# Using Infrared Spectroscopy to Examine the Influences of Stabilizers on the Molecular Structure of Stabilized Contaminated Clay Soils

**Khitam Abdulhussein Saeed and Sabah Hassan Fartosy**

**Abstract** An experimental evaluation on artificially contaminated clay soils with different amounts of heavy metals, which were then stabilized with two types of standard additives, was carried out. To examine the effect of those additives on the contaminated soils' molecular system, vibrational (infrared) spectroscopy was employed. It is well known that contaminants in soil lead to inadequate engineering properties for contaminated soils. Thus, it can change the impact of these contaminants on clayey soil's geotechnical characteristics soils over the mechanism of chemical stabilization that produces appropriate material that is preferable for construction uses. In this study, artificial polluted clay soils were prepared and then mixed with different proportions of heavy metals like (Pb and Zn) and stabilizers like quick lime CaO and ordinary Portland cement (OPC). The changes in the structure of soil molecular because of stabilizers and heavy metals were investigated based on Fourier Transform Infrared Spectroscopy (FTIR). The obtained results allow exploring the major vibrational modes in kaolin clay soil samples in which two active bands were observed at 3696.0 and 3620.0 $cm^{-1}$. These bands were related to the octahedral (OH) stretching vibrations and identified the kaolinite minerals. The bonding mode vibration of water-molecules (H–O-H) was discovered at 1638.0 $cm^{-1}$. It decreased with time because of the water consumption during the cement hydration and lime dissolution due to producing pozzolanic compounds, which are responsible for improving the strength properties of comminated soils. It was also investigated that heavy metals were at the absorbance band at 1384.0 $cm^{-1}$. So, it can be concluded from the importance of the applied FTIR test to evaluate the effect of stabilizers on the molecular structure of contaminated clay soils.

**Keywords** Contaminated soils · Portland cement · Kaolin clay · Hydrated lime · Physico-chemical behavior

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## 1 Introduction

This study's background problem is preventing hazardous pollutants from damaging the environment, which is related to disposal and waste production. This pays more attention to the importance of today's heavily industrialized world [1]. Therefore, the interest toward the contaminated soils grows to encourage environmental activities that depend on responsible reusable applications and avoid expensive landfill disposal. Stabilization/solidification (S/S) is among the treatment options required to consolidate the contaminants and solid wastes by adding traditional cement-based additives, such as cement, fly-ash, etc. hydrated-lime [1–4]. The mechanism of solidification/stabilization exerts a toxic chemical waste stream to a stable insoluble form (stabilization) or captures the waste through a solid cement-based structure (solidification) [5]. Hence, the quality of binder-based solidified waste elements are controlled by this mechanism [6, 7].

Nevertheless, to understand the expected effectiveness for the alteration of specific engineering characteristics of the site's polluted soil, it is essential to observe the mechanical time-dependence and the interconnection of molecular with soil stabilizers as a function of heavy metals. Infrared spectroscopy was utilized as an alternative method to describe the clay soil's interactive influence with organic matter, commonly used in soil analysis [8]. However, it can produce unique information about the mineral structure, for example; specimen set to any group of minerals which belongs to, the consistency degree inside the matrix, the uniformity level within the matrix, the nature of isomorphic substituents, also the uniqueness of molecular water from constitutional hydroxyl, and the existence of the non-crystalline and crystalline impurities [9].

The assessment and identification of different chemical reactions involved in the stabilization process of the contaminated clayey soils are the aims of this study. Therefore, the molecular structure requires examination in the expression of local bonding to evaluate the penetration extent of the crystalline structure of heavy metals and stabilizers within clay soil and its in-between layers [3]. On the other hand, the appliance FTIR technique is necessary to examine the molecular properties of polluted soil. This technology has a great history as a complementary method of X-ray diffraction (XRD.) and other clay investigation techniques, as reported in [10].

## 2 Experimental Program and Materials

**Soil and Stabilizers**. The type of soil that was used in this research was a pure brown Kaolin with a low amount of acid. A quantity of the soil was bought from the Tapah area, located in the West of Malaysia Peninsula. The physical properties and chemical ingredients for this soil are shown in Tables 1 and 2, respectively [7].

**Table 1** Physical properties for selected brown kaolin clay soil

| Physical properties | Values | Physical properties | Values |
|---|---|---|---|
| Cation exchange capacity (CEC) (meq/100) | 19.2 | Specific gravity | 2.65 |
| pH (L/S = 2.5) | 4.34 | Liquid limit, LL (%) | 41 |
| ICL (%) | 2.0 | Plastic limit, PL (%) | 23 |
| Max. dry density (g/cm$^3$) | 1.5 | Plasticity index (PI) | 18 |
| Optimum moisture content (%) | 24.3 | BS Classification | CL |
| Unconfined compressive strength (kPa) | 130 | – | – |

**Table 2** Chemical composition for brown kaolin clay soil

| Chemical compositions oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | $CO_2$ |
|---|---|---|---|---|---|---|---|---|
| Value (%) | 49.5 | 30.31 | 1.02 | 0.79 | 8.78 | 4.03 | 2.05 | 1.4 |

Figure 1 shows a FESEM image of natural kaolin clay. The neatly arranged, book-like kaolinite particles are a predominant characteristic of intact soil [11], while in general, kaolin owns the edge-to-edge intermittent structure and a two-faced aggregate [12].

On the other hand, the observation of Fig. 2, depicts an energy image of dispersive X-ray spectrometer (EDAX), reveals the high level of concentrations for silicon (Si) and aluminum (Al) proceeded by lower concentrations of potassium (K), iron (Fe), and magnesium (Mg) were evident, with less intensity for calcium (Ca) in natural kaolin clay. The results from Fig. 2 confirm what was previously presented in Table 2.

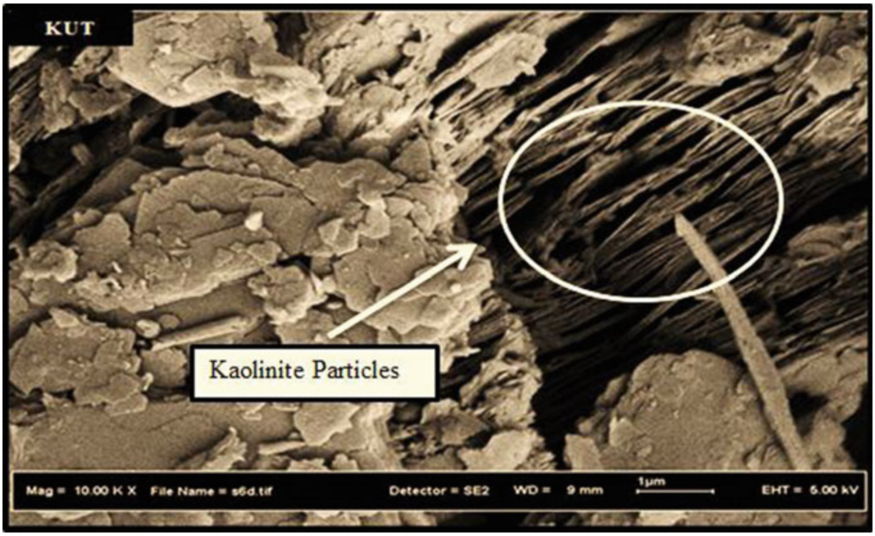

**Fig. 1** FESEM image of untreated kaolin clay soil

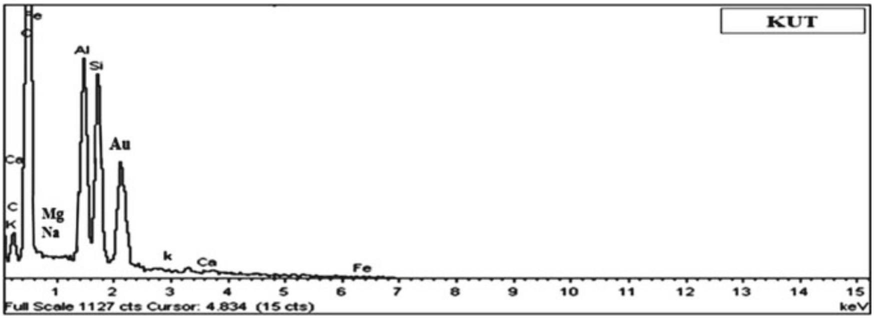

**Fig. 2** EDAX spectrum of natural kaolin clay soil

To the effectiveness of the work, two kinds of traditional stabilizers were selected for comparison and detection, which are significantly more potent in treating the contaminated clay soil. The first stabilizer that used in this research was the ordinary Portland cement. It was selected because it was cost-effective, easy to obtain, and appropriate for various wastes. These factors make this type of stabilizer the most extensively used binder in the stabilization technique [13]. Cement-based stabilization produces chemical alterations that can be used for stabilization and modification applications. The second stabilizer was quick lime (calcium oxide) obtained in the form of powder brought from a lime factory located in an area known Pasir Gudang, Johor. Previous studies mentioned that lime works effectively with clayey soils, especially with soils that own plasticity index (medium to high, PI > 15.0) [1, 7, 14]. Because of the absence of aluminates and silicates in silts and granular material pozzolanic responses, which did not occur, the lime did not interact appropriately.

Furthermore, the lime used in this study was retained in the oven under elevated temperature to prevent particles from agglomeration gradually so that the proportionate chemical composition did not change. The lime testing is implemented in compliance with the standard BS 1924.0: Part 2:1990 (Clause 5.4.60), so the lime quality is not changed. According to that standard, 5.0 g of lime was mixed with 100.0 ml distilled water free of $CO_2$ by using a magnetic stirrer for a period (1) hour. Then, it had been placed on the suspension for 24 h in an airtight container. Its pH value should be at 25ºC based on the following formula:

$$\mathbf{pH}_{25^{\circ}\mathrm{C}} = \mathbf{pH}_{\mathbf{T}} + 0.03(\mathbf{T} - 25) \tag{1}$$

This test was repeated no less than three times until obtaining the average pH25.0 value of 12.40, that compliance with the range of 12.35–12.45 that specified in the standard. However, it is necessary to mention that cement is preferable to lime with granular material and silt [15]. According to ACI 230.1R-90 1990: cement is suitable for all types of soils, and it is preferable to stabilize any soil, except for soils contain organic content of greater than 2%. The chemical composition of Portland cement and lime is shown in Table 3.

**Table 3** Chemical composition for the Portland and quick lime

| Quick lime (CaO) | | Ordinary Portland cement (OPC) | |
|---|---|---|---|
| Chemical composition | Values (%) | Chemical composition | Values (%) |
| Calcium oxide, CaO | 74.23 | Calcium oxide, CaO | 64.73 |
| Phosphorus oxide, $P_2O_5$ | 0.08 | Potassium oxide ($K_2O$) | 0.57 |
| Magnesium oxide, MgO | 0. 74 | Magnesium oxide, MgO | 1.1 |
| Calcium sulfate, $CaSO_4$ | 0.12 | Sulfur trioxide, $SO_3$ | 2.01 |
| Ferric oxide, $Fe_2O_3$ | 0.17 | Ferric oxide, $Fe_2O_3$ | 3.1 |
| Aluminum oxide | 0.11 | Aluminum oxide | 5.2 |
| $Al_2O_3$ silica, $SiO_2$ | 0.14 | $Al_2O_3$ silica, $SiO_2$ | 21.1 |
| Loss on ignition, LOI | 24.35 | Loss on ignition, LOI | 0.8 |

The reactions of stabilizer ions in the short and long-term depending on the concentration of the stabilizer. Therefore, the stabilizer content has a significant effect on the initial cementation and alteration of the treated specimens related to the reactions that occur in the (short – long) term. Furthermore, to simulate the real field conditions, it is imperative to mix reasonable quantities of cement and lime to all design mixtures. This study compares the reaction between soil and heavy metals using two types of stabilizers. It reduces the cost of high stabilizer content, the same content for minimum and maximum concentrations for lime and cement that has been used. This research was implemented on synthetic polluted soils, which are prepared under laboratory conditions and containing 5% based on the dry soil weight for both lead ($Pb^{+2.0}$), and zinc ($Zn^{+2.0}$) (based on the dry soil weight. The purpose of adding these reagents was to simulate the contamination of non-organic metal, and they were selected because of their prevalence in many polluted areas [16].

**Preparation of Samples**. Under air-dried conditions which satisfied using the oven, the soil specimens were prepared. This drying condition can remarkably change soil compaction and plasticity properties, as reported in [17]. Similar amounts of cement and lime mixture (10%) were percentages based on the dry soil weight. It is necessary to mention that the synthetic soil specimens mixed with heavy metals were prepared by adding lead nitrate ($Pb(NO_3)_2$) and zinc nitrate ($Zn(NO_3)_2$) to emulate contaminant sources in intact brown kaolin clay. Furthermore, the prepared contaminated soil samples were compacted in 38.0 × 76.0 mm molds with a cylindrical cross-section. The procedure of preparation was implemented in compliance with clause 4.1.50 of BS 1924: Part 2: 1990b to obtain the designated maximum dry density and optimum water content. After curing the sample for two hours, then extracted from the mold, placed in a thin-walled PVC tube, a thin-plastic cover was used to wrap the sample, and finally, the sample was sealed using tight rubber-lids. Later, the specimens were placed in a room with a controlled temperature (27.0 ± 2 °C) for curing till conducting all experiments after a period of (7, 100, and 200 days).

**Fig. 3** Perkin Elmer spectrum 2000 instrument (FTIR)-UTM-FS-Skudi-Johor-Malaysia

## 3 Testing Program

The research project depends on the FTIR technique used to investigate the changes related to the intact specimens' molecular structure and treated with contamination. The amount of soil that dried in the oven (2 mg) was blended with 200.0 mg of potassium bromide (KBR) to obtain a homogeneous powder, then compacted into a hard disk (solid pellet) [3]. This diaphanous KBR solid pellet was then placed in a specimen holder and scanned using a Perkin Elmer Spectrum 2000 appliance to yield a beam mode moved transferred inside the 400.0–4000.0 cm$^{-1}$ specimen, Fig. 3.

## 4 Results and Discussion

The effect of two selected stabilizers on the molecular structure of the intact soil specimens and specimens treated with contamination was investigated using Infrared spectroscopy. Typical FTIR spectra of intact Brown Kaolin clayey soil near (400.0–4000.0 cm$^{-1}$) are shown in Fig. 4. Two active bands near 3696.0 and 3620.0 cm$^{-1}$ were identified as kaolinite related to octahedral stretch vibrations from (OH). Further, sharp bands were also noticed near 1115.0, 1031.0 and 1007.0 cm$^{-1}$ which can be related to Si–O stretching.

The band at 912.0 cm$^{-1}$ was attributed to the deformation of OH that belongs to the hydroxyl groups. Most of the other bands, for example, the vibrations of Si–O

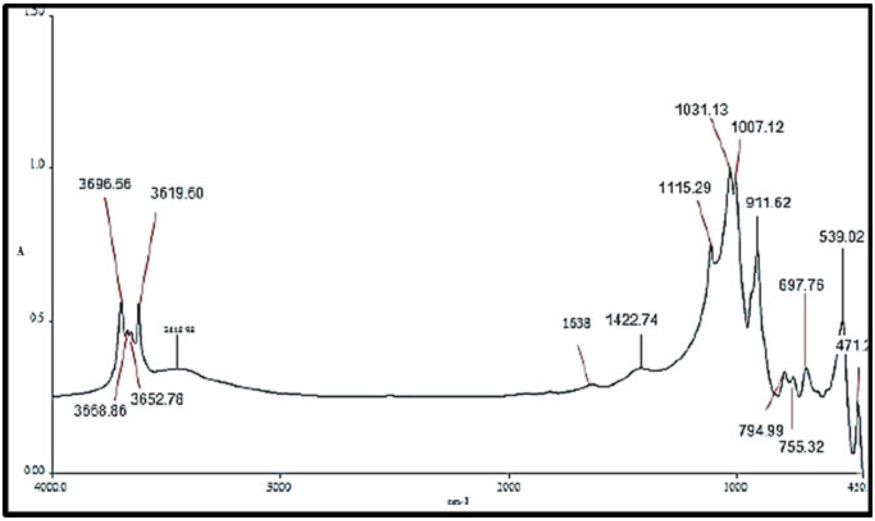

Fig. 4 FTIR spectra of intact brown kaolin clayey soil

were noticed near 794.0, 698.0, 540.0 and 470.0 cm$^{-1}$ also approved the presence of kaolinite, and another small band at 1422.0 cm$^{-1}$ highlighted the existence of calcite, while bands near 1638.0 cm$^{-1}$ pointed out the bonding vibrations of water-molecules (H–O-H). Figure 5 presents spectra of FTIR in natural vs. cement treated

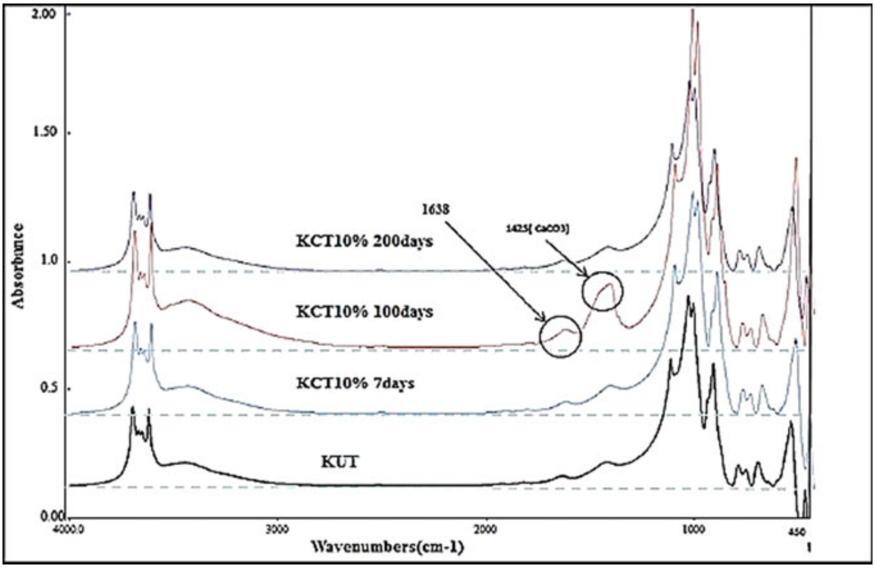

Fig. 5 FTIR spectrums of natural and cement treated kaolin clay at different time intervals

with Kaolin clay soils at different curing periods. Remarkable alterations happened in FTIR spectra for cement-treated cured Kaolin samples at one hundred days because of the increase in Si–O intensity, which is stretching at 1031 and 1007 cm$^{-1}$, respectively. These may have been related to the initiation of cement hydration and the development of primary cementitious compounds, which, in turn, increased polymerized Si–O units. As indicated previously by XRD, Portland was the primary source of hydration compounds during this stage of curing.

Furthermore, the significantly increased absorption at 1425 cm$^{-1}$ and shift to higher energy was attributable to calcite, which then dropped remarkably by 200 days. The decrease was likely because of the development of the non-crystalline compound, Calcium Aluminum Oxide Carbonate Hydrate, which negatively influences the molecular structure of cured specimens, as shown in Fig. 5. Therefore, the observed decrease in FTIR spectra intensity peaks at this stage of curing; likely may attribute to the reduction of inter-layered water-molecules (H–O-H) being consumed due to the progress hydration process of cement.

Figure 6 shows spectra of FTIR from both lead and zinc contaminated cement-Kaolin cured samples. This figure reveals decreasing in intensity at 1031 and 1007 cm$^{-1}$, V4 and V1; all of which reflected possible reactions of lead and zinc ions added to the cement-treated soil of reactions or adsorption of these metals that impact the polymerization phenomena of silicates. The intensity of band 3445 cm$^{-1}$ was attributed apparently to the agent OH-nitrates that increased after the addition of metallic nitrates. This decrease progressed as metallic nitrates reacted with hydroxides during cement hydration to produce new compounds, which, in turn, influenced

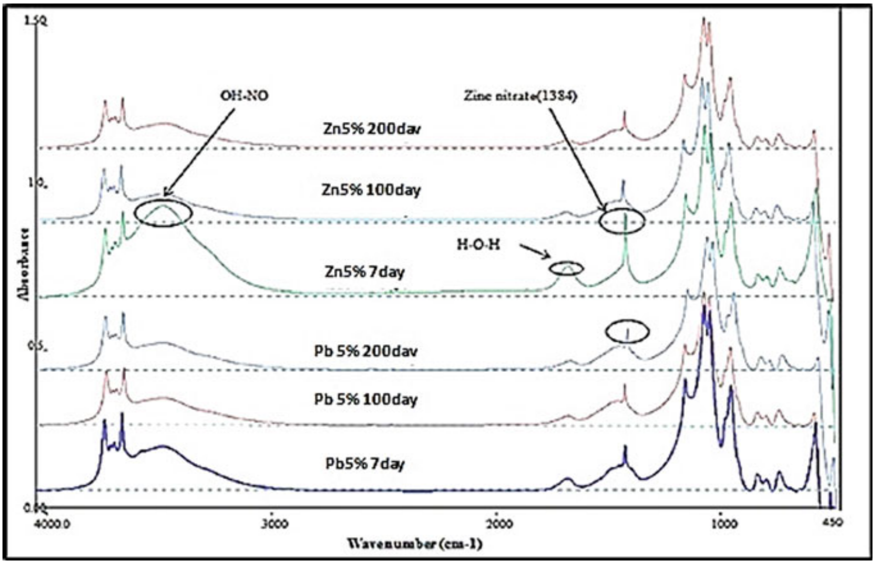

**Fig. 6** FTIR spectrums of lead and zinc added to the cement-treated Kaolin Clay at various time intervals

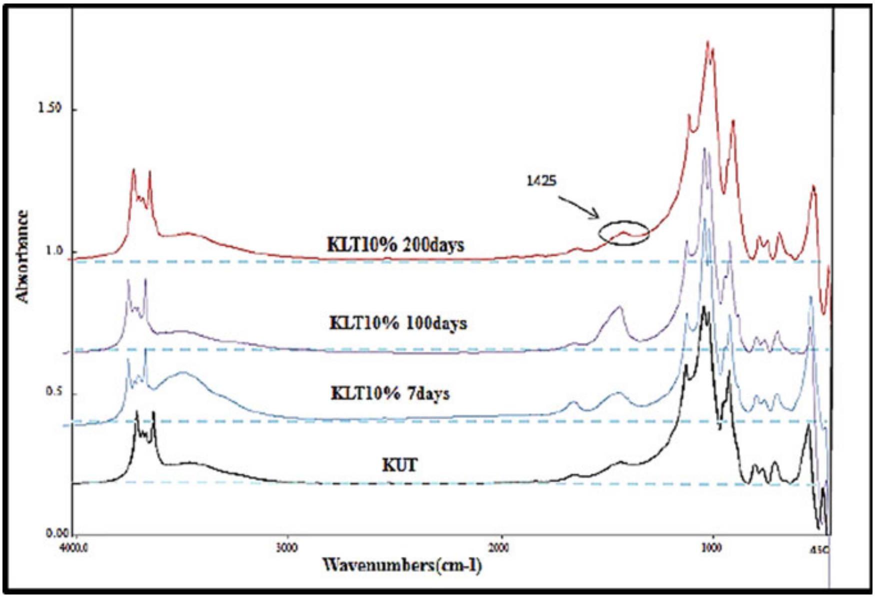

**Fig. 7** FTIR spectrums of natural and lime treated kaolin clay at different various intervals

cement hydration, as stated previously. Over time, decreased intensity of lead–zinc nitrates confirmed heavy metal reactions within the cement-soil matrix that produced the new compounds observed earlier by XRD.

Also, FTIR spectroscopy was implemented on Kaolin clay specimens treated with lime, as appeared in Fig. 7. FTIR spectra were not shown any significant changes for lime in comparison to soil samples treated with cement. Nevertheless, the rise in absorption intensity at band 1425 $cm^{-1}$ is related to improving calcium sources provided by lime. Moreover, the stretching of Si–O causes a trivial increase in their intensities beyond the polymerization that progresses. Figure 8 illustrates molecular structures of interactions with lead and zinc within a lime-treated Kaolin matrix compared to FTIR spectra of the cement-treated matrix. Only minor differences, especially with zinc, were observed. As shown in Fig. 8, compared to treated uncontaminated samples, more significant percentages of decreasing Si–O intensity are observed in lime-treated samples than in cement-treated samples, especially with zinc. Otherwise, no significant alteration of functional groups in contaminated samples was noticed except for metallic nitrates' appearance for both lead and zinc at wave number 1426 $cm^{-1}$.

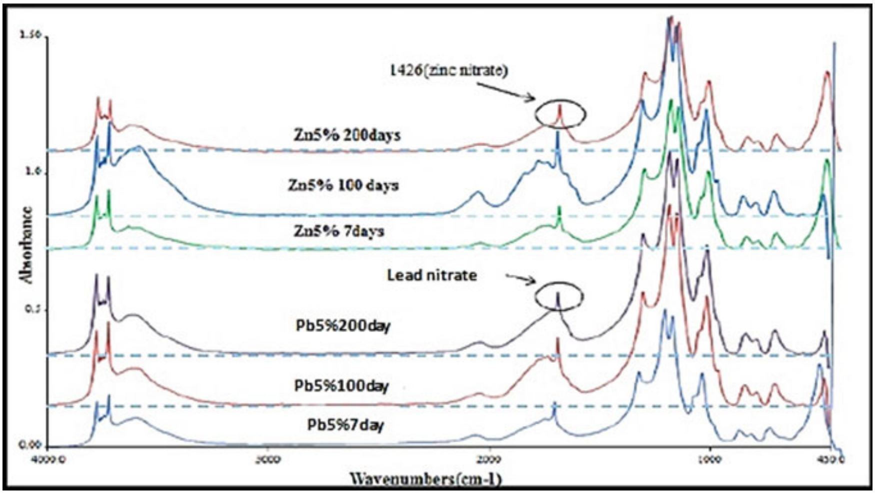

**Fig. 8** FTIR spectrums of lead and zinc doped with lime treated Kaolin Clay at various time intervals

# 5 Conclusions

The mechanism of additives (cement and lime) used to treat contaminated clay soil achieved in current research depends primarily on the physico-chemical behaviors of treated-contaminated soils regarding a detailed analysis of their molecular characterizations. The molecular studies by Fourier Transform Infrared Spectroscopy (FTIR) on both lime and cement treated brown kaolin clay samples were revealed the following results. Two strong bands were observed near 3696.0 and 3620.0 $\text{cm}^{-1}$, referred to the octahedral OH stretching vibrations; these bands identified the kaolinite minerals. In addition, other bands appeared because of the quartz and hematite existence.

- The existence of calcite was observed at the vibrational band at 1422 $\text{cm}^{-1}$.
- The bonding mode vibration of water-molecules (H–O–H) was noticed near 1638.0 $\text{cm}^{-1}$. It decreased with time because of water consumption through the hydration of cement and the dissolution of lime.
- The lead and zinc nitrates existences were investigated at the absorbance band at 1384 $\text{cm}^{-1}$.

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