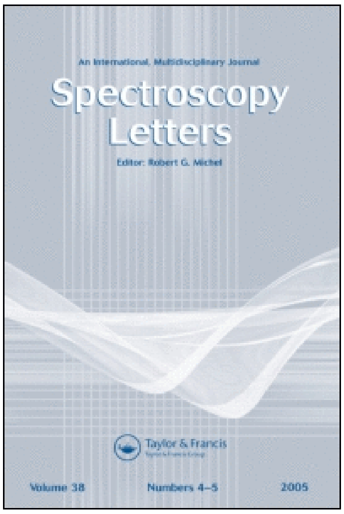

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Near Infrared Spectroscopy of Benzoic Acid Adsorbed on Montmorillonite

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ABSTRACT The adsorption of benzoic acid on both sodium and calcium montmorillonites has been studied by near infrared spectroscopy complimented with infrared spectroscopy. Upon adsorption of benzoic acid, additional near-infrared bands are observed at 8665 cm^{-1} and assigned to an interaction of benzoic acid with the water of hydration. Upon adsorption of the benzoic acid on Na-Mt, the NIR bands are now observed at 5877, 5951, 6028, and 6128 cm^{-1} and are assigned to the overtone and combination bands of the CH fundamentals. Additional bands at 4074, 4205, 4654, and 4678 cm^{-1} are attributed to CH combination bands resulting from the adsorption of the benzoic acid. Benzoic acid is used as a model molecule for adsorption studies. The application of near-infrared spectroscopy to the study of adsorption has the potential for the removal of acids from polluted aqueous systems.

KEYWORDS adsorption, benzoic acid, montmorillonites, near infrared spectroscopy, structured water

INTRODUCTION

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area, and resulting strong adsorption/absorption capacities. One highly utilized application is the use of clays as adsorbents. In expanding clays, the most common dioctahedral smectite is montmorillonite, which has two silica-oxygen tetrahedral sheets sandwiching an aluminium or magnesium octahedral sheet, where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls. Because of substitution of silicon by aluminium in the tetrahedral layers or similar substitution of aluminium by magnesium, montmorillonite layers are negatively charged.[1–4] Thus, cations like sodium, potassium, and calcium are attracted to the mineral interlayer space to neutralize the negative layer charges. Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature.[5,6] This makes natural clays suitable as effective sorbents for organic compounds.

At present, there are many applications of montmorillonites as sorbents in pollution prevention and environmental remediation such as treatment of

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spills, waste water and hazardous waste landfills.[7–16] Some studies have showed that replacing the inorganic exchange cations of clay minerals with organic cations can result in greatly enhanced capacity of these materials to remove organic contaminants from soils and industrial effluents.[17,18] The use of NIR spectroscopy for the determination of minerals was first elucidated by Hunt et al.[19–25] NIR spectroscopy has been applied to clay minerals.[26–30] NIR spectroscopy has proven particularly useful for soil analysis.[31,32] To date there have been few reports of the use of NIR spectroscopy to determine the adsorption of organic molecules on clays and organoclays.[33]

In this work we extend these adsorption studies to the determination of adsorbed benzoic acid on montmorillonite. Montmorillonite clay was chosen as the model adsorbent on basis of the following reasons: 1) it is used widely in agriculture, dyes/pigments, engineering polymers, and pharmaceuticals and as fungicide for leather, production of parathion and organic synthesis[34] and 2) the U.S. Environmental Protection Agency (USEPA) claimed the organic acids as one of the main organic contaminations.[35] Our present study demonstrates that NIR is a powerful technique to determine the adsorption of these organic pollutants on clay and the resulting clay materials. It is of high importance to understand well the adsorption mechanism of clay materials to organic pollutants and for the application of clay-based materials in pollution prevention and environmental remediation.

EXPERIMENTAL

Materials

The montmorillonites used in this study were supplied by The Clay Mineral Society and were standard minerals labeled as SWy-2 (Na-rich montmorillonite) Crook County, Wyoming, USA and STx-1 (Ca-Montmorillonite, white) Gonzales County, Texas, USA.

Method of Adsorption

Five grams of benzoic acid were dissolved and made up to 300 mL with toluene. 10 g Ca/Na montmorillonite were weighted into a 500 mL an ampoule. 250 mL of the acid solution were pipetted into the ampoule with a magnetic stir bar. The samples were stirred for 8 h in 35 ± 2°C. The solids were recovered by centrifugation, washed once with toluol, twice with ethanol, and thereafter once with acetone. After each washing, the solids were separated from the liquid by centrifugation. The product was allowed to dry at room temperature.

Near and Mid Infrared Spectroscopy

NIR spectra in reflectance mode use a Nicolet Nexus FT-IR spectrometer with a Nicolet Near-IR Fibreport accessory (Nicolet Nexus, Madison, WI, USA). A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 12000 to 4000 cm^{-1} (909 to 2,500 nm) by the co-addition of 64 scans at a resolution of 8 cm^{-1}. A mirror velocity of 1.2659 m/s was used. The spectra were transformed using the Kubelka-Munk algorithm ($f(R_\infty) = (1 - R_\infty)^2/2\,R_\infty$) for comparison with absorption spectra.

Mid-infrared and NIR spectra were obtained using an FT spectrometer (Nicolet Nexus, Madison, WI, USA) with a single bounce diamond ATR cell. Spectra over the 4000 to 500 cm^{-1} (2,500 to 20,000 nm) range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s.

The spectral manipulations of baseline adjustment, smoothing, and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was carried out using Peakfit software (Jandel Scientific, Postfach 4107, D-40688 Erkrath, Germany). Lorentz-Gauss cross product functions were used through out and peak fit analysis undertaken until squared correlation coefficients with R^2 greater than >0.995 were obtained.

RESULTS AND DISCUSSION

For convenience, the NIR spectra of montmorillonite (Na-Mt), montmorillonite with adsorbed benzoic acid, calcium montmorillonite with and without adsorbed benzoic acid may be divided into sections according to the spectral region where NIR intensity is observed:

1. The 7900 to 9100 cm^{-1} region (Fig. 1)
2. The 5800 to 7400 cm^{-1} region (Fig. 2)
3. 4000 to 5500 cm^{-1} region (Fig. 3).

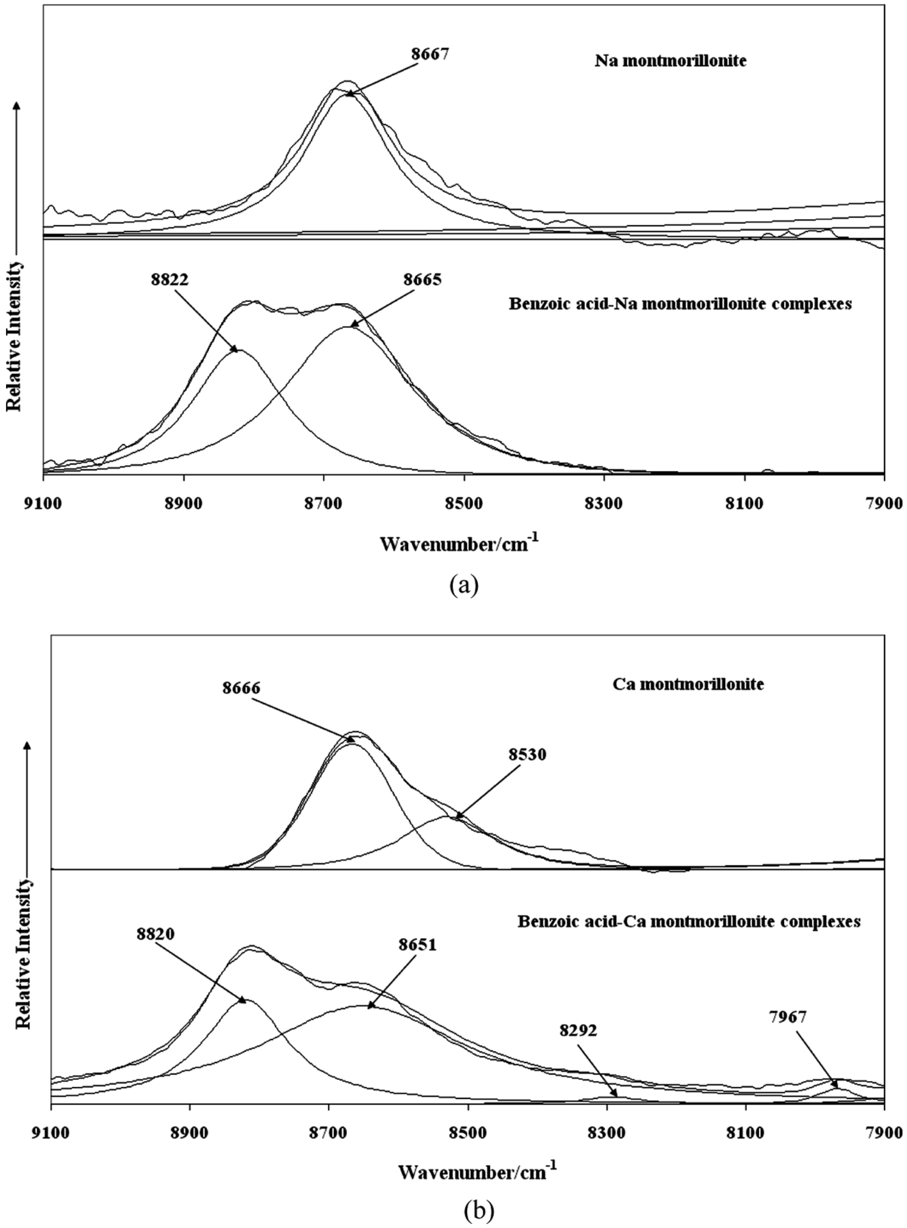
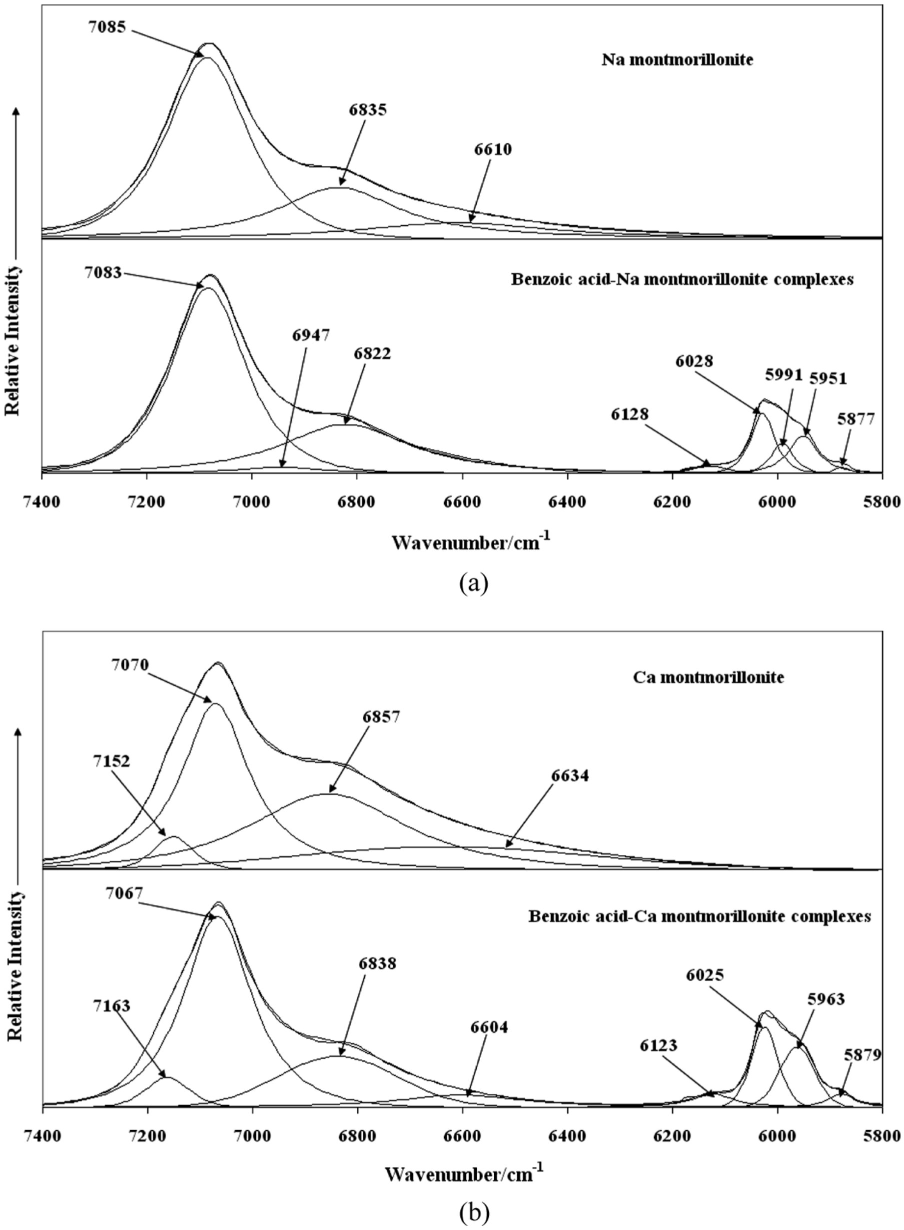


FIGURE 1 NIR spectra of (a) sodium montmorillonite and benzoic acid adsorbed on sodium montmorillonite and (b) calcium montmorillonite and benzoic acid adsorbed on calcium montmorillonite in the 7900 to 9100 cm^{-1} region.

The infrared spectra of the OH and CH stretching regions of the montmorillonite, montmorillonite with adsorbed benzoic acid are illustrated in Figs. 4 and 5, respectively.

NIR spectroscopy is often referred to as proton spectroscopy. Bands which occur in the NIR spectrum are the result of overtone and/or combination bands of bands that are observed in the mid-infrared spectra. Thus the bands in the NIR spectra of the montmorillonite clays with adsorbed benzoic acid will result from the overtones of OH or CH bands. In this experiment the benzoic acid is being used as a model molecule to test the NIR measurement of the adsorption on montmorillonite.

NIR bands in the high wavenumber region between 7900 and 9100 cm^{-1} are shown in Fig. 1. For Na-Mt a band is observed at 8667 cm^{-1} and for Ca-Mt two bands are observed at 8530 and 8666 cm^{-1}. One possibility is that these bands are due to electronic transitions, however, this seems unlikely as the clay does not contain any transition metal cations. The assignment of the bands is therefore given to OH combination bands. The band might be due to the combination of $2\nu_1 + 2\delta$OH. This



(a)

(b)

FIGURE 2 NIR spectra of (a) sodium montmorillonite and benzoic acid adsorbed on sodium montmorillonite and (b) calcium montmorillonite and benzoic acid adsorbed on calcium montmorillonite in the 5800 to 7400 cm^{-1} region.

would be approximately $2 \times 3500 + 2 \times 800 = 8600\,\text{cm}^{-1}$. Another alternative is that the bands are due to OH stretching bands combined with water vibrations. One may conclude that the second band at 8530 cm^{-1} is a result of differences in hydration of the calcium in the montmorillonites interlayer. Upon adsorption of the benzoic acid on the Na-Mt an additional band at 8665 cm^{-1} is observed. This additional band is evidence for the interaction of the benzoic acid with the hydroxyl surface or the water of hydration of the cation. Alternatively the benzoic acid has interacted with the hydration sphere of the sodium and this has altered the summation of bands proposed above. In the NIR spectrum for calcium montmorillonite, bands are observed at 6634, 6857, 7070, and 7152 cm^{-1}. These bands are in the region of the first overtone of the OH fundamental and are therefore assigned to bands due to $2\nu_1$, $2\nu_3$, and $\nu_1 + 2\nu_3$.

For the adsorption of benzoic acid on the Ca-Mt additional bands additional bands are observed at 7967, 8292, and there is a shift in the 8530 cm^{-1} band to 8651 cm^{-1}. It is concluded that the benzoic acid has interacted with the water of hydration

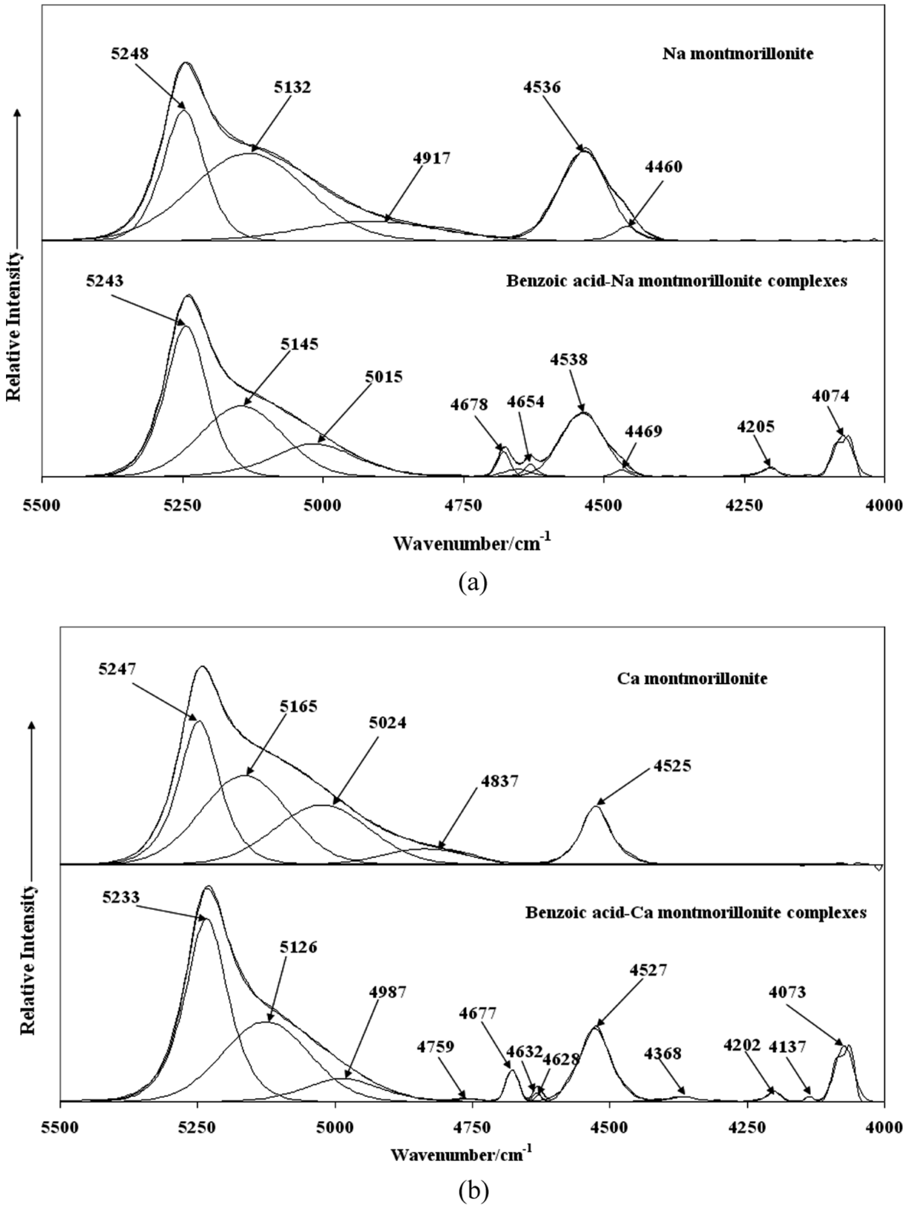
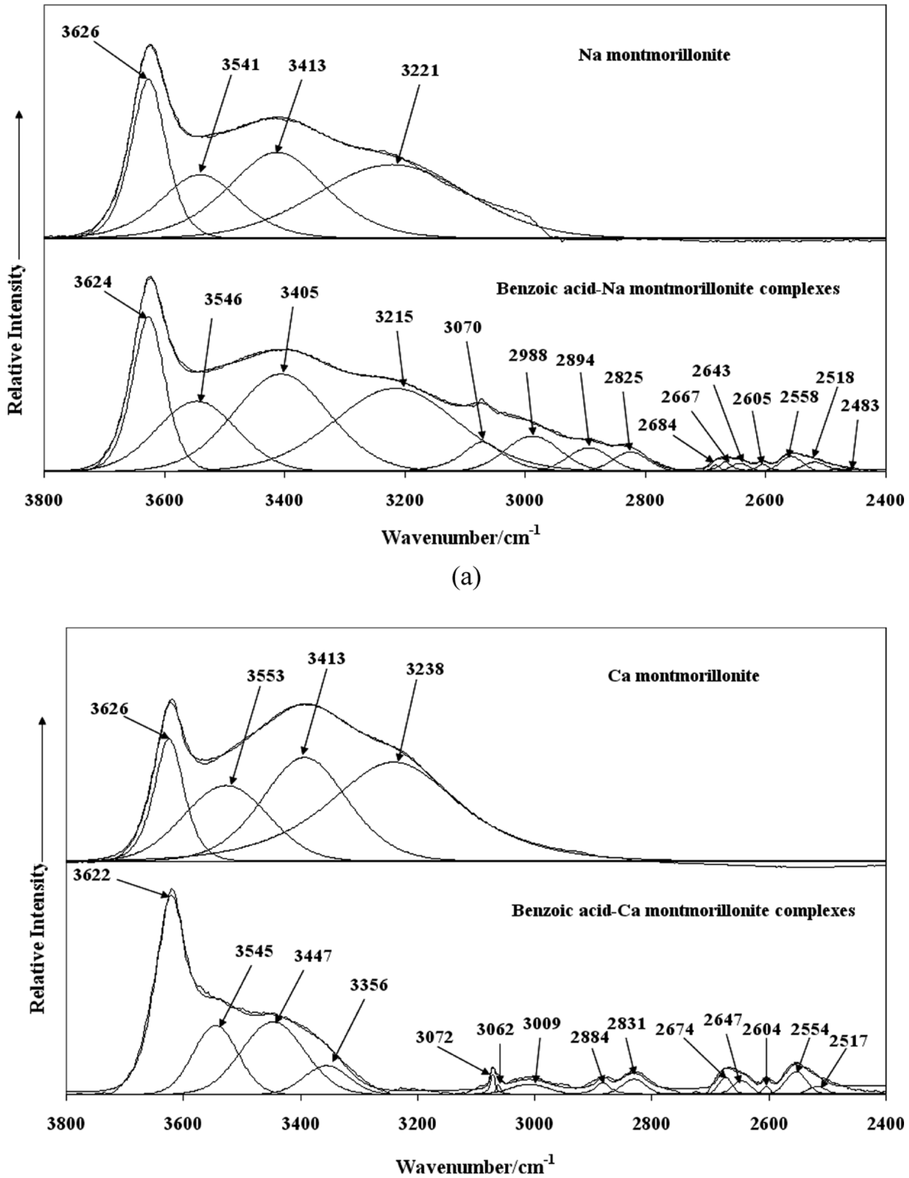


FIGURE 3 NIR spectra of (a) sodium montmorillonite and benzoic acid adsorbed on sodium montmorillonite and (b) calcium montmorillonite and benzoic acid adsorbed on calcium montmorillonite in the 4000 to 5500 cm^{-1} region.

of the calcium cations in the montmorillonites interlayer.

The NIR spectra in the 5800 to 7400 cm^{-1} are reported in Fig. 2. This spectral region is the region of the first overtone of the hydroxyl fundamental and results from $2\nu_1$. It must be remembered that in NIR spectroscopy all combinations of bands are allowed. Thus bands $= 2\nu_3$ and $\nu_1 + \nu_3$ are allowed. Thus for Na-Mt three bands are observed at 6610, 6835, and 7085 cm^{-1}. Similarly for Ca-Mt three bands are observed at 6634, 6857, and 7070 cm^{-1}. Upon adsorption of the benzoic acid on Na-Mt, the NIR bands of the clay are found at 6822, 6947, and 7083 cm^{-1}. Additional bands are now observed at 5877, 5951, 6028, and 6128 cm^{-1}. These bands are assigned to the overtone and combination bands of the CH fundamentals. These bands are not observed in this spectral region and provide evidence of the adsorption of the benzoic acid on the montmorillonite. A similar set of bands are observed for the Ca-Mt with bands at 5879, 5963, 6025, and 6123 cm^{-1}. The bands are in similar positions for both the Na-Mt and Ca-Mt adsorptions.

The NIR spectra in the 4000 to 5500 cm^{-1} are shown in Fig. 3. This spectral region is where combination bands from water and the montmorillonites are found.



(a)

(b)

FIGURE 4 IR spectra of (a) sodium montmorillonite and benzoic acid adsorbed on sodium montmorillonite and (b) calcium montmorillonite and benzoic acid adsorbed on calcium montmorillonite in the 2400 to 3800 cm^{-1} region.

Three bands are observed for Na-Mt at 4917, 5132, and 5248 cm^{-1} and are attributed to water combination bands. Two bands at 4460 and 4536 cm^{-1} are assigned to OH combination bands from the montmorillonite. For Ca-Mt the water combination bands are found at 4837, 5024, 5165, and 5247 cm^{-1}. The OH combination band is found at 4525 cm^{-1}. Upon adsorption of the benzoic acid on Na-Mt additional bands are found at 4074, 4205, 4654, and 4678 cm^{-1}. These bands are attributed to CH combination bands resulting from the adsorption of the benzoic acid. For the Ca-Mt, these additional bands are found at 4073, 4137, 4202, 4368, 4628, 4677, and 4759 cm^{-1}. These additional bands prove the adsorption of benzoic acid on montmorillonites surfaces.

The infrared spectrum of the Na-Mt and the Ca-Mt with and without the adsorption of benzoic acid is reported in Fig. 4. Four bands are observed for Na-Mt at 3221, 3413, 3541, and 3626 cm^{-1}. This latter band is assigned to the inner hydroxyl group of the montmorillonites. The first three bands are attributed to water in the montmorillonite interlayer. A similar set of bands is found for the Ca-Mt. The additional bands are clearly due to the adsorption of benzoic acid. In Fig. 5, the spectral region between 1350 and 1800 cm^{-1} is displayed. For Na-Mt, an infrared

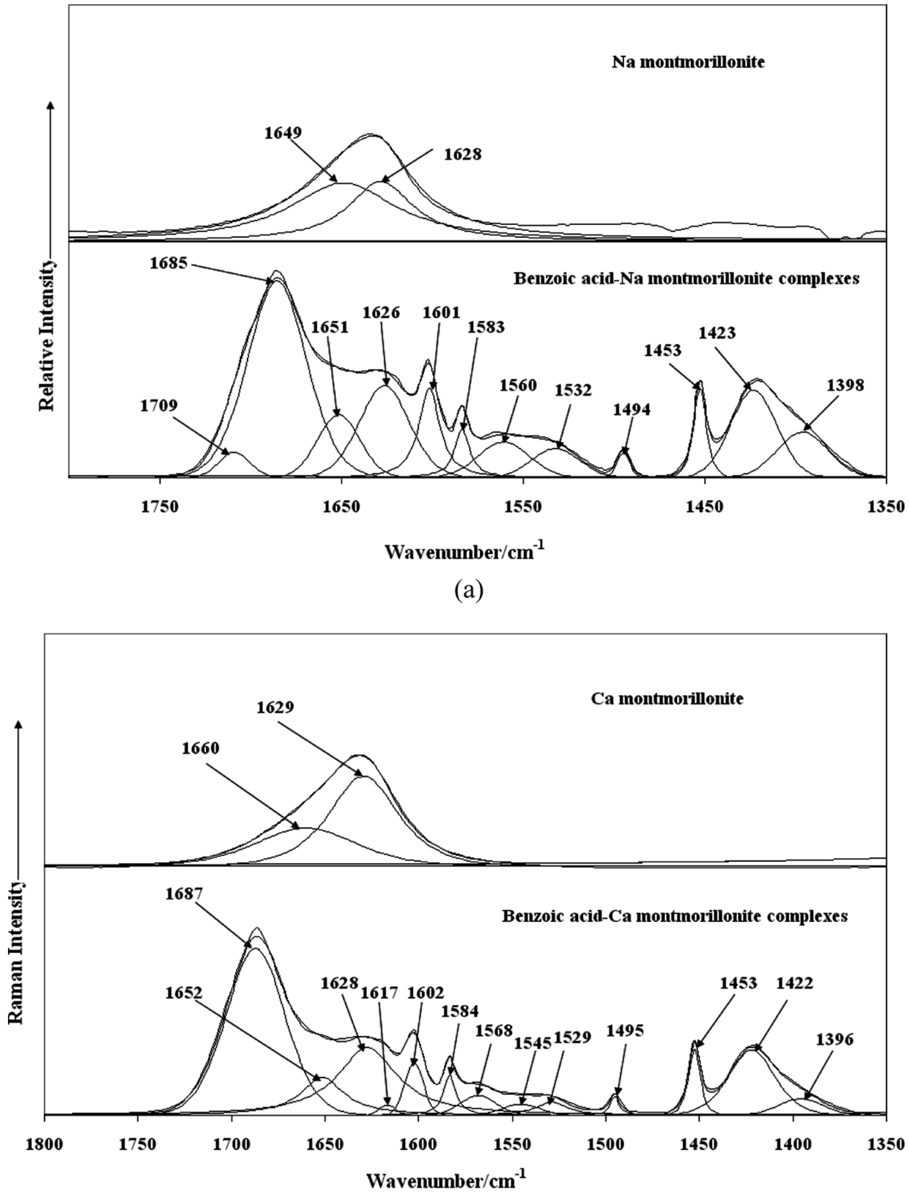


FIGURE 5 IR spectra of (a) sodium montmorillonite and benzoic acid adsorbed on sodium montmorillonite and (b) calcium montmorillonite and benzoic acid adsorbed on calcium montmorillonite in the 2400 to 3800 cm^{-1} region.

band is observed at around 1635 cm^{-1}, which may be resolved into component bands at 1628 and 1649 cm^{-1}. These bands are assigned to the water HOH bending mode. For Ca-Mt, the two bands are found at 1629 and 1660 cm^{-1}. The observation of a higher energy component is indicative of water which is strongly hydrogen bonded such as in the hydration sphere of the Na or Ca ions. The band at 1629 cm^{-1} is assigned to the bending mode of water bonded to water. Upon adsorption of the benzoic acid additional bands are observed as observed in Fig. 5. Interestingly the water bending mode is now observed at around 1687 cm^{-1}. This indicates that upon adsorption of the benzoic acid the hydrogen bond between the water in the hydration sphere is stronger. This suggests that the benzoic acid is adsorbed into the interlayer of the montmorillonites. Such a conclusion fits well with the conclusions of Yariv et al.[36]

In this work we have shown the potential for NIR spectroscopy for the determination of adsorbed acids on montmorillonitic clays. Since many pollutants are acidic, benzoic acid was selected as a molecule to represent these possible pollutants. NIR spectroscopy is a rapid technique which with modern portable hand-held spectrometers enables an assessment of pollutants to be quickly made. Other techniques such as X-ray diffraction do not offer such instant results.

CONCLUSIONS

This research has focused on the study of the adsorption of benzoic acid upon sodium and calcium montmorillonites using near-infrared spectroscopy. Montmorillonites are noted for their swelling properties and the water of hydration of the cations in the interlayer. Differences in the NIR spectra of sodium and calcium montmorillonites are attributed to the differences in the water in the hydration sphere. This is observed in the hydroxyl combination and first overtones of the OH fundamentals. NIR spectroscopy offers methodology for the easy analysis of acids adsorbed on clays. Other techniques including XRD are not suitable for these adsorption studies.

The adsorption of the benzoic acid is readily observed by comparing the spectra of the montmorillonites with and without adsorbed benzoic acid. The adsorption of benzoic acid results in the observation of additional NIR bands in the 5800 to 6150 cm^{-1} region. NIR bands at 5877, 5951, 6028, and 6128 cm^{-1} are observed. These bands are assigned to overtones of the CH vibrations. Additional NIR bands at 4074, 4205, 4654, and 4678 cm^{-1} are attributed to CH combination bands resulting from the adsorption of the benzoic acid.

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