Near infrared spectroscopy as a tool to monitor contaminants in soil, sediments and water—State of the art, advantages and pitfalls

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ABSTRACT

Public awareness related with environmental issues (e.g. soil and water contamination) is on the increase, determining the advent of more astringent safety standards where new analytical methods are required to complain with these guidelines. Infrared (IR) spectroscopy is originated from the absorption measurements of different IR frequencies and has become a very attractive technique to measure heavy metals and other contaminants in soils, sediments and water. The aim of this review is to provide with an overview of different applications of near infrared (NIR) spectroscopy addressing issues related with contamination in soil, sediments and water. A discussion on the main factors or variables that affect the results of this type of applications is provided.

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1. Introduction

There are several contaminated soil sites in the world, and with an increasing population and associated health risk there is a growing pressure to remediate them [1–3]. Public awareness of environmental issues (e.g. soil and water contamination) is also on the increase, determining the advent of more astringent safety standards where new analytical methods are required in order to complain with these guidelines [1–3]. In addition, due to extensive

oil exploitation, refining and transportation, oil pollution has also become a major source of water and soil contamination [1–3]. Although a number of standard procedures and methods are currently in use in order to quantify total petroleum hydrocarbons (TPHs) and other contaminants in soils, sediments and water, these methods require time- and labor intensive sample preparation steps, where in many cases the use of solvents and reagents are needed and not adequate for in field monitoring [3].

Contaminants include a wide range of natural and synthetic metallic and organic compounds, minerals, hydrocarbons, and radioactive wastes that can be found in soil and ground water samples representing a serious threat to health and safety [4]. Detecting and monitoring these contaminants is therefore a challenging task [4,5]. Traditional site characterization methods involving drilling and sampling (e.g. soil, groundwater) and often

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require laboratory analysis that are time-consuming, laborious, expensive and expose personnel to contaminated media [3–4].

In recent years, emphasis has been placed on the development of rapid methods and sensors to monitor different contaminants in soils, water and air. For example, for the analysis of soil samples a variety of sensors have been evaluated such as temperature and pH probes, pressure transducers, miniature camera, electrical resistivity, laser induced fluorescence, infrared (IR) and Raman spectroscopy [3–6]. Two recent papers have reviewed the use of vibrational spectroscopy methods including near (NIR) and mid infrared (MIR) spectroscopy as well as other sensors used to monitor and measure heavy metals and other contaminants in soil and water [3,4].

The aim of this review is to provide with an overview of different applications of near infrared (NIR) spectroscopy addressing issues related with contamination in soil, sediments and water. In addition, a discussion on the main factors or variables that affect the results of this type of applications is also provided.

2. General overview of near infrared spectroscopy

Infrared (IR) spectroscopy is originated from the absorption measurements of different IR frequencies by a sample positioned in the path of an IR beam (e.g. NIR and MIR beams) when the frequency of a specific vibration is equal to the frequency of the IR radiation directed at the molecule, this molecule absorbs the radiation [7–11]. Generally speaking absorption spectroscopy is based on the Beer–Lambert law stating that for a homogeneous and non-scattering liquid sample, the concentration of an absorber is proportional to the sample absorbance [7–11]. Near IR is characterised by the overlapping of many different overtone and combination vibrations (vibrational modes of C—H, N—H, and O—H chemical bonds) resulting in broad bands resulting in NIR spectra data with low structural selectivity compared with mid infrared (MIR) spectra where fundamentals are more resolved, allowing the structure of a sample to be better elucidated [7–11]. The overtones in the NIR region correspond to energy transitions that are higher than those for fundamentals (MIR) and in particular the frequencies of the first and second overtones correspond to about two or three times that of the fundamentals observed in the MIR region [7–11]. Combination bands result from transitions involving two or more different vibrational modes of one functional group occurring simultaneously where the frequency of a combination band is the sum or the multiples of the relevant frequencies [7–11]. The absorption intensity decreases when the overtone level increases. The higher energy of NIR radiation and the presence of combination vibrational bands made NIR spectroscopy a better tool when complex and wet samples (soils and sediments) are analysed compared with MIR spectroscopy [7–11]. Overall, NIR spectroscopy is widely adapted to determine organic matter constituents in several types of samples (e.g. liquids, solids, gas) [7–11].

3. Applications of near infrared in the detection and monitoring of contaminants

3.1. Heavy metals

The application of NIR reflectance spectroscopy was reported for the prediction of heavy metals in freshwater sediments from Canada by Malley and Williams [12]. Samples were analysed in the NIR range (1100 and 2500) and partial least squares (PLS) regression was used to develop calibration models for the heavy metals in the sediments [12]. The coefficient of determination (R^2) between NIR data and the concentration of heavy metals measured using reference methods were for Cd 0.63, for Cu 0.91, for Zn 0.93,

for Pb 0.81, for Ni, 0.88, for Mn 0.93 and for Fe 0.86 [12]. The analysis of the wavelengths derived from the PLS models indicated that most of the variance in the heavy metal concentration was attributed to the presence of proteins, cellulose, and oil in the matrix of the sediments [12]. According to these authors the first PLS factor accounted for 75–95% of the variability in the data for each metal, except for Cd (50%). The different behavior for Cd was also attributed to its much shorter geological time in the lake and to its proportionately greater association with inorganic ligands as compared with the other metals [12]. A multivariate calibration method combining PLS regression and reflectance spectra in the visible (VIS) and NIR regions was used to characterise soil properties such as organic matter (OM) and clay content that are inter-correlated with concentration levels of Cd and Zn [13]. Several spectral pre-processing methods such as normalisation, multiplicative scatter correction (MSC), derivatives and standard normal variate (SNV) transform were explored by these authors in order to improve the robustness and performance of the calibration models [13]. No pre-processing method gave the best results for Cd and Zn with a root mean standard error in cross validation (RMSECV) equal to 0.68 and 80.97 mg kg^{-1}, respectively [13]. The combination of VIS–NIR spectroscopy was also reported to predict the concentrations of As, Cd, Cu, Fe, Hg, Pb, S, Sb, and Zn in the samples [14]. The prediction of heavy metals was achieved by stepwise multiple linear regression analysis (SMLR) and artificial neural networks (ANN) [14]. The R^2 reported by these authors were for As 0.84, for Fe 0.72, for Hg 0.96, for Pb 0.95, for S 0.87 and for Sb 0.93 [14]. No correlation was obtained for Cd (0.51), Cu (0.43), and Zn (0.24). Analysis of the PLS correlation coefficients indicated that absorptions features of iron and iron oxides contributed to explain the calibration results obtained [14].

Soil samples representing a wide range in pH, soil organic carbon (SOC) and textures (clay, sand and silt) were analysed using in the VIS and NIR range (400–2500 nm) [15]. The R^2 reported by these authors were 0.97, 0.94, 0.80, 0.99 and 0.96 for Fe, Cd, Cu, Ni and Zn, respectively [15].

The determination of Hg concentration in suburban agricultural soils from the Nanjing region was achieved using VIS–NIR spectroscopy [16]. Several spectral pre-treatments (absorbance, Kubelka–Munk transformations and derivatives) were applied to the reflectance spectra to optimize the accuracy of the prediction models [16]. The prediction of Hg concentration was achieved by univariate regression and principal component regression (PCR). The optimal model ($R = 0.69$, RMSEP = 0.15) for the predicting of Hg was achieved using the PCR regression with Kubelka–Munk transformation [16]. Correlation analysis revealed that Hg concentration was positively correlated with the absorption of goethite and clay minerals, suggesting that Hg-sorption by clay-size mineral assemblages in soils was the mechanism by which to predict spectrally featureless Hg [16].

The capability of measuring heavy metals and their effect on the chemical composition of forest soil was explored using VIS–NIR spectroscopy [17]. These authors proposed a quantitatively tool to determine total (TOT) and exchangeable (EXC) concentrations of Zn and Pb (Zn-TOT, Pb-TOT, Zn-EXC, Pb-EXC) as well as other chemical and microbial properties in forest soil samples polluted with heavy metals [17]. Samples were analysed using VIS–NIR (400–2,500 nm) spectroscopy and principal component (PC) scores and PLS regression was used to develop the calibration models [17]. For quantitative estimations, the best calibration model was obtained for the ratio between SOC and N-TOT ($R = 0.98$) [17]. The models for SOC, N-TOT, and microbial properties were satisfactory but less accurate. NIR spectroscopy failed to accurately predict S-TOT, ratio SOC and S-TOR, Zn-TOT, Pb-TOT, Zn-EXC, and the ration Pb-EXC to SOC [17].

The use of VIS–NIR spectroscopy was used to predict As contamination in soil samples [18]. PLS regressions as well as