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Application of Fourier Transform Infrared (FTIR) Spectroscopy to Analysis of Clays ¹

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Abstract

The present paper should be considered as a study of the application of Fourier Transform Infrared (FTIR) Spectroscopy for surface clay characterization. The application of surface clay materials for water treatment, oil adsorption, excipients or as active using in drugs has largely increased these recent years. The surface clay material presents hydroxyl groups, which can link very easily water molecules. These hydroxyl groups can react with organic groups and by their vibration in the infra-red region, FTIR can be easily used as a technical method for surface clay characterization. In this paper, the basic clay mineral specimens (bentonite, sepiolite, kaolinite and perlite) were examined and shows the chemical compositions of the clay where alumina oxide and silica oxide are present in major quantity.

Keywords: Clay Minerals, FTIR Spectroscopy, Characterization,

Fourier Dönüşümlü Kızılötesi (FTIR) Spektroskopisinin Killerin Analizlerinde Kullanılması

Öz

Bu makale, killerin yüzey karakterizasyonu için Fourier Dönüşümlü Kızılötesi (FTIR) Spektroskopisi uygulamasının bir çalışmasıdır. Killerin su arıtma, yağ adsorpsiyonu gibi yüzey işlemlerinde ya da yardımcı maddelerde ve ilaçlarda aktif olarak kullanımı son yıllarda büyük ölçüde artmıştır. Killerin yüzeyinde bulunan hidroksil grupları, su molekülleri ile kolayca bağlayabilmektedir. Bu hidroksil gruplar organik gruplarla reaksiyona girerler ve onların kızıl ötesi bölgedeki titreşimleriyle tespit edilebilirler. Bu nedenle FTIR, killerin yüzey karakterizasyonunda kolayca kullanılabilen teknik bir yöntemdir. Bu makalede, temel kil minerali numuneleri (bentonit, sepiyolit, kaolin ve perlit) incelendi ve kimyasal bileşimlerinin büyük miktarda alüminyum oksit ve silisyum oksit içerdiği gözlemlendi.

Anahtar Kelimeler: Kil Mineralleri, FTIR Spektroskopisi, Karakterizasyon

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1. Introduction

Clays are hydrous aluminosilicates commonly defined as minerals forming colloid fraction of soils, sediments, rocks and water and may consist of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Clay materials have structures arranged in layers and are categorized by these different layered structures [1-3]. Clay materials fall under various types like pyrophyllite - talc, smectites - bentonite, mica - illite, kaolinite, serpentine, vermiculite and sepiolite [4]. Figure 1 shows the structure of a typical clay. The chemistry which occurs on the surfaces of clay gives them high flexibility in adsorption processes. Surface chemistry includes the structure, ion exchange capacity, specific surface area, mechanical-chemical stability, water-holding capacity and surface reactivity that affect the physical and chemical properties of clay minerals [5]. Generally, these clay materials are naturally used as they are without being chemically modified. Synthetic or natural clay minerals are an important, abundant and low-cost material class with unique swelling, intercalation, and ion-exchange properties [6].

The important roles of clays in natural environments, the structure of crystal structure, mineralogy and surface chemistry are important for useful environmental and industrial applications. The pioneering work of Ross, in 1927, [7] Hendricks and Fry, in 1930, and Pauling, in 1930 [8,9] introduced the crystallinity in the structures of clay minerals. The majority of clay minerals consist of layers of silicates and phyllosilicates, including silica and alumina layers. These groups can be subdivided according to the type of layer structure. Clays consist of a interconnected silicates sheet combined with a second sheet like grouping of metallic atoms, oxygen, and hydroxyl Elmoubarki et al., [10]. The basic structural units are divided into silica sheets and brucite or gibbsite sheets [11]. The 1:1 clay mineral type consists of one tetrahedral sheet and one octahedral sheet [12]. Octahedrons consist of two hydroxyl ion planes, typically octahedral, which extend to the plane of a magnesium or aluminum ions coordinated by the hydroxyl plates. These octahedrons are also arranged in a hexagonal pattern which called octahedral sheets. The 2:1 (three layer) layer lattice silicates consist of two silica tetrahedral sheets between which is an octahedral sheet. The 2:1 clay minerals include the mica and smectite groups, which are the most abundant among the clay minerals. The serpentine and mica group is subdivided on the basis of dioctahedral and trioctahedral type. The phyllosilicate surfaces contain two basic types, i.e., siloxane surface and hydroxyl surface. 2:1 clay minerals (e.g., smectite group minerals) contain only siloxane surfaces, while the 1:1 clay minerals (e.g., kaolinite group minerals) contain both types' surfaces [5-12].

Bentonite consists essentially of hydrous magnesium-calcium aluminum silicate called montmorillonite, a clay mineral of the smectite group. It is highly colloidal and plastic clays composed of very fine particles, which produced by in situ devitrification of volcanic ash. Bentonite and montmorillonite have similar mineral properties. Bentonite has an excessive negative charge in its cage and is characterized by a three-layer structure with two silicate layers covering an aluminate layer. This occurs as a result of the partial replacement of tetravalent Si with trivalent Al that leads to the replacement of trivalent Al with divalent Ca. The ideal mineral formula for bentonite is $(\text{OH})_4(\text{Al}_2\text{Fe}_4\text{Mg}_4)\text{Si}_8\text{O}_{20}\text{H}_2\text{O}$ [14,15].

Sepiolite, $(\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O})$ with as unit cell formula is a natural hydrated magnesium silicate clay mineral and structurally formed by an alternation of blocks and tunnels growing up in the fiber direction (c-axis) [16,17]. Its structure is quite different from that of smectites. Each structure is built up of two tetrahedral silicate layers "in sandwich" with a central magnesia layer, in a way similar to that which occurs in other 2:1 silicates, although the discontinuity of silica layers leading to these structural tunnels in sepiolite. This arrangement determines that silanol groups (Si-OH) are present at the border of each block at the outer surface of the silicate. These silanol groups, together with the water molecules coordinated to the Mg ions at the borders of the structural blocks, are the main active centers for adsorption [18].

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ with the chemical formula is a naturally occurring inorganic polymer with a layer structure consisting of siloxane and gibbsite-like layers. The siloxane layer consists of SiO_4 tetrahedron bonded in a hexagonal array. The bases of the tetrahedra are approximately coplanar and the apical oxygen atoms are linked to a second layer containing aluminum ions and OH groups (the gibbsite-type layer). Kaolinite is a dioctahedral 1:1 phyllosilicate formed by superposition of silicon tetrahedral sheets and aluminum octahedral layers. Adjacent layers are linked by van der Waals forces and hydrogen bonds. This interlayer induces limited access to the interlamellar aluminol groups (Al-OH) which can be used for grafting reactions. The most reactive functional groups in kaolinite are hydroxyl groups which may be involved in ion exchange processes as well as many chemical reactions. Kaolin with a wide range of applications especially in paper filling and coating pigment is an important industrial material. It is used as an expander in aqueous based paints and inks, is a functional additive in polymers and is the main component in ceramics [19, 20].

Perlite is a commonly light gray, glassy volcanic rock with rhyolitic composition and 2 to 5% combined water. Chemically, perlite ore consists of SiO_2 , Al_2O_3 , and lesser amounts of several metal oxides (sodium, potassium, iron, calcium, and magnesium). It contains 70-75% SiO_2 which is chemically inert in many environments, and is therefore the perfect filter aids and fillers in various processes and materials. Perlite is basically the mineral obsidian. Perlite mineral deposits exist in many countries around the world, but the expanding product is only available in countries with commercial expansion plants. The production of perlite around the world is that in descending order of production, Turkey, Greece, and The United States, 41%, 26%, %18, respectively. When looked around the world, the reserve of perlite is more in Turkey. The amount of perlite reserve is considerably higher than the world; show us that it can contribute substantially to the economy of Turkey. World perlite reserves are estimated to be around 8 billion tons and 5.7 billion tons of it exist in Turkey corresponding to more than about 70% of the world reserves [21].

The new method based on the absorption of infrared radiation by minerals was developed from the middle of the last century for clay minerals [22]. However quantitative infrared spectrometry has not been widely applied in geology for many decades, as quantitatively accurate analysis of minerals routinely become possible only in the last decades [23]. Analytical accuracy now reached a certain level, where very fine changes in the clay's structure could be detected. The use of FTIR spectroscopy in the study of clay minerals has been historically undertaken by XRD to support mineral identification. However, the OH stretching vibrations, $\nu(\text{OH})$ of layer silicates have been shown to be sensitive to changes in the cations in the tetrahedral and especially, octahedral sites, and also the interlayer. Other useful applications of FTIR spectroscopy include the intercalation of these minerals with organic molecules [24].

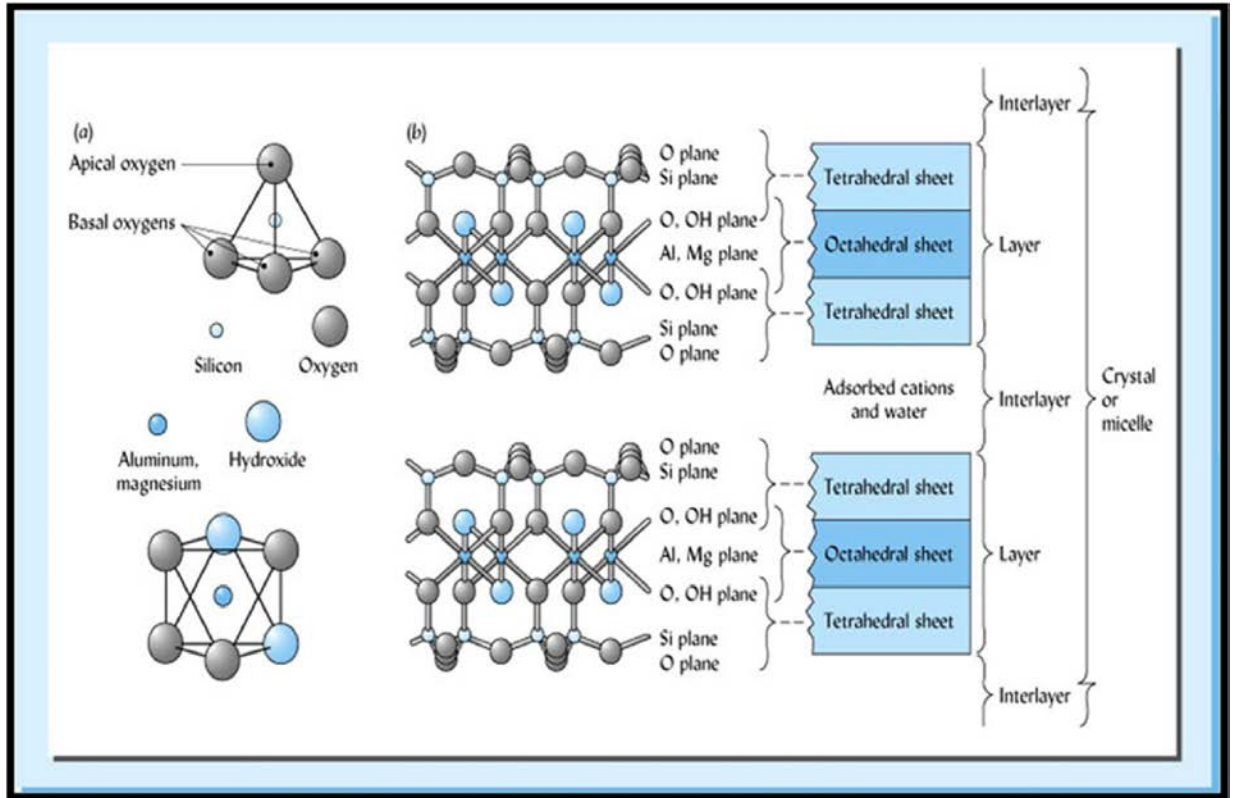


Figure 1. Structure of a typical clay material [13]

2. Materials and Methods

2.1. Clays

The clay mineral specimens (bentonite, sepiolite, kaolinite and perlite) were examined by FTIR-spectroscopy. The bentonite was obtained from Reşadiye (Turkey). The chemical composition of the bentonite is % 60.22 SiO_2 , 17.8 % Al_2O_3 , 3.14 % Na_2O , 2.52 % Fe_2O_3 , 3.39 % CaO , 1.12 % K_2O , 2.22 % MgO and 7.45 % loss ignition. The CEC of the bentonite was 76 meq/100 g [25].

The sepiolite sample was obtained from Sivrihisar/Eskişehir region. The chemical composition of sepiolite clay obtained by X-ray fluorescence (XRF) is 49 % SiO_2 , 24 % MgO , 0.02% Na_2O , 0.02 % SO_3 , and 26.18% loss ignition. The CEC of the sepiolite was 6.62 meq/100 g.

The kaolinite sample was obtained from Güzelyurt (Aksaray, Turkey). The cation exchange capacity of kaolinite was determined as 13meq/100g by the ammonium acetate method. The chemical composition of this clay obtained by X-ray fluorescence (XRF) is 53.00% SiO_2 , 26.71% Al_2O_3 , 0.62% Na_2O , 0.37% Fe_2O_3 , 0.57% CaO , 1.39% K_2O , 0.28% MgO and 17.20% loss ignition [15].

The perlite samples were obtained from Cumaovası Perlite Processing Plants of Etibank (İzmir, Turkey). The chemical composition of the perlite is 71-75 % SiO_2 , 12.5-18 % Al_2O_3 , 2-4 % Na_2O , 0.1-1.5 % Fe_2O_3 , 0.5-2 % CaO , 4-5 % K_2O , 0.03-0.2 % MgO . The cation exchange capacities (CEC) of the perlite was 37.20 meq/100 g [26].

Clay samples were treated before using in the experiments in order to obtain a uniform size sample of solid follows: the suspension containing 10 g L^{-1} clay was mechanically stirred for 24 h, after waiting for about a couple of min the supernatant suspension was filtered through filter paper. The solid sample was dried at 105 °C for 24 h, ground then sieved by 150 μm sieve.

2.2. DRIFT Spectroscopy

FTIR analysis was performed using a Perkin Elmer 100 FTIR spectrometer to determine absorption peak values. Infrared instruments measure the vibration spectrum of a sample by passing infrared radiation through it and recording the extent to which the wavelengths are absorbed. Since the amount of absorbed energy is a function of the number of molecules present, the infrared device provides both qualitative and quantitative information. The recorded spectrum is a plot of the transmittance of the sample versus the frequency (or wavelength) of the radiation. This spectrum is a fundamental property of the molecule and can be used both to characterize the sample and to determine its concentration.

The FTIR spectra of the clays were recorded in a Perkin Elmer 100 FTIR spectrometer in the range of 4000 to 400 cm^{-1} wavelength using the DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. FTIR spectrometer equipped with DTGS (Deuterated Tri Glycine Sulfate) detector, it is of interest to use detectors working at room temperature. A spectrum of the clay was obtained using KBr dilution, and finely powdered KBr was used as reference. For each sample 64 scans were obtained at a resolution of 4 cm^{-1} with a transmission mode. The DRIFT does not require any sample preparation. Approximately 3 weight % ground clay was dispersed in 100 mg oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5-20 μm . Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse reflectance accessory used was designed exclusively for Perkin Elmer 100 FTIR spectrometer. It includes two four-position sample slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an agate mortar and pestle in 1-3 % concentration. Clays and KBr were heated in the oven overnight at 150°C to minimize the water adsorbed on KBr and the clay sample.

3. Results and Discussion

FTIR-spectroscopy allows to obtain the necessary information about individual minerals, noncrystalline admixtures and to simultaneously determine the presence of organic matter. The absorption of infrared radiation by clay minerals depends critically on atomic mass, and the length, strength and force constants of inter-atomic bonds in the structures of these minerals. It is also controlled by the constraints of the general symmetry of the unit cell, and the local site symmetry of each atom within the unit cell. The absorption of infrared radiation is also strongly influenced by a number of crystal patterns and the size and shape of the mineral particles. In general, the constituent units of clay minerals include hydroxyl groups, tetrahedral silicate/aluminate anions, octahedral metal cations, and interlayer cations. The large broad bands between 3000 and 3750 cm^{-1} are due the presence of O-H stretching in silanol groups and water. Metal-O-H bending modes occur in the 600-950 cm^{-1} region. Si-O and Al-O stretching modes are found in the 700-1200 cm^{-1} range. Si-O and Al-O bending modes dominate the 150-600 cm^{-1} . Lattice vibrational modes in the far-IR range (33 to 333 cm^{-1}) are related to the interlayer cations. All silicas present an intense peak related to siloxane-stretching in siloxane group at 1100 cm^{-1} , and a band assigned to Si-O stretching frequency of silanol group at 900 cm^{-1} [27]. These peaks were illustrated in Table 1: absorption bands of clay samples.

FTIR studies of these solids help in the identification of various forms of the minerals present in the clay. The combined vibrations are noteworthy due to the presence of various compounds. Nevertheless, observed bands (in the range, 4000–400 cm^{-1}) have been tentatively assigned. Clay contains four different types of water molecules: (i) hygroscopic, (ii) zeolitic, (iii) bound and (iv) hydroxyl water [28].

Table 1. Important IR bands of clay along with their possible assignments.

Band (cm ⁻¹)	Assignments
3750-3000 cm ⁻¹	Al---O-H stretching
3660 ± 90 cm ⁻¹	Al---O-H (inter-octahedral)
3520 ± 200 cm ⁻¹	H-O-H stretching
1650 cm ⁻¹	H-O-H stretching
1020 cm ⁻¹	Si-O-Si, Si-O stretching
900-850 cm ⁻¹	Al---O-H stretching
1400 cm ⁻¹ and 525 cm ⁻¹	Si-O stretching, Si-O-Al stretching
3718 – 3680 cm ⁻¹	(Al, Mg)---O-H.
1250-800 cm ⁻¹	Si-O- (Mg, Al) stretching
790-750 cm ⁻¹	Si-O stretching, Si-O-Al stretching
630 cm ⁻¹	Si-O stretching, Si-O-Al stretching
540-420 cm ⁻¹	Si-O stretching, Si-O-Fe stretching

The FTIR spectrum of clays presented in Figure 2 reveals the bands belonging to bentonite: the broadband at 3620 cm⁻¹ is due to Al(Mg)-O-H stretching indicative of montmorillonite-rich smectite clay. Peaks at 3410 cm⁻¹ is due to H-O-H stretching (for H₂O) H-OH bonds located in water molecule cations. The band at 1635 cm⁻¹ belongs to the stretching vibration of the H-O-H bending. The shoulders and broadness of the -OH bands are mainly due to contributions of several structural -OH groups occurring in smectite [29]. In this spectrum also the bands at 840, 980, 1030 and 1277 cm⁻¹ which can be probably attributed to Si-O vibrations of other silicates, such as kaolinite or/and illite present in the samples as impurities can be seen. The bands near 470, 525, and 685 cm⁻¹ are assigned to the hydroxyl bending vibrations of water and stretching vibration of the structural hydroxyl group of smectites, respectively. The band at 470 cm⁻¹ was from Si-O-Si groups of the tetrahedral sheets. The band at 525 cm⁻¹ was from Si-O-Al (where Al is an octahedral cation), in the bentonite [25].

The bands in the IR spectrum of the sepiolite (Figure 2) may be summarized as follows: the band of the triple bridge group Mg₃OH band at 3725–3565 cm⁻¹ characterized by weak bonding strength is ascribed to the presence of OH groups in the octahedral sheet and the OH stretching vibration in the external surface of sepiolite. On the other hand, the 3230 and 1660 cm⁻¹ bands are respectively assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The band at 1452 cm⁻¹ developed due to the hydroxyl bending vibration again reflects the presence of bound water. The Si-O coordination bands at 1213 and 1090 cm⁻¹ represent the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheet. The lattice vibrations at 442 cm⁻¹ arising from the Si-O-Mg of the octahedral-tetrahedral linkage and at 655 cm⁻¹, Mg₃OH-bending [30].

The spectrum in Figure 2 demonstrates kaolinite clay. The triclinic layer structure of kaolinite reveals four well resolved (-OH) bands in IR spectrum. Three of these bands are assigned to the stretching vibrations of surface hydroxyl groups (3650, 3670, and 3690 cm⁻¹) while the fourth (3620 cm⁻¹) is attributed to the vibrations of inner hydroxyl groups. The typically broad OH-stretching band at 3620 cm⁻¹, which is an average envelope for wide range of Al-Al-OH and Al-Mg-OH environments in the highly substituted and distorted structure of montmorillonite. This band occurs close to the inner OH groups in kaolinite, but can be distinguished by its much greater breadth. Bands due to $\nu(\text{AlFeOH})$ at 2925 and at 2850 cm⁻¹ are typical of Fe bearing kaolinites. The OH deformation bands of kaolinite are

situated at 1635 cm^{-1} (Al-Al-OH) and 1035 cm^{-1} (Al-Mg-OH). Supporting bands at 535 cm^{-1} (Si-O) and 465 cm^{-1} (Si-O) are diagnostic for kaolinite, too [15].

The FTIR spectra of the perlite (Figure 2) show absorption bands at 455 , 770 and 1070 cm^{-1} , being characteristically of amorphous silica and a broad band ranging between 2870 , 2995 and 3550 cm^{-1} due to surface hydroxyl groups. The changes in the intensity of the latter absorption band could explain the effect brought about by each treatment on the -OH groups of the perlite. The band at 3760 cm^{-1} forms, as a result of OH- stretching vibration of the silonal (Si-OH) groups. The band at 1070 cm^{-1} represents the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheets. The band at 1634 cm^{-1} is attributed to the hydroxyl bonding vibrations because of bound water. The absorption bands at 455 cm^{-1} and 789 cm^{-1} are characteristics of amorphous silica arising from Si-O vibrations. A broad band ranging between 3200 and 3700 cm^{-1} is due to surface hydroxyls. The band at 3760 cm^{-1} forms, as a result of OH-stretching vibration of the silonal (Si-OH) groups. The band at 1070 cm^{-1} represents the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheets. The band at 1634 cm^{-1} is attributed to the hydroxyl bonding vibrations because of bound water. The asymmetric stretching vibrations of Si-O-Si bridges were observed at 1180 cm^{-1} . The peak at 985 cm^{-1} indicates the presence of Si-O-Al bonds [26,31].

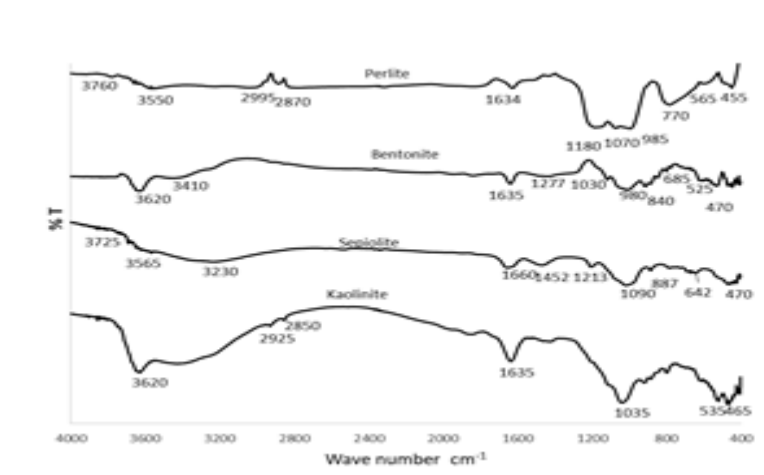


Figure 2. FTIR spectrum of the clay samples

4. Conclusion

About the hydration characteristics, interlayer cations and moisture content in the clays vibrational spectroscopic investigations yield useful information. In addition, it is a useful tool to study changes in the Si-O vibrations resulting from changes crystal symmetry due to swelling. FTIR spectroscopy is a very sensitive technique provides information on the chemical composition of the analyzed material, applied to the study of clays. The splitting of the band indicates presence of more than one type of hydroxyl bonds, due to their different absorption frequencies. The absorption bands present in the spectrum those are relevant to each bond types and necessary for the identification of the clay minerals.

Different absorption bands in clay minerals constituents of the interlayer space in middle infrared spectra (400 - 4000 cm^{-1}) are related to the tetrahedral, octahedral layer. Clay contains four different types of water molecules: (i) hygroscopic, (ii) zeolitic, (iii) bound and (iv) hydroxyl water. When considered a spectroscopy of clays, which are absorbed the energy at particular wave numbers. The band included spectral bands of clays: stretching bands of structural hydroxyl groups (around 3600 cm^{-1}), broad stretching band of water (around 3400 cm^{-1}), deformation band of water (around 1650 cm^{-1}), band of Si-O stretching (around 1000 cm^{-1}), deformation bands of Al-Al-OH vibration (around 900 cm^{-1}), deformation bands of Al-Mg-OH vibration (around 850 cm^{-1}), Si-O stretching band of silica (

around 800 cm^{-1}), coupled out-of-plane vibration band of Al-O and Si-O (around 625 cm^{-1}) and deformation bands Al-O-Si, Si-O-Si, respectively (around 525 cm^{-1} and 470 cm^{-1}).

The sample preparation protocol based on their DRIFT-FTIR spectra which eliminates the effect of adsorbed water, makes the objective comparison of different clay minerals possible. For different clay minerals, the extents of band areas of O-H and Si-O stretching in spectrum is also characteristic. Characteristic absorption bands are used during qualitative identification of clay minerals and their components, which could help fingerprinting clay minerals in natural mixtures. On the basis of these developments, it seems reasonable to increase the application of infrared spectrometry in the analysis of clays in many areas of industry and also revisiting samples already analyzed with other traditional analytical techniques. Methodology could potentially be quite beneficial for the analysis of core samples and could make it more cost-effective and less time-consuming.

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Uzun Özet

Giriş

Killer, genel olarak toprak, tortu, kayaların kolloid kısmından oluşan mineraller olarak tanımlanan sulu alüminosilikatlardır. Kil malzemeleri katmanlar halinde düzenlenmiş yapılara sahiptir ve bu farklı tabakalı yapılara göre kategorize edilir. Genelde, bu kil malzemeleri kimyasal olarak değiştirilmeden doğal olarak kullanılırlar. Sentetik veya doğal kil mineralleri, benzersiz şişme, birleşme ve iyon değiştirme özelliklerine sahip, önemli, bol bulunabilen ve düşük maliyetli malzemelerdir. Killer kristal yapıları, mineralojileri ve yüzey kimyaları nedeniyle çevresel ve endüstriyel uygulamalar için önemlidirler.

Bentonit ve montmorillonit benzer mineral özelliklere sahiptir. Bentonit, kafesinde aşırı negatif yüke sahip olan bir alüminat tabakasını kaplayan iki silikat tabakalı üç katmanlı bir yapı ile karakterize edilir. Bentonitin ideal mineral formülü $(OH)_4(Al_2Fe_4Mg_4)Si_8O_{20}H_2O$ dir. Sepiyolit, $(Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O)$ şeklindeki birim hücre formülüne sahip doğal hidratlanmış magnezyum silikat kil mineralidir. Yapısal olarak, elyaf yönünde (c eksen) büyüyen blok ve tünellerin değişmesiyle oluşur. Kimyasal formülü $Al_2Si_2O_5(OH)_4$ olan kaolin, siloksan ve gibsit benzeri tabakalardan oluşan, doğal inorganik bir polimerdir. Perlit, riyolitik bileşimli ve % 2 ila 5 oranında bileşik halinde suya sahip, yaygın olarak açık gri, camsı bir volkanik kayadır. Kimyasal olarak, perlit cevheri SiO_2 , Al_2O_3 ve daha az miktarda metal oksitlerden (sodyum, potasyum, demir, kalsiyum ve magnezyum) oluşmaktadır.

Kızılötesi radyasyonunun mineraller tarafından absorplanmasına dayanan yeni metot kil mineralleri için geçen yüzyılın ortalarından itibaren geliştirilmiştir. Bununla birlikte, minerallerin kantitatif olarak doğru analizi yalnızca son on yılda mümkün olduğundan, kantitatif kızılötesi spektrometresi jeolojide uzun yıllardır yaygın olarak uygulanmamaktadır. Şu an analitik doğrulukta, kilin yapısındaki çok ince değişikliklerin tespit edilebildiği belirli bir seviyeye ulaşmıştır.

Bu makale, killerin yüzey karakterizasyonu için Fourier Dönüşümlü Kızılötesi (FTIR) Spektroskopisi uygulamasının bir çalışmasıdır. Killerin su arıtma, yağ adsorpsiyonu gibi yüzey işlemlerinde ya da yardımcı maddelerde ve ilaçlarda aktif olarak kullanımı son yıllarda büyük ölçüde artmıştır. Killerin yüzeyinde bulunan hidroksil grupları, su molekülleri ile kolayca bağlayabilmektedir. Bu hidroksil gruplar organik gruplarla reaksiyona girerler ve onların kızıl ötesi bölgedeki titreşimleriyle tespit edilebilirler. Bu nedenle FTIR, killerin yüzey karakterizasyonunda kolayca kullanılabilen teknik bir yöntemdir. Bu makalede, temel kil minerali numuneleri (bentonit, sepiyolit, kaolin ve perlit) incelendi ve kimyasal bileşimlerinin büyük miktarda alüminyum oksit ve silisyum oksit içerdiği gözlemlendi.

Metod

Kil numuneleri, deneyde kullanılmadan önce, aynı boyutta numune elde etmek için muamele edilmiştir: 10 g L⁻¹ kil içeren süspansiyon 24 saat mekanik olarak karıştırıldı, birkaç dakika bekledikten sonra üst faz filtre kâğıdından süzülür. Katı numune 105 °C de 24 saat kurutuldu, öğütüldü ve daha sonra 150 µm lik elek ile elendi.

Absorpsiyon tepe değerlerini belirlemek için, FTIR analizi, Perkin Elmer 100 marka FTIR spektrometresi kullanılarak gerçekleştirildi. Kızılötesi aletler bir numunenin titreşim spektrumunu, içinden kızılötesi radyasyon geçirerek ve dalga boylarının ne ölçüde absorplandığını kaydederek ölçer. Absorbe edilen enerji miktarı, mevcut molekül sayısının bir fonksiyonu olduğundan, kızılötesi cihaz hem kalitatif hem de kantitatif bilgi sağlar. Kaydedilen spektrum, numunenin geçirgenliğinin radyasyonun frekansına (veya dalga boyuna) karşı bir grafiğidir. Bu spektrum, molekülün temel bir özelliğidir ve hem numuneyi karakterize etmek hem de konsantrasyonunu belirlemek için kullanılabilir.

Sonuçlar ve Tartışma

Kil minerallerinin, orta kızıl ötesi spektrumunda (400-4000 cm⁻¹) yer alan farklı absorpsiyon bantları, kil minerallerindeki ara kat boşluğunu oluşturan, tetrahedral ve oktahedral tabakaları ile ilgilidir. Kil dört farklı tipte su molekülü içerir: (i) higroskopik, (ii) zeolitik, (iii) bağlı ve (iv) hidroksil su dur. Killerin spektroskopisi göz önüne alındığında, belirli dalga boylarındaki enerjiyi absorplarlar. Killerin spektrumunda: 3600 cm⁻¹ civarında, yapısal hidroksil gruplarının gerilme titreşimlerinden bant, 3400 cm⁻¹ civarında, suyun -OH gerilmesinden kaynaklı geniş bant, 1650 cm⁻¹ civarında suyun deformasyon bandı, 1000 cm⁻¹ civarında Si-O gerilme bandı, 900 cm⁻¹ civarında, Al-Al-OH titreşiminin deformasyon bandı, 850 cm⁻¹ civarında Al-Mg-OH titreşiminin deformasyon bandı, 800 cm⁻¹ civarında silikanın gerilme bandı, 625 cm⁻¹ civarında, Al-O ve Si-O'nun düzlem dışı titreşim çift bandı, 525 cm⁻¹ ve 470 cm⁻¹ civarında sırasıyla Al-O-Si ve Si-O-Si bantları gözlemlenmiştir.

Adsorbe edilmiş suyun etkisini ortadan kaldıran DRIFT-FTIR spektrumlarına dayanan örnek hazırlama protokolü, farklı kil minerallerinin objektif olarak karşılaştırılmasını mümkün kılar. Farklı kil mineralleri için, spektrumda uzanan O-H ve Si-O bant alanlarının kapsamı da karakteristiktir. Kil minerallerinin ve bileşenlerinin kalitatif tanımlanması sırasında karakteristik absorpsiyon bantları kullanılır, ki bu doğal karışımlardaki kilin parmak izi bölgesinin bulunmasını sağlar. Bu gelişmelerin ışığında, sanayinin birçok alanında killerin analizinde kızılötesi spektrometresi uygulamalarını artırmıştır. Yöntem, daha düşük maliyetli ve daha kısa süreli olduğundan, örneklerin analizinde oldukça faydalıdır.