![Figure 6](image_url)

**Figure 6.** Scatter plot of actual and predicted N using MSC spectra data.

Judging from the prediction performance for both K and N contents determination in mixed soil and biochar samples, it is recommended to correct the spectral data prior to prediction models development. The multiplicative scatter correction can be chosen to seek the optimum spectra data and suitable for bulk samples like soil. Several algorithms were also widely available to be used as spectra correction methods from which each spectra method has its particular characteristics that might be suitable for respective type of studied samples.

4. **Conclusion**

Presented study aimed to apply the near infrared spectroscopy approach in determining two related properties of soil mixed by biochars. Prediction models used to determine K and N contents of studied samples by means of raw and enhanced spectra data. The results showed that mixed soil samples with biochar properties (K and N) can be determined simultaneously with maximum correlation coefficient are 0.86 and 0.77 for K and N respectively. Based on this obtained performance, it may conclude that SW-NIRS approach can be applied to determine related properties of mixed soil biochar samples rapidly.

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