Research Article

The Use of ATR-FTIR Spectroscopy for Quantification of Adsorbed Compounds

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Quantification of adsorbed amounts requires in most cases several assumptions. Adsorption of organic compounds, for example, is usually measured indirectly, by mass balance calculations based on the evaluation of the remaining chemical in solution. Such procedure might yield overestimates when precipitation or degradation of the adsorbate occurs and underestimates when separation of the sorbent material (e.g., clay particles) with the adsorbed chemical is not effective. This study presents a simple quantification procedure based on the ratio between IR absorption bands of the sorbate and the adsorbate. The advantages of the procedure are (a) direct evaluation of the adsorbed amount and (b) accurate measurement of chemicals that are hard to quantify, as those that do not absorb light in the UV-Visible range, or require expensive chromatography procedures.

1. Introduction

Quantification of adsorbed amounts of compounds on sorbates in general and clays in particular is usually performed by evaluating mass balance based on chromatography [1], UV-Visible spectroscopy [2, 3], elemental analysis [4], or any other analytical technique that measures the remaining concentration of the analyte in solution. The general procedure when using those techniques is that if the added concentration is known (C_{added}) and the remaining and not-adsorbed equilibrium concentration (C_{equ}) is measured by one of those analytical procedures, the adsorbed amount can be calculated by subtracting ($C_{\text{added}} - C_{\text{equ}}$) and dividing it by the amount of sorbent.

One of the problems of such techniques is that several other processes that reduce concentration in equilibrium solution might be wrongly ascribed as adsorption. For example, Rytwo and coworkers [5] described apparent “adsorption” of crystal violet on Texas vermiculite that after a more detailed analysis was revealed as degradation of the dye on the surface of the mineral, and the amount adsorbed as crystal violet was considerably lower than

the initial estimations. Overestimated adsorbed amounts may also stem from precipitation or evaporation of the adsorbate in case. Such erroneous quantifications might be avoided by measuring the adsorbate content not in the solution but directly on the sorbate. An example of such technique is the use of CHNSO analyzer that might yield the amount of organic compounds adsorbed on a mineral [3, 6]: considering the sorbent in most cases does not include carbon, nitrogen, or sulfur, all the amounts of those elements measured are ascribed to the organic compound adsorbed. In cases where the sorbent contains some of those elements more cumbersome evaluations can be performed to take that into consideration [7]. However, large discrepancies between different techniques are in some cases measured: Aznar and coworkers [3] had shown a 20% difference between elemental analysis of the adsorbed amount and mass balance by UV-Vis. Elemental analysis will also not detect degradation on the surface, as disclosed by the study mentioned above [5], if the products remain bound to the sorbate.

Vibrational spectrum of a compound is considered to be a unique characteristic of the molecule; thus, infrared (IR) spectroscopy is used as a fingerprint technique for

identification [8]. It has been used for decades in clay mineralogy to derive information concerning clay minerals structure, composition, and structural changes upon chemical modification [9]. It is an economical, nondestructive, rapid, and common technique that helps in mineral identification and give also unique information about clay minerals [10], including quantitative mineral analysis and composition of sediments and clays [11, 12], wetting/drying changes and their influences [13, 14], clay-organic interactions [7, 15], and even orientation of organic molecules on the mineral [16, 17]. The increased sensitivity of Fourier transform infrared (FTIR) spectrometers makes the attenuated total reflectance (ATR) method a simple and routine technique. ATR has been used extensively to investigate adsorption of organic substances on minerals. Its main advantage is that it allows measurement of dispersions, gels, liquids, and pastes, very fast, with no extra preparation procedures [10].

This study reports an ATR-FTIR quantification technique performed on the sorbate and based on the quantitative evaluation of the ratio between adsorption bands of the adsorbate (in several cases an organic compound) and the sorbate (in the examples presented in this study a clay mineral). The technique is compared with results obtained by other analytical procedures such as gravimetry, UV-Visible spectroscopy, and CHN elemental analysis.

2. Materials and Methods

2.1. Materials. Volclay KWK Food Grade bentonite clay (American Colloid Company, Arlington Heights, IL) was supplied by Mr. Micha Vaadia (Galil Mountain Winery). S9 “Pangel” sepiolite was purchased from Tolsa SA (Madrid, Spain). Wyoming Na-montmorillonite (SWy-2) was obtained from the Source Clays Repository of The Clay Minerals Society (Columbia, MO). Berberine chloride and egg-yolk L- α phosphatidylcholine (PC) were purchased from Sigma-Aldrich (Rehovot, Israel). Crystal violet (CV) was purchased as chloride salt from Fluka Chemie AG (Buchs, Switzerland). Mustard and *Melaleuca* essential oils were kindly supplied by Dr. Dan Gamrasni. All materials were used without further treatment or purification.

2.2. Comparison with Gravimetric Measurements: Hygroscopic Water Content on Clay. To mimic sorbents with different water content, KWK bentonite-berberine-clay with amounts ranging from 0.1 to 0.8 mmole berberine per g clay was prepared as described by Rytwo et al., 2005. At those added concentrations complete adsorption of the berberine is observed [18]. This was confirmed by measuring remaining berberine with an HP 8452A diode array UV-Vis spectrophotometer (Hewlett-Packard Co., Palo Alto, CA) at 344 nm, (ϵ of berberine $22800 \text{ M}^{-1} \text{ cm}^{-1}$). In all samples optical density (OD) was lower than the limit of detection ($\text{OD} < 0.01$, equivalent to less than $4.4 \times 10^{-7} \text{ M}$ berberine remains). Organoclays were freeze-dried and left to equilibrate at ambient conditions for 72 h. The water content was measured gravimetrically by weighing the air-dried and oven-dried

(at 105°C for 24 h) organoclay, respectively, on an analytical balance. Experiments were executed in triplicate.

2.3. Comparison with Mass Balance by UV-Vis Spectroscopy: Cationic Dyes Adsorption. Adsorption isotherms of crystal violet on SWy-2 montmorillonite were prepared and measured as described above for the berberine experiments. The concentration of the dye in each of the filtrates was determined by measuring the absorption at 588 nm (ϵ of $83000 \text{ M}^{-1} \text{ cm}^{-1}$) using the HP 8452A spectrophotometer previously mentioned. The detection limit of the dye was $2.7 \times 10^{-7} \text{ M}$ corresponding to an optical density of 0.01. Experiments were carried out in triplicate.

2.4. Comparison with CHNSO Measurements: Adsorption of Phosphatidylcholine. Phosphatidylcholine (PC) was adsorbed on clays (SWy-2, sepiolite) as liposomes from aqueous dispersions. Liposomes were prepared by the extrusion method; PC was dissolved in chloroform, which was subsequently evaporated under a stream of nitrogen. The dried lipid cake was rehydrated in 5 mM NaCl solution at the desired concentration. The resultant suspension was repetitively extruded through polycarbonate membranes from Whatman with pore sizes of 400, 200, and 100 nm, respectively. The final liposome diameter was ca. 130 nm as confirmed by dynamic light scattering measurements (Malvern Instruments Zetasizer Nano ZS). For adsorption on the clays, liposome dispersions of 0.1–2.4 mM PC concentration were contacted with the sorbates (at 2 mg mL^{-1} clay concentration) and stirred overnight. The clay-PC materials were recovered by centrifugation, washed, and subjected to ATR-IR and CHN elemental analysis (PerkinElmer 2400 Series II CHNS/O Elemental Analyzer), respectively. For quantitative PC analysis by ATR-IR the PC/clay absorption intensity ratios were calibrated by collecting IR spectra of physical mixtures of clay with known amounts of PC.

2.5. Kinetic Evaluations: Essential Oils Evaporation from Clays and Organoclays. Measurements of essential oils were performed directly or by direct mixing with sorbents (SWy-2 or organoclays based on CV or berberine adsorbed on SWy-2 at 0.8 mmole dye per g clay) at a 1:10 weight ratio oil:sorbent. ATR-FTIR measurements were performed as described below.

2.6. ATR-FTIR Measurements. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of all the experiments described above were measured on a Nicolet Avatar 320 FTIR (Nicolet Analytical Instruments, Madison, WI), using a MIRacle ATR device with a diamond crystal plate (Pike Technologies, Madison, WI). Spectra were recorded at 4 cm^{-1} nominal resolution with mathematical corrections yielding a 1.0 cm^{-1} actual resolution and 100 measurements were averaged. OMNIC 8.1 (Thermo Fisher Scientific Inc.) software analytical procedures were used to convert the spectra from ATR to absorbance and to perform additional analysis such as peak resolution. Quantification

FIGURE 1: (a) FTIR spectrum of KWK raw clay (full line) and clay with 0.1 (dashed line), 0.25 (dotted line), and 0.75 (dashed dotted) mmole berberine per g KWK clay; (b) gravimetric water content of berberine-KWK organoclays and its relation to the ratio of IR absorption of adsorbed water (A_{3450}) to structural OH (A_{3620}).

based on the absorption intensity of different peaks was performed using TQ analyst EZ 8.0.2.97 software (Thermo Fisher Scientific Inc.). Absorbance (A) intensities for each relevant wavelength (e.g., 3450 cm^{-1}) is denoted by A_{3450} . The quantitative evaluation of the amounts of adsorbed compound was based on the ratio between absorbance intensities at bands clearly ascribed to the adsorbate and the sorbate. This ratio is denoted, for example, by A_{3450}/A_{3620} for adsorbed O-H at 3450 cm^{-1} and structural O-H at 3620 cm^{-1} .

3. Results

3.1. Comparison with Gravimetric Measurements: Hygroscopic Water Content on Clay. The hygroscopic water content of clays decreases as the amount of adsorbed organic cation increases. The explanation of the effect is that the residual water content depends highly on the hydration shell of the adsorbed cations: exchanging inorganic hydrated cations by large organic molecules, with no hydration layers, leads to the formation of hydrophobic organoclay complexes, reducing the amount of hygroscopic water [19]. Adsorbed water on clay is observed at approximately 1600 cm^{-1} and a broad peak at approximately 3400 cm^{-1} corresponding to angle bending and stretching vibrations, respectively [20]. Vibrations due to OH moieties in the lattice structure of montmorillonite and bentonites exhibit a clear absorption band at approximately 3620 cm^{-1} [10]. Figure 1(a) shows the FTIR spectra of raw KWK clay and clay with adsorbed berberine at different amounts, normalized to the latter peak.

A relative decrease of the adsorbed water stretching peak can be clearly observed. Similar results were presented for heated MX80 bentonite self-supporting films [20] and

ascribed to a gradual decrease in water content due to the heating. In order to quantify this effect, we define the ratio A_{3450}/A_{3620} as a quantitative indicator between the adsorbed water and structural OH groups. For example, when added berberine is 0.1 mmole berberine per g KWK clay, $A_{3450} = 0.0653$ and $A_{3620} = 0.1092$, yielding $A_{3450}/A_{3620} = 0.5977$. Figure 1(b) shows the relationship between this ratio and the hygroscopic water content of the berberine-KWK organoclays, as measured gravimetrically. It can be seen that a very good linear fit between both parameters is observed. Thus, by calibrating the measurement with a known water content, the ratio A_{3450}/A_{3620} can be a good indicator for the water content of bentonite clays.

3.2. Comparison with Mass Balance by UV-Vis Spectroscopy: Cationic Dyes Adsorption. The most widely used evaluation technique of adsorbed amounts is based on mass balance calculations following measurement of the remaining concentration (not adsorbed) in solution. In most cases, when the adsorbate is an organic molecule with a large chromophore, the remaining concentration is measured by UV-Vis spectroscopy. As mentioned in the Introduction, this technique is prone to artifacts due to degradation, precipitation, or metachromatic changes in the spectrum of the adsorbate.

For the case of adsorption of crystal violet (CV) on bentonite clays, this technique is well established [21], even though degradation of the dye on vermiculite was reported [5]. Adsorption experiments of CV on SWy-2 montmorillonite were performed, with added dye between 0 and 1.6 mmole g^{-1} , equivalent to 0–200% of the cation exchange capacity (CEC) of the clay. Adsorbed amounts were measured by mass balance as described in Section 2.3.

FIGURE 2: (a) ATR-FTIR spectra of SWy-2 raw clay and clay with added amounts of CV as denoted in the figure (in mmole g^{-1} clay). All spectra normalized by the absorption band of the Si-O vibration at 990 cm^{-1} . (b) CV adsorbed as a function of the amount added. Points represent average adsorbed amounts evaluated by FTIR ratios of CV to clay absorption bands. Small dots and the dashed line represent the amount as measured by UV-Vis spectroscopy and mass balance calculation.

Figure 2(a) presents the ATR-FTIR spectra of the freeze-dried organoclay powder. The absorption band of the mineral ascribed to Si-O stretching [10] can be observed at about 1000 cm^{-1} , whereas the additional bands observed in the spectra are ascribed [22] to moieties in triarylmethane dyes, as ring vibrations (1590 cm^{-1}), C- ϕ stretching (1170 cm^{-1}), and N-ring vibrations (1350 cm^{-1}). By using for calibration the data point of 100% CEC added CV, where all the dye is adsorbed [23], ratios between those bands and the clay Si-O peaks ($A_{\text{CV},1590}/A_{\text{Si-O}}$, $A_{\text{CV},1350}/A_{\text{Si-O}}$, and $A_{\text{CV},1170}/A_{\text{Si-O}}$) were evaluated and related to the calibration data point. Results of the three ratios were averaged. Figure 2(b) exhibits the adsorbed amounts by ATR-FTIR evaluation compared with the values measured by UV-Vis and evaluated by mass balance. A relatively good fit can be observed ($R^2 = 0.9894$) with slight discrepancies at large added concentrations, where the ATR-FTIR technique yields slightly lower (5–10%) adsorption values than the usual practice. A similar reasonable fit between the ATR-FTIR and the UV-Vis mass balance results was also measured for other cationic dyes (methylene blue, berberine, etc.) adsorbed on SWy-2 and other clays (KWK, S9 sepiolite, SHCa-1 hectorite, etc.).

3.3. Comparison with CHNSO Measurements: Adsorption of Phosphatidylcholine. Adsorption of phospholipids on clays is widely studied and used for several applications [6, 24]. Since its absorption light in the UV-Vis range is only at 205 nm , its quantification is usually determined by CHN measurements. Its vibrational spectrum has several specific absorption bands caused by the different functional groups:

C=O stretching at 1720 cm^{-1} , P=O asymmetric stretching bands at $1220\text{--}1240\text{ cm}^{-1}$ [25], methylene (CH_2) bending at $1440\text{--}1480\text{ cm}^{-1}$, and the C-H stretching region at $2800\text{--}3000\text{ cm}^{-1}$ [8]. All those bands can be used to quantify its adsorption, relative to significant bands of the sorbent as the Si-O band at approximately 1000 cm^{-1} or the O-H vibrations in the lattice structure of the clay at approximately 3600 cm^{-1} [10]. Figure 3 shows three of the four adsorbate bands, at several added amounts of phosphatidylcholine (PC) on SWy-2 montmorillonite, normalized to the sorbent as the Si-O band at approximately 1000 cm^{-1} . It can be seen that all PC peaks increase with the added amount, indicating increase in the adsorption.

Figure 4 shows the results of the adsorption of PC on SWy-2 as evaluated by the average of ratios between four PC peaks (C=O, CH stretching, phosphate asymmetric vibration, and CH bend) and the O-H vibrations in the lattice structure of the clay FTIR peaks, as a function of results measured by CHN analyzer for the same samples (A_{1720}/A_{3620} , A_{2900}/A_{3620} , A_{1230}/A_{3620} , and A_{1460}/A_{3620}). The reason the O-H peak was preferred is that a PC peak at 1060 cm^{-1} might interfere in the accurate evaluation of the clay if the Si-O peak at 1100 cm^{-1} is used. A very good fit between the CHN and FTIR quantification is observed in Figure 4. Similar results were obtained for adsorption of PC on sepiolite clay.

3.4. Kinetic Evaluations: Essential Oils Evaporation from Clays and Organoclays. Essential oils are highly volatile substances isolated by a physical process from an odoriferous plant [26]. In recent decades essential oils and their components have

FIGURE 3: FTIR spectra of SWy-2 clay with added amounts of PC as denoted in the figure. All spectra normalized by the absorption band of the Si-O vibration at approximately 1000 cm^{-1} .

FIGURE 4: PC adsorbed on montmorillonite evaluated by FTIR ratios of PC to clay absorption bands, as a function of the measured adsorbed amounts by CHN analysis of the same samples.

been of great interest as they have been the sources of natural products [27]. Australian tea tree oil (TTO) is obtained from the foliage and terminal branches of species of *Melaleuca*, and its composition is given in the International Standard (ISO 4730-2004) [28]. Its main components are terpinen-4-ol (30–48%, CAS 562-74-3, and v.p. 0.0438 mm Hg), γ -terpinene (10–28%, CAS 99-85-4, and v.p. 1.08 mm Hg), and α -terpinene (5–13%, CAS 99-86-5, and v.p. 1.64 mm Hg). As

FIGURE 5: ATR-FTIR spectra of tea tree oil immediately after application (TTO) and after 18 m (TTO 18 m), adsorbed on berberine-SWy-2 organoclay after 18 m (TTO/OC 18 m).

terpenes are two orders of magnitude more volatile than terpinen-4-ol, the relative evaporation of those components might be monitored. In order to evaluate the contribution of the several compounds to the TTO mixtures, samples of the pure chemicals were purchased and measured. Pure γ -terpinene exhibits peaks at 780, 815, and 830 cm^{-1} , whereas pure terpinen-4-ol presents absorption bands at 889, 864, and 799 cm^{-1} . Figure 5 shows the FTIR spectrum of TTO immediately after application and after 18 min (TTO 18 m). A relative decrease of the more volatile γ -terpinene compared to the less volatile terpinen-4-ol can be clearly observed. It is interesting to notice that the adsorption of TTO on a hydrophobic organoclay (berberine-SWy-2 montmorillonite) reduces terpinene evaporation, and its peaks remain substantial after 18 min (TTO/OC 18 m).

By performing several measurements at different periods of time a detailed kinetic evaluation can be performed and by doing that the “slow release” effect obtained by the adsorption of the essential oil on the organoclay can be clearly observed. Figure 6 displays the natural logarithm of the ratio between the intensity of the γ -terpinene to the terpinen-4-ol absorption bands, as a function of the time from application. It can be seen that a reasonable fit to linear curves can be observed for all cases. A pseudo-first-order process behaves according to $d[A]/dt = -k[A]^1$, in which $[A]$ is the ratio between the peaks at a given time and k is the kinetics coefficient of the process. Integration of this equation leads to $[A] = [C]/[C]_0 = e^{-kt}$, which can be linearized to $\ln[A] = -kt$. Thus, a linear representation of the logarithm of $[A]$ as

FIGURE 6: Natural logarithm of the ratio between the absorption bands of γ -terpinene to the terpinen-4-ol as a function of time for nonadsorbed tea tree oil, tea tree oil adsorbed on clay, and on berberine-montmorillonite (OC) organoclay.

a function of the time will yield the fit to a 1st-order process, and the slope will be the kinetic coefficient, which in this case represents the evaporation rate. Half-life can be calculated as $t_{1/2} = -\ln(1/2)/k = \ln 2/k$ and is independent from the initial concentration [29].

Evaporation rate of γ -terpinene from tea tree yields a half-life time of 11.7 min. Adsorbing the oil on raw clay or organoclay yields half-life time of 23.1 and 44.8 min, respectively, demonstrating the slow release effect achieved by the hydrophobic berberine-SWy-2 hybrid platform.

An even more significant slow release effect is observed in mustard oil. The main component of this oil is allyl-isothiocyanate, which has a very distinctive IR absorption band at about 2100 cm^{-1} . Figure 7 shows the evaporation of mustard oil as it can be seen from the almost complete disappearance of the isothiocyanate peak. The evaporation rate of the nonadsorbed oil is 0.193 m^{-1} ($t_{1/2} = 216\text{ s}$). The adsorption of the oil on berberine-SWy-2 organoclay slows down the process by 40 folds, yielding an evaporation rate of $4.77 \times 10^{-3}\text{ m}^{-1}$ ($t_{1/2} = 8720\text{ s}$). Similar effects were measured with other essential oils and specific nanocomposites (Rytwo, 2014, unpublished results).

4. Discussion

Results presented in this study demonstrate a good fit between quantification based on ATR-FTIR measurements and other methods. Two main problems should be emphasized when using the proposed technique: (a) the quantitative determination of the technique proposed here depends on

FIGURE 7: ATR-FTIR spectra of the isothiocyanate band of mustard oil immediately and 14 m after application (full and dashed dotted, resp.) compared to mustard oil adsorbed on berberine-SWy-2 organoclay immediately and 14 m after application (dotted and dashed lines, resp.).

the use of accurate calibration data; (b) there are several cases when adsorption of a compound causes changes in part of the FTIR absorption bands due to interactions with the adsorbent [18].

It is obvious that all measuring techniques are prone to biases and depend on accurate calibration. UV-Vis mass balance, for example, demands accurate determination of the ϵ values of the analyte and the lack of interferences at the wavelength of measurement. Furthermore, it should be recalled that at high added concentrations usually considerable dilutions of the filtrate are needed, making mass balance subtractions more sensitive to errors. CHNSO and chromatography measurements rely also on calibrations performed sometimes on standards and matrices that differ completely from the analyte.

Thus, it is hard to determine which technique is more accurate, and each method should be used with caution and considering its limitations. However, considering the fact that differences between the presented methods hereby are minor and (for example) both UV-Vis mass balance and the proposed technique detected the saturation effect at high added concentrations of adsorbed organic dyes, the ATR-FTIR method might be considered a possible alternative for fast quantification.

5. Conclusions

- (i) ATR-FTIR is a fast, nondestructive, and relatively cheap technique that might allow direct semiquantitative measurements of components in mixtures, as

in the case of adsorbed compounds, or of chemicals evaporating at different rates.

- (ii) By using calibration samples, such measurements become quantitative.
- (iii) The advantage of the technique is its lower susceptibility to over- or underestimations.
- (iv) As any other analytical techniques, suitable preliminary tests are needed to ensure there are no significant changes in the intensity or the energy of the specific absorption bands used for the quantification.

Abbreviations

A_{xxx} :	Absorbance at a wavelength of $xxx\text{ cm}^{-1}$
ATR:	Attenuated total reflectance
CEC:	Cation exchange capacity
CV:	Crystal violet [4-[bis[4-(dimethylamino)phenyl]methylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium
FTIR:	Fourier transform infrared
KWK:	Volclay KWK Food Grade bentonite clay
OD:	Optical density
PC:	Phosphatidylcholine
SWy-2:	Wyoming Na-montmorillonite
$t_{1/2}$:	Half time life
TTO:	Australian tea tree oil
UV-Vis:	Ultraviolet-visible.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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