NEAR-INFRARED SPECTROSCOPY AS A RAPID AND SIMULTANEOUS ASSESSMENT OF AGRICULTURAL GROUNDWATER QUALITY PARAMETERS
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NEAR INFRARED SPECTROSCOPY SEBAGAI METODE CEPAT DAN SIMULTAN UNTUK PREDIKSI KUALITAS AIR TANAH LAHAN PERTANIAN

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ABSTRACT
Groundwater quality in agricultural area is highly affected by human activities. To determine groundwater quality, several methods are widely applied. Yet, most of them are based on standard laboratory analysis which is normally time consuming, expensive, and involve chemical materials from which may cause another environmental pollution. Thus, a rapid, effective and simple alternative method is required to assess groundwater quality. Fourier transform near-infrared spectroscopy (FT-NIRS) is considered to be employed due to its advantages. The main purpose of the present study, is to evaluate the feasibility of FT-NIRS technology in assessing groundwater quality parameters: total dissolved solids (TDS) and Sulfate concentration (SC). Transmission spectra data were acquired for groundwater samples from 8 different wells in wavelength range from 1000 to 2500 nm. Spectra data were corrected by multiplicative signal correction (MSC), while TDS and SC prediction models were established by using partial least squares regression (PLSR) and validated by full cross validation method. Obtained results showed that FTIR is able to detect and predict TDS and SC rapidly. Achieved maximum correlation coefficient (r) and RPD index were 0.86; 1.82 for TDS and 0.83; 1.76 for SC prediction respectively. It may be concluded that FT-NIRS combined with proper multivariate approach, can be used to assess groundwater quality parameters rapidly and simultaneously.

ABSTRAK
Studi ini bertujuan untuk menerapkan metode teknologi inframerah sebagai metode alternatif baru yang cepat dan simultan untuk prediksi dan penentuan kualitas air tanah lahan pertanian di area Banda Aceh dan Aceh Besar. Data spektrum untuk sampel air tanah direkam dalam bentuk transmisi dengan panjang gelombang 1000 – 2500 nm. Spektrum diperbaiki dengan metode MSC, sedangkan model prediksi TDS dan SC dibangun dengan metode PLSR. Hasil studi menunjukkan bahwa teknologi inframerah dapat memrediksi secara cepat dan simultan kadar TDS dan SC dengan koefisien korelasi dan indeks kehandalan: 0.86; 1.82 untuk TDS dan 0.83; 1.76 untuk SC. Dapat disimpulkan bahwa teknologi sinar inframerah dapat diterapkan sebagai metode alternatif yang cepat dan akurat untuk penentuan kualitas air tanah di lahan pertanian.

INTRODUCTION
Water is one of the most important natural resources to all living maters. Besides being used for drinking, water is also used for washing, building, irrigating, cleaning and many other activities. Water descends from clouds as rain and drops onto the earth (*Fritzsche et al., 2019)*. Water beneath the earth surface is called groundwater. It is defined as the water found underground in the cracks and spaces in soil, sand and rock (*Serranti et al., 2018*). It is stored in and moves slowly through geologic formations of soil, sand and rocks that are called aquifers. Generally speaking, groundwater is normally treated and processed by filtering so that it can be used as drinking water. It plays important roles in maintaining human race. It is used by more than 80 percent of the people worldwide, including almost everyone who lives in rural areas.

Groundwater is mostly used for irrigation, fertilization, etc. *(Gandariasbeitia et al., 2017; Sahamishirazi et al., 2017*).

Furthermore, groundwater can normally be found in almost any place. The water table can be deep or shallow, and may rise or fall depending on many factors.

Heavy and strong rains or snow melting can cause the rise of water table, or heavy pumping of groundwater supplies may cause the water table to fall *(Fritzsche et al., 2019*). Water in aquifers is brought to the surface naturally through a spring or can be discharged into lakes and streams. Groundwater can also be extracted through a well drilled into the aquifer. A well is a pipe in the ground that fills with groundwater. This water can be brought to the surface by a pump. Shallow wells may go dry if the water table falls below the bottom of the well. Some wells, called artesian wells, do not need a pump because of natural pressures that force the water up and out of the well *(Fritzsche et al., 2019; Zhu et al., 2018)*.

Aquifers normally consist of gravel, sandstone, sand, and fractured rock or stone, Water can move and deliver through these subsequent materials. The speed at which groundwater flows depends on the size of the spaces in the soil or rock and how well the spaces are connected *(Lu et al., 2018; Sano et al., 2018*). People need to be ensured that they are provided with pure, healthy and non-toxic water for daily used, especially for drinking. Groundwater quality is quite related to soil conditions since groundwater flows inside beneath porous rocks and soil or aquifers. Thus, groundwater needs to be analysed as it acts as water resource. Groundwater quality is highly affected by many factors, including human activities.

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 may affect plant growth in soils contaminated with heavy metals *(Chakraborty et al., 2017; Soriano-Disla et al., 2019*).

Agricultural crops (fruits, grains, and vegetables) for livestock for human consumption, growing on contaminated soil, can potentially uptake and accumulate toxic materials in their edible plant parts, and may be affected by groundwater quality, and thus, be harmful to animal and human health through the food chains. From this point of view, it is necessary to determine groundwater quality, monitor its condition and further take preventative actions to avoid any harmful impacts. A reliable and environmentally friendly method is therefore needed to rapidly detect and determine groundwater quality (*Fritzsche et al., 2019*).

The conventional and standard methods for determining groundwater quality are based on regular field data samplings and followed by reinforced chemical analyses in the laboratory or known as wet chemical analysis. It sometimes also involves complicated procedures. However, this method may be costly and time-consuming as a result of the intensive groundwater samplings in-situ and the analyses in the laboratory. Moreover, such investigations can only provide limited information on specific locations and moments in time (*Munawar et al., 2016; Pasquini, 2018*).

During the last few decades, infrared technology has been widely used and has become the most promising method of analysis in many field areas including soil science and agriculture due to its advantage; simple sample preparation, fast, and environmentally friendly since no chemicals are used *(Deng et al., 2018; Munawar et al., 2016; Pasquini, 2018; Samadi et al., 2018; Yusmanizar et al., 2019*). More importantly, it has the potential ability to determine multiple parameters simultaneously (Agussabti et al., 2020; Agus Arip et al., 2019). Therefore, the main purpose of this present study is to investigate the feasibility and apply infrared spectroscopy based on Fourier transform in determining groundwater quality parameters in terms of total dissolved solids (TDS) and sulfate concentration (SC). Prediction models were established by performing calibration and full cross validation using partial least squares regression (PLSR) with enhanced and corrected spectra data using multiplicative scatter correction (MSC) robustness.

MATERIALS AND METHODS

Spectra data acquisitions

Infrared spectra data for groundwater samples were taken by irradiation halogen lamp onto a 40 mL of water samples derived from different locations in Banda Aceh and Aceh Besar areas. Groundwater samples cover different land-use type and acceptable locations. Spectra data were recorded in form of transmission data in wavelength range from 1000 to 2500 nm or in wavenumbers 4000 – 10000 cm^{-1} (A A Munawar et al., 2019; Yunus et al., 2019). Spectra data were saved in two different file formats (*.SPA and *.CSV) that were used for further analysis (Saputri et al., 2019; Sudarjat et al., 2019).

Total dissolved solids (TDS) and sulfate concentration (SC) measurements

Actual TDS and SC data were measured and collected using standard laboratory analysis. TDS data were obtained by using gravimetric analysis according to SNI 06-6989, 27 – 2005, whilst SC data were measured based on SNI 06-6989, 20 – 2004.

Outlier removal

Spectra data were firstly projected on principal component analysis (PCA) followed by *Hotelling* T^2 ellipse for outlier detection. If there are any data outside the ellipse, then these spectra data are noted as outlier and removed prior to further analysis (*Arendse et al., 2018; Cozzolino, 2014)*.

Spectra data enhancement

Once outlier data were removed, spectra data were corrected and enhanced using multiplicative scatter correction (MSC) in order to eliminate noises due to light scattering, sensor curvature and inside temperature (*Ma et al., 2018*).

TDS and SC prediction models

Both these groundwater quality parameters were predicted using partial least squares regression (PLSR) models and validated using full cross validation. Spectra data used for models were raw un-corrected spectra and enhanced spectra data by MSC (*Darusman et al., 2019; Munawar et al., 2019; Suci et al., 2019)*. Obtained results were then compared. The prediction accuracy and robustness were judged by the following statistical parameters: coefficient of determination (R^2), correlation coefficient (r), root-mean-square error (RMSE) and residual prediction deviation (RPD) *(Ghosh et al., 2019*).

Relevant and optimum wavelength

Relevant wavelength for TDS and SC parameters prediction were inspected and observed using regression coefficient plot derived from the best and the most accurate PLSR model. Optimum wavelengths were located in the highest peak and lowest valley of the respective spectra plot dataset.

RESULTS

Groundwater spectra features

Typical spectra data features of groundwater samples are given in Fig 1. As shown in these figures, the strong absorbance and transmittance bands are located at around 1460 nm and 1920 nm. TDS and SC are chemical parameters and bond with C-H-O or S-O, O-H structures. Thus, it is possible for FTIRS to predict them since these structured chemical bonds are vibrated in IR wavelength region.

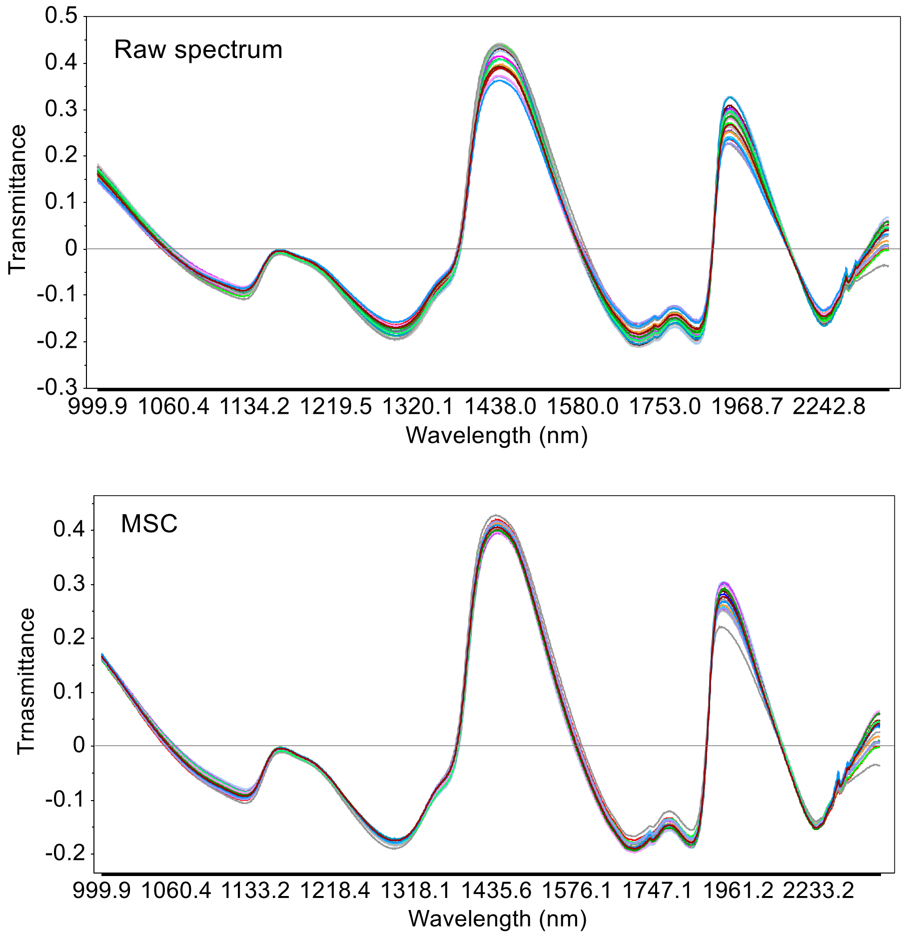

Fig. 1 - Typical raw and MSC spectrum of groundwater samples

All spectra data were projected onto principal component analysis (PCA) followed by Hotelling T^2 ellipse for outlier detection as shown in Fig.2. Some data are noted and removed because they are potential outliers. Thus, remaining data were 23 spectra data and also TDS and SC parameters.

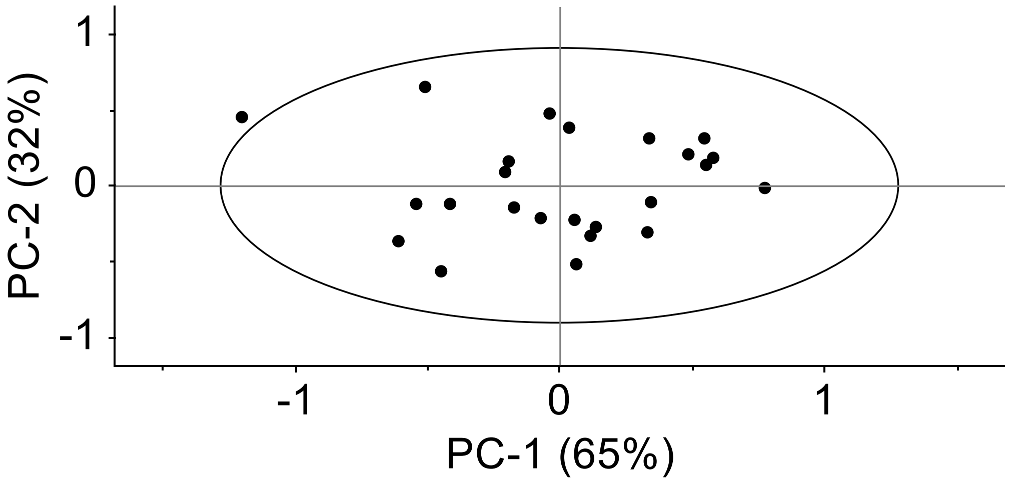

Fig. 2 - PCA projection and *Hotelling* T^2 ellipse for outlier detection

TDS and SC prediction

Actual TDS and SC parameters derived from standard laboratory measurements are presented in Table 1. As shown in the table below, the maximum TDS and Sulfate content of respective site locations are maximum 681.16 and 22.09 mg/L respectively. They were still under allowed maximum concentration based on SNI standard for groundwater quality parameters. The allowed TDS maximum is 1500 mg/L and allowed Sulfate is 400 mg/L respectively.

Table 1

Descriptive statistics for actual TDS and SC parameter

Descriptive Statistic	**Sulfate SO_4 (mg/L)**	**TDS (mg/L)**
Mean	12.32	332.71
Max	22.09	681.16
Min	3.86	122.83
Range	18.22	558.33
Std. Deviation	4.27	162.10
Variance	18.26	26277.34
RMS	13.05	368.55
Skewness	0.55	0.69
Kurtosis	0.60	-0.08
Median	11.63	341.18
Q1	9.77	186.61
Q3	14.31	421.10

Based on the descriptive table above, it can be seen from Skewness value, that both TDS and SC contents are in the range -1.69 - +1.69 which are inferred as normally distributed data. Yet, for multivariate analysis, this indictor was not obligatory. Thus, partial least squares regression still can be employed to develop prediction models. At first, raw un-corrected spectra data were used to develop prediction model for TDS and SC prediction. Then, MSC corrected spectra were used also to develop models for both groundwater quality parameters. Prediction result for TDS prediction is presented in Table 2, while for SC prediction is presented in Table 3.

Table 2

Prediction result for TDS parameter

Spectrum	Statistical parameters			
	R^2	r	RMSE	RPD
Raw	0.89	0.94	50.15	3.23
MSC	0.95	0.97	33.46	4.84

Table 3

Prediction result for Sulfate parameter

Spectrum	Statistical parameters			
	R^2	r	RMSE	RPD
Raw	0.60	0.77	2.67	1.60
MSC	0.63	0.79	2.52	1.70

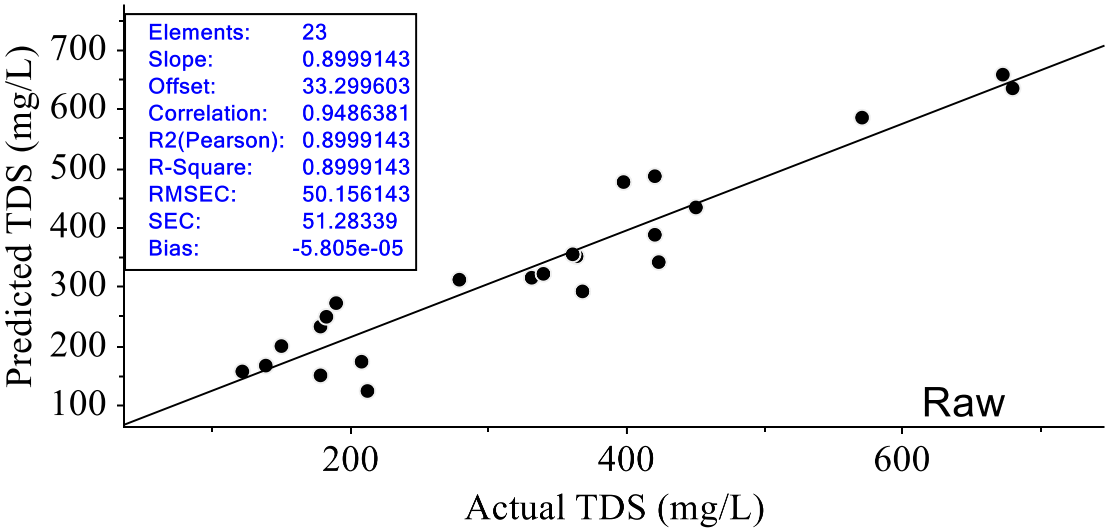

Fig. 3 - TDS Prediction results based on Raw spectrum

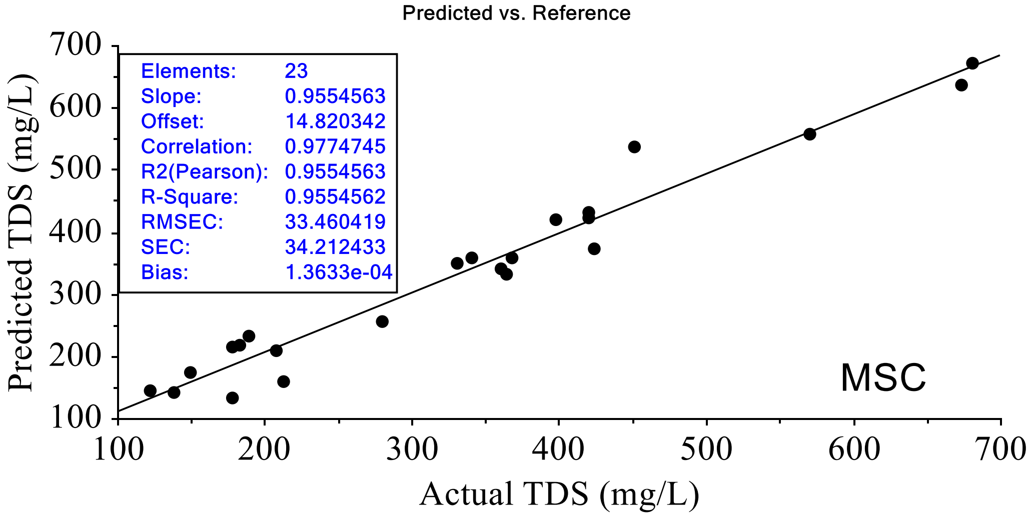

Fig. 4 - TDS Prediction results based on MSC spectrum

Based on prediction results, it can be seen that even using raw un-corrected spectra data, TDS can be predicted very well with coefficient correlation of 0.94 and the coefficient of determination is 0.89. Moreover, the residual prediction deviation (RPD) index achieved was 3.23. It can be inferred that TDS can be predicted accurately and robustly. Prediction results for TDS parameter was increased when spectra data were corrected using MSC method. The coefficient of determination and correlation were improved to 0.95 and 0.97 respectively. Moreover, the RPD index was also increased to 4.84 which can be categorized as excelent model performance.

Similar findings were also obtained for Sulfate content, when spectra data were corrected using MSC spectra correction method. As shown in Figure 5, the maximum achieved correlation and determination coefficient were 0.79 and 0.63 respectively. However, the maximum RPD index is 1.70 which can be infered as a coarse prediction performance.

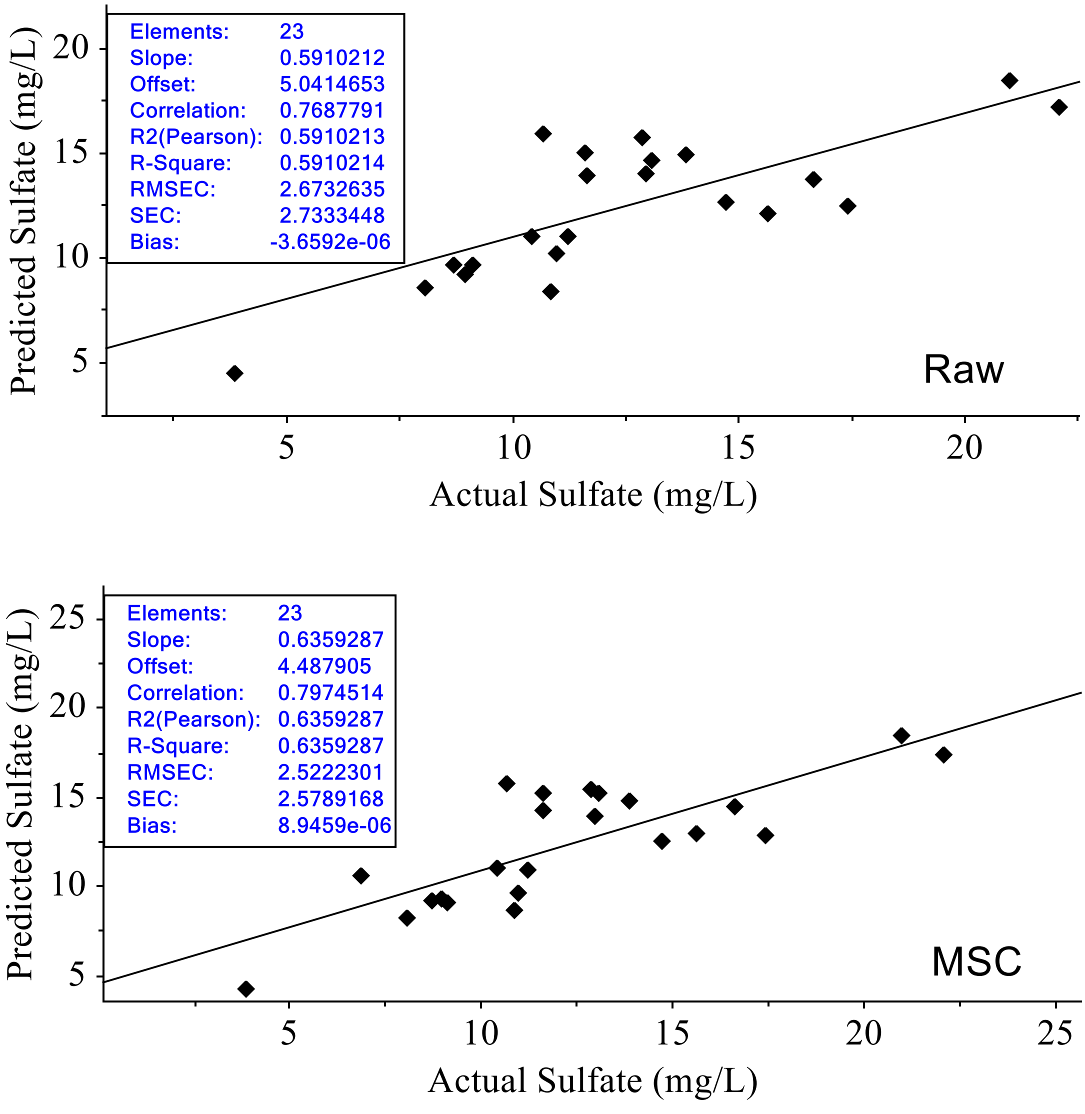

Fig. 5 - Sulfate prediction results based on Raw and MSC spectrum

Judging from YDS and SC prediction performances, it seems that Fourier transform infrared spectroscopy can be used and applied as an alternative method to predict groundwater quality indices on agricultural area. However, some improvements are still needed to enhance and improve prediction accuracy and robustness of those models. Nevertheless, infrared technology based on spectra data of FTIR can be employed as alternative fast and simultaneous method to predict groundwater quality parameters in agricultural areas and other environmental area as well.

CONCLUSIONS

In this work, we researched the FTIR technique as a rapid and non-destructive method for groundwater quality prediction in terms of TDS and Sulfate contents. We employed MSC spectra correction and PLSR method to develop prediction models. Based on the obtained results, we may conlude that FTIR is able to predict TDS of groundwater with excelent performance (RPD = 4.86) and coarse and sufficient prediction model performance (RPD = 1.70).

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