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Adsorbents regeneration under microwave irradiation for dehydration and volatile organic compounds gas treatment

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ABSTRACT

In adsorption processes, adsorbent regeneration is by far the most time and energy consuming step for which microwave technology offers many advantages. Nevertheless, desorption under microwave is a complex process: electromagnetic energy conversion into heat is strongly linked to several other phenomena such as thermodynamic equilibrium, heat and mass transfers as well as transport. This study points out the key parameters controlling desorption under microwave irradiation. In this paper, an experimental study is presented using several types of adsorbents (silica, activated alumina, NaX and NaY zeolites) and various adsorbates (water, toluene, *n*-heptane and methylcyclohexane). Theses solids and liquids have been selected for their contrasted dielectric and structural properties. Water desorption from several adsorbents exhibits very different behaviours linked, not only to the evolution of their dielectric properties with temperature and water content, but also to the structure of the adsorbents and more especially to the quantity and position of the exchange cations. Simulated temperature profiles in the solid bed show that, in some cases, desorption can be effective and rapid without reaching very high temperatures in the solid. Results obtained with a zeolite NaX show that desorption rates and effectiveness strongly differ from an adsorbate to another, and seem to be mainly controlled by the microwave absorbed power profile. Morphology-dependent resonances could be responsible for some high rates of heating and accelerating desorption. Microwave heating appears to be a promising technology for adsorbent regeneration processes which is completely dependent on the appropriate choice of the adsorbent–adsorbate couple as well as the reactor's shape and size.

1. Introduction

Adsorption on microporous solids is a powerful technique for trapping selectively undesirable gaseous molecules. Considering the pollutant emissions standards that are becoming more and more severe, this flexible and low cost technique already used for dehydration applications or volatile organic compound (VOC) emissions control, is a promising technique [1,2]. The most limiting step of the process is often the regeneration step which is time and energy consuming. In this context, the use of microwave technology appears to offer a potential solution [3].

Microwave heating has found its way into a number of applications, particularly in the food industry [4] as well as material drying or the processing industry [5]. Industrial microwave technology for chemical processes is still developing [6]. Concerning adsorbent regeneration, patents on microwave-assisted processes are available [7,8]. Three industrial processes of adsorbent regeneration under microwave heating are reported in Bathen [3]. The first two deal with the recovery of solvents from a polymeric adsorbent or of VOC adsorbed on activated carbon. The last one deals with alumina regeneration in an air-drying process. Canada Ontario Hydro Technologies has built a pilot plant of a 30 kg/h capacity for the recovery of VOC from activated carbon used in gold ore beneficiation. Microwave technology has also proven useful for the destruction of chlorinated and non-chlorinated organic pollutants on a pilot scale by Cha and Carlisle [9]. These researchers have designed and constructed a microwave air purification system based on granulated activated carbon and zeolite adsorption where microwaves are used for desorption as well as for final catalytic oxidation of the pollutants.

Transferring microwave processes from a laboratory to an industrial scale is not necessarily straightforward. While the electric field is often considered homogeneously distributed in small cavities, microwave propagation in an industrial setting has to be taken into account and combined with the chemical and physical transformations of the process. A recent work on methanol desorption from a zeolite in a 1 m waveguide column [10] demonstrates the feasibility of this process. It also studies the instantaneous

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Table 1
Adsorbent properties.

Adsorbent	Alumina	Silica	NaX G5	NaY	NaX powder
Average diameter (μm)	1500–3000	1000–3000	650	650	2
Particles density (kg/m^3)	1255	566	1100–1200	1100–1200	1365
Bed density (kg/m^3)	870	480	650	630	
Specific surface B.E.T (m^2/g)	274	552	685	639	792
Microporous volume N_2 (cm^3/g)	0	0	0.283	0.271	0.326
Mesoporous volume N_2 (cm^3/g)	0.406	0.875	0.034	0.045	0.022
Mesoporous volume Hg (cm^3/g)	0.286	0.433	0.042	0.047	
Macroporous volume Hg (cm^3/g)	0.036	0.031	0.269	0.259	
Mesoporous pores mean diameter N_2 (nm)	6.4	6.7	–	–	
Macroporous pores mean diameter Hg (nm)	1019	104	333	165	–
Adsorption capacity at ambient temperature ($kg_{water}/kg_{dry\ solid}$)	0.15	0.16	0.27	0.21	0.32
Si/Al ratio	0	∞	1.3	2.4	1.3

and transitory behaviour of temperature and the propagation of microwave energy. This kind of work helps to further microwave process modelling and industrial transfer.

Microwave advantages for adsorbent regeneration have mainly been established at a laboratory scale. (1) During dielectric heating, electromagnetic energy is directly converted by the material itself into heat. It provides a fast and volumetric warming of the material which limits heating the container. (2) Temperature profiles can be inverted to the ones obtained in the adsorbent pellets with traditional heating, which is favourable to energy savings [11]. (3) Microwave regeneration of adsorbents is considered a repeatable and sustainable method. Ohgushi and Nagae [12] showed that microwave treatment can induce a small degradation of the adsorption capacity of the adsorbent (zeolite X) but the total amount of water adsorbed by a microwave treated zeolite during its lifetime remains 10 times higher than the one of a classical commercial dessicant (calcium chloride). Despite all these encouraging observations and advantages, microwave technology is not directly applicable to any desorption system without a preliminary analysis of all the phenomena interfering at the micro, meso and macroscale. Desorption under microwave is a complex process involving: (1) electromagnetic energy conversion into heat which is ruled by the overall dielectric properties of the adsorbent and adsorbate materials and by the electric field distribution in the microwave applicator, (2) thermodynamic equilibrium which is temperature dependant, (3) transport phenomena in the pellets depending on the solid structure and the molecule's size and shape, (4) heat and mass transfer as a function of hydrodynamics.

The local distribution of the electric field in the applicator is described by Maxwell's propagation equations in which the dielectric properties of the media interfere. Dielectric properties named as permittivities are composition, temperature and microwave frequency dependant. In polyphasic systems for which a condensed phase (adsorbate) is in contact with a solid adsorbent, dielectric permittivities are not easily deduced from the permittivity values of the pure components. During desorption applications, they are modified by the changing temperature and composition. Adsorbents as well as adsorbates themselves can exhibit very contradictory permittivity behaviours with temperature. Thus, each adsorbent–adsorbate couple will possess its own variation in dielectric properties during desorption under microwaves, leading to a difficulties in predicting the overall behaviour of the system.

The aim of this study is to point out the key parameters controlling desorption under microwave. A better understanding is required in order to predict the applications of adsorbent regeneration for which microwave technology is the most interesting. Our objective is then to determine for a few applications, what mainly controls desorption under microwaves.

An experimental study of desorption under microwaves is presented using several types of adsorbents and adsorbates, for which the dielectric and structural properties are very contrasted. Four adsorbents have been selected considering their good adsorption capacities for water or VOC [13,14]: silica, activated alumina, NaX and NaY zeolites. Both zeolites are faujasites, offering the same crystalline structure but different Si/Al ratios (1.3 versus 2.4). The NaX zeolite is then more ionic and should possess higher dielectric permittivities than the NaY zeolite. Both zeolites offer a large microporosity and macroporosity, due respectively to the crystalline structure, with the two existing types of cavities (sodalite β-cages and supercages) [1], and to the binder. Mesoporosity is normally low but can sometimes be developed by microwave heating when zeolite is fabricated by microwave-mediated desilication at high temperature [15]. The two other solids are amorphous and also polar. They are essentially mesoporous which leads to lower specific areas BET and adsorption capacities than zeolites. Nevertheless, when intraparticle diffusion is a limiting factor, mesoporosity can be advantageous compared to microporosity because it favours diffusion of the desorbed molecules inside the pores of the solid. Comparing these four solids should help us in understanding the relative importance of dielectric properties and micro or mesoporous structures.

Four adsorbates have also been selected: water, for its high polarity and well known ability to heat under microwave, and three less polar or non-polar VOC (toluene, methylcyclohexane and *n*-heptane). Each of these three organic compounds possesses seven atoms of carbon but their molecular structures are very different (aromatic cycle, saturated cycle, linear). These contrasted steric properties affect thermodynamic equilibrium and internal diffusion into the pores of the solid. The comparison of the four adsorbates should help us to conclude on the role of their dielectric and steric properties.

2. Experimental

2.1. Adsorbents and adsorbates characteristics

Commercial beads of adsorbents were used and their main characteristics are given in Table 1. Activated alumina (A.A. 1,5-3) was provided by Axens, silica (X254) by Grace, NaX zeolite (G5) and NaY zeolite (CBV100 by Zeolyst) by CECA. Binder free NaX (13X) powder, used for dielectric properties measurements was also provided by CECA. Classical characterization of theses samples was carried out by nitrogen adsorption at 77 K (Micromeritics ASAP 2010) and by mercury porosimetry. Prior to measurements, the samples were outgassed at 773 K for 12 h. The microporous volume was calculated using the Dubinin–Raduskevitch equation and the mesoporous volume was obtained either by the difference between the nitrogen-adsorbed volume at a relative pressure P/P_0 equal to 0.99 and the microporous volume or by the one determined from the *t*-plot method. The mesoporous mean diameter was calculated by the classical Barret, Joyner and Halenda method. The macroporous mean diameter was estimated from mercury porosimetry curves

Table 2
Dielectric properties of saturated adsorbents with water and liquid adsorbates – 20 °C and 2.45 GHz (ε' real part and ε'' imaginary part) – Error: ±0.05.

Adsorbents saturated with water			Liquid adsorbates		
	ε'	ε''		ε'	ε''
Activated Alumina	5.05	0.70	Water	79.00	11.00
Silica	2.70	0.35	Toluene	2.50	0.05
NaX G5 zeolite	5.25	1.10	*n*-Heptane	1.90	0.01
NaY zeolite	3.75	0.70	Methylcyclohexane	2.00	0.01

by the Washburn relation. Adsorption capacities were measured in situ at room temperature following the procedure described in Section 2.3.

Adsorbates are ultrapure water (Barnstead Easy Pure Rodi), toluene, *n*-heptane and methylcyclohexane of more than 99% purity, from Alfa Aeser or Acros.

2.2. Dielectric properties measurements

Dielectric properties at room temperature (20 °C) of the liquid adsorbates, as well as the saturated with water adsorbents ones are given in Table 2. They were measured at 2.45 GHz using a reflecting method (Network analyser Agilent N5230A 10 MHz to 20 GHz). For the adsorbents, solids were ground into a very fine powder and compacted before measurement following the instructions given by Agilent for the use of the semi-solid or high temperature open ended coaxial probe 85070 E.

The small perturbations method in resonant cavity at 2.45 GHz was used to achieve adsorbents permittivities with temperature. This method is described in detail in a previous work [16]. Dielectric properties of silica, pure NaX powder and NaX beads (G5) were measured as a function of temperature. The sample was first heated from room temperature to 200 °C in an open tube. The water content of the sample, which decreased during heating due to desorption, was evaluated before and after the experiment by classical thermogravimetry. The initial water contents were 8% for silica, 32% for NaX powder (that is to say fully saturated), and only 6% for NaX G5 beads. In a second step, the sample was cooled from 200 °C to room temperature in a closed but pierced tube to prevent water adsorption from ambient surrounding air and to maintain atmospheric pressure. For NaX powder and NaX beads, there was a second heating of the dried sample in the open tube. Permittivities profiles are given in Figs. 1–3.

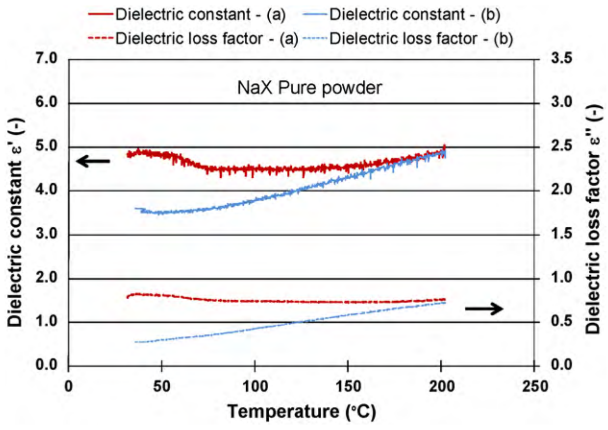

Fig. 1. Effect of temperature on the dielectric permittivities at 2.45 GHz of NaX pure powder during – (a) heating with dehydration from 32% to 4% of water content and (b) heating at a constant water content of 4%.

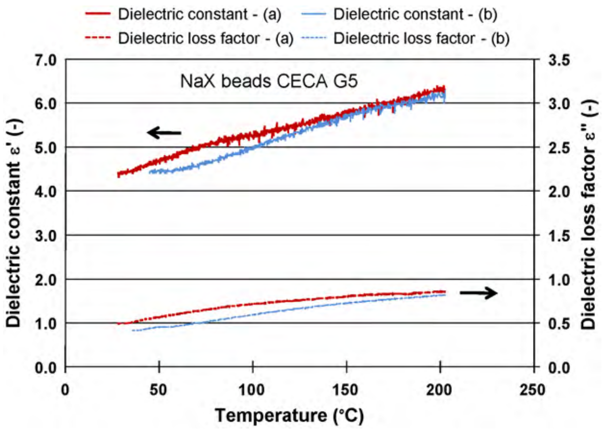

Fig. 2. Effect of temperature on the dielectric permittivities at 2.45 GHz of NaX beads CECA G5 during – (a) heating with dehydration from 6% to 2% of water content and (b) heating at a constant water content of 2%.

2.3. Microwave apparatus and procedure

Adsorption and desorption cycles were conducted in a fixed bed reactor consisting of a glass tube of 2.9 cm internal diameter, introduced in the chimneys of a standard waveguide (Fig. 4). The adsorbent bed height is about 3.75 cm corresponding to the one of the irradiated zone. The reactor is supported on a microbalance which records its weight change with time. During the adsorption step, full saturation of the solid is obtained by bubbling the vector gas (nitrogen) in an adsorbate-containing vessel before flowing it through the adsorbent bed. During desorption step under microwave irradiation, the vector gas flowrate of 30 NL/h firstly passes through a desiccant bed of zeolite NaA before being introduced at the bottom of the reactor. An optical fiber (0–200 °C range) is used in the irradiation area to measure the solid temperature inside the bed or the gas temperature a few millimetres above the bed surface.

The microwave heating system consists of a magnetron functioning at 2.45 GHz with a maximal power of 1950 W. Microwaves are carried out in a WR 340 waveguide applicator for a resonant single mode TE_{013}. The applicator length is manually adjusted at the beginning of the experiment to achieve a minimum reflected power. The circulator protects the magnetron by conducting reflected power into a water load. Reflected and incident powers are measured and recorded and the absorbed power (P_{abs} in W) is deduced by calculating the difference. The experiments were led

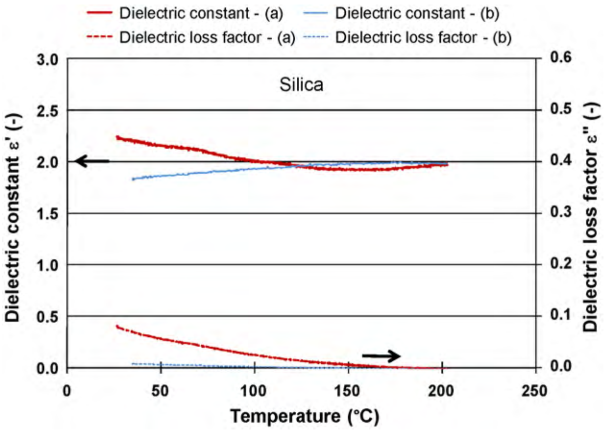

Fig. 3. Effect of temperature on the dielectric permittivities at 2.45 GHz of silica during – (a) heating with dehydration from 8.7% to 0.8% of water content and (b) cooling at a constant water content of 0.8%.

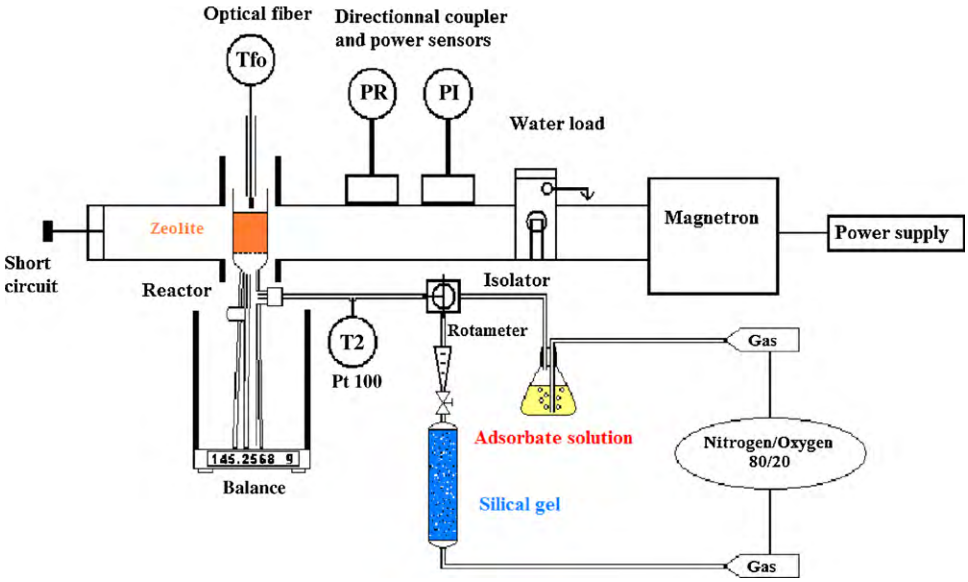

Fig. 4. Experimental apparatus.

in a continuous mode of microwave irradiation with an incident power of 50 W.

3. Results and discussion

3.1. Dielectric properties analysis

According to Pointing's Theorem, the average microwave absorbed power (P_{abs} in W) is related to the dielectric properties of the medium and the local electric field magnitude (E in V m^{-1}) [17,18] by:

$$P_{abs} = V\pi f \varepsilon_0 \varepsilon'' E^2$$

where V is the volume of the sample (m^3), f the microwave frequency (Hz) and ε_0 the free space permittivity (F/m). The local electric field satisfies the Maxwell's equations and is coupled to the relative dielectric constant (ε') and relative dielectric loss factor (ε'') values.

In order to elucidate the contribution of the dielectric properties, and more especially of the loss factor on the absorbed microwave power in our experiments, the dielectric properties of NaX zeolite and silica given in Figs. 1–3 are helpful. Fig. 1 indicates that both relative dielectric properties ε' and ε'' of pure NaX powder remain nearly constant from room temperature to 200 °C while dehydrating from 32% to 4%. On the contrary, they increase with temperature when the solid is "dry", at a water content of about 4%. This trend is confirmed in Fig. 2, by the increasing values of ε' and ε'' with temperature, obtained with NaX G5 beads very lowly saturated with water (from 6% to 2%). At a given temperature, permittivity values are higher for "dry" NaX G5 beads compared to "dry" NaX pure powder due to the presence of the binder (usually clay).

On the contrary, ε' and ε'' for dry silica barely change with temperature and the dielectric loss factor ε'' is nearly equal to zero indicating that silica itself is relatively transparent to microwaves. During dehydration from 8.7% to 0.8%, the decrease in ε' and ε'' can be fully attributed to water loss. These measurements demonstrate that dielectric properties of the medium are regulated by the water adsorbed content and the temperature of the system.

It is assumed that dehydration takes place in two distinct phases: (1) desorption of the molecules bound to the surface and (2) internal diffusion of the water molecules inside the pores of the structure. At any time of the desorption, water is present in two forms inside the solid: the bound molecules which are less free than water in a liquid state and circulating molecules in the form of water vapour. One can then question the contribution of each of these phases on the effective permittivities.

First, capillary condensation was examined in our conditions using the Kelvin equation [19]. Calculations were performed at room temperature for the smallest mesoporous pore diameter that we can consider, 3 nm. They show that a water partial pressure of 16.2 mbar should be reached to observe capillary condensation whereas our water desorption rates (even during microwave dehydration) lead to a maximum partial pressure of 2.3 mbar. Therefore, in any case, capillary condensation does not occur. Pore sizes (given in Table 1) are large enough to consider the desorbed water molecules in a gas phase. The dielectric permittivity of a gas phase is always extremely low because molecules are no longer linked enough to each other to convert electromagnetic energy into heat by rotational polarization. As also concluded by Roussy et al. [20] and Thiebaut et al. [21], once they are desorbed from the surface, the circulating adsorbate molecules inside the pores of the solid do not contribute to microwave energy absorption any more. Electromagnetic energy is absorbed by the solid itself and the bound molecules at the surface. The dielectric properties of the medium change as a ponderate additive function of the water adsorbed molecules and the dry adsorbent dielectric properties. In our study, dry adsorbent behaviours are very contrasted with temperature leading to radically different variations in resulting loss factors during dehydration, from one adsorbent to another.

3.2. Hydrodynamic conditions in the fixed bed reactor

Preliminary calculations were made in order to determine the hydrodynamic regime at the surface of adsorbent particles during desorption under microwave. Depending on the particles mean diameter and the temperature of the bed, the particle Reynolds' number varied from 0.31 to 1.2 indicating a Stokes or a Van Allen intermediate regime. The effect of gas flowrate on the desorption rate was then experimentally studied by varying the nitrogen gas flowrate from 2 to 30 NL/h corresponding to a gas velocity ranging from 0.1 to 1.26 cm/s. For even faster desorption conditions (dehydration of NaX zeolite), no significant gas flowrate effect was observed on the weight loss of the bed and the desorption rates

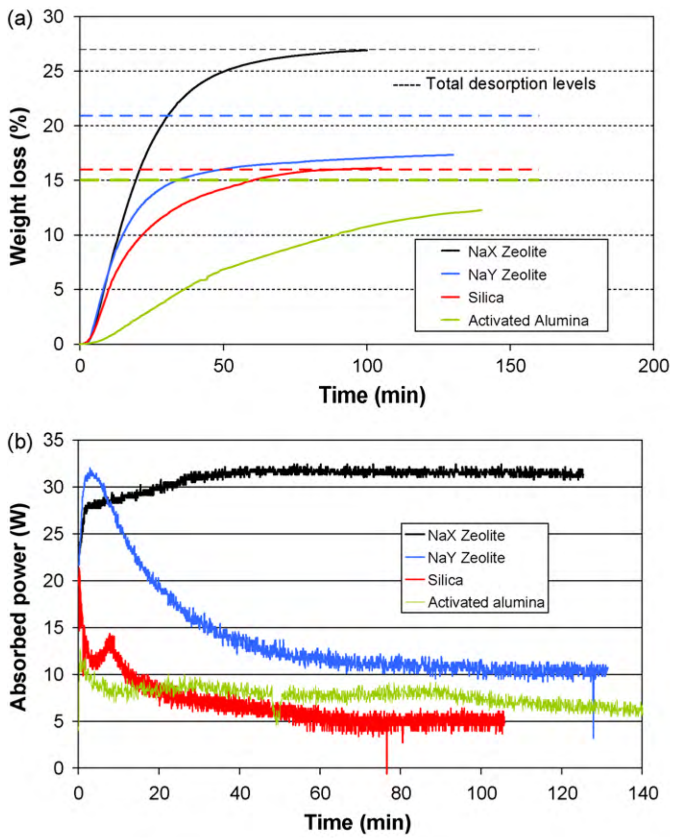

Fig. 5. Dehydration under microwaves of various adsorbents – P_{incident} = 50 W – (a) weight loss (% of dry solid weight) and (b) microwave absorbed power (P_{abs}) profiles.

indicating that external heat and mass transfer was not limiting in our conditions.

3.3. *Dehydration of various adsorbents*

Fig. 5a shows that water is not desorbed at the same rate and with the same efficiency for the four solids tested. At the end of the experiment, only silica and NaX zeolite were fully dehydrated while NaY zeolite and activated alumina were partially dehydrated. If experiments would have last longer, water molecules would have finally been removed by elution by the dry nitrogen flow, and full dehydration would also have been reached. The curves confirm that elution is kinetically very slow compared to desorption by a thermal effect. At the end of our experiments, microwave energy absorption is not effective enough to heat the solid further and provoke additional desorption for alumina and NaY zeolite.

The faster rates of desorption are obtained for both zeolites for which the pore size is the lowest compared to silica and alumina which develop a large mesoporosity (see mesoporous volumes in Table 1). Adding the fact that proportionally higher desorption rates can be obtained for higher microwave input powers [11], internal diffusion does not seem to be a limiting phenomena in our conditions and cannot explain the observed differences in weight loss profiles.

Microwave absorbed power profiles over time (Fig. 5b) demonstrate contrasted behaviours of the four solids towards the electromagnetic energy conversion into heat. For alumina, the absorbed power slightly decreases during the whole experiment while for silica, the decrease is more pronounced. There is a small peak around 8 min but the curve reaches a stable value as soon as full water desorption is achieved. On the contrary, for both zeolites, the absorbed power increases quickly during the first minutes of the experiment. While it keeps on increasing for NaX zeolite until reaching a stable and quite high value, it decreases dramatically for NaY zeolite during the dehydration process.

All theses trends are fully concordant with the permittivities variations analysed in Section 3.1. The dielectric loss factor of the medium is governed by the loss factor of the solid itself varying more or less with temperature and the loss factor of the adsorbed molecules, the quantity of which decreases during desorption.

For silica, the decreasing absorbed power follows the water loss profile remaining stable as soon as water desorption is fully achieved (after 60 min) and at a very low level. The small peak at $t = 8$ min, can be explained by a small change in the position of the applicator length: tuning the cavity was necessary considering the rapid decrease in the absorbed power in the first minutes. Despite this artefact, one can conclude that energy is transferred selectively to the surface via the adsorbate (water) and the decreasing microwave absorbed power directly follows the decreasing water content in the solid. Our results are concordant to the ones of Vallee and Conner [22] who also worked with silica and silicalite but additionally with organic compounds as adsorbates. They interpreted their results by estimating the “effective” temperature of the surface where adsorption occurs, which is always greater than the measured solid or gas temperature because of local and selective features of the microwave heating. In their study, the surface temperature was increased for adsorbates having higher permittivity.

Alumina follows a similar trend. According to Estel et al. (2003) [16], the dielectric loss factor of dry alumina fluctuates little from 0.6 to 0.55 between 30 and 70 °C and one can suppose that it remains true to 120 °C, the temperature reached in our dehydration. Absorbed power directly follows the slowly decreasing water content.

Zeolite NaX (G5) does not behave like silica or alumina because this solid is much more able to heat under microwave. First, at room temperature when solids are fully hydrated, ε'' value (in Table 2) is the highest for NaX and implies the high initial level of microwave energy conversion. Then, desorption occurs and temperature increases. The decreasing water content contributes to a decrease in the dielectric loss factor of the medium. This decrease is counterbalanced by an increase in the dielectric loss factor of the dry NaX zeolite itself with increasing temperature (Fig. 2).

The comparison of the final state for both NaX and NaY zeolites shows that the dehydrated NaX zeolite at elevated temperature converts microwave energy into heat while dry NaY does so at a much lesser extent. This result suggests that the dehydrated NaX permittivity is probably more dependent on temperature than the NaY zeolite’s. Unfortunately, dielectric properties with temperature of the dry commercial NaY zeolite used are not available in literature. Nevertheless, some measurements conducted in our laboratory using the reflecting method always gave lower ε'' values for dry pure NaY compared to pure NaX zeolite in the range of 20–50 °C. The microwave absorbed power for both saturated zeolites increases quickly at the beginning of the experiment due to the rapid heating of the surface of the solid by the large amount of bounded water molecules absorbing microwave energy. The decreasing water content contributes to a decrease in dielectric permittivity of the system. This decrease is counterbalanced by an increase in the dielectric permittivity of the dry NaX zeolite itself with increasing temperature which does not seem to be the case for NaY. NaY zeolite permittivity during dehydration is mainly controlled by the water content profile. These solids of same structure and similar properties differ in their aluminium quantity, their number of exchange cations (two times less in the NaY zeolite) and the absence of very mobile exchange cations in the supercage (type

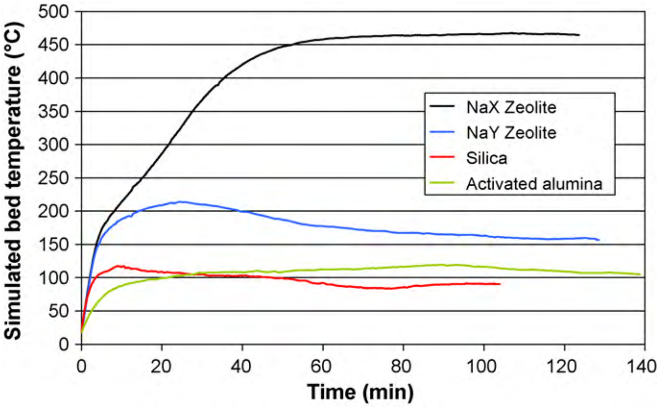

Fig. 6. Simulated temperature of the bed during dehydration under microwaves with various adsorbents.

III site) for the NaY zeolite. These existing cations in the NaX zeolite supercages are probably responsible for the higher dielectric permittivity of the NaX than of the NaY zeolite [23,24]. They can also favour ionic conductivity at elevated temperatures and provoke the heating of the solid by Joules effect.

Temperature profiles inside the solid bed have been simulated by solving the simple thermal balance described in Polaert et al. [11] and are given in Fig. 6. While high temperature is reached in the NaX zeolite bed, much lower levels are shown for the other solids, essentially due to the lower values of absorbed powers. The temperature profile conditions desorption effectiveness through the thermodynamic equilibrium reached at the surface at any time. Once desorption is completed and final thermal equilibrium is reached, the absorbed power is only used for maintaining the system temperature while balancing thermal loss.

From these comparisons, it can be concluded that water desorption in some solids can be effective (100% of dehydration for silica and 81% for NaY zeolite) and rapid without reaching very high temperature levels. Energy savings can then be achieved and solid degradation can be avoided. The cooling time of the bed is usually a limiting factor in industrial applications. An interesting compromise can be found between the dehydration effectiveness required and the maximum temperature reached in the bed. Adsorbent behaviour can be very contrasted for a given adsorbate: the adsorbent will have to be chosen considering the variation of its dry solid dielectric permittivity with temperature.

3.4. *VOC desorption on NaX zeolite*

Fig. 7a shows that desorption is fully achieved for the four tested adsorbates on NaX zeolite. On the contrary, microwave absorbed power profiles are very different (Fig. 7b). In the case of VOC desorption, initial microwave absorbed power levels are much lower than those obtained with solids saturated with water. This can be easily explained by the low values of dielectric loss factors of these adsorbates (Table 2). The microwave absorbed power strongly increases during the experiment, even showing an accelerating profile for toluene and *n*-heptane. It is advisable to think that the decreasing VOC content barely affects the dielectric loss factor of the medium regarding to the very low ε'' values for the hydrocarbons used. Of course, the increasing ε'' value of NaX zeolite over temperature is, at least partially, responsible for the increasing absorbed power.

Nevertheless, one can question this accelerating phenomenon and try to determine how it is provoked. A heterogeneous temperature distribution in the solid, even at a molecular scale [25,26] has often been described. Equilibrium molecular dynamics and simulations on non-equilibrium molecular dynamics made on bare zeolites and on loaded zeolites with methanol and/or benzene [27] confirmed that some atoms (like Na in bare zeolites), sorbent framework or adsorbate molecules can be maintained at different steady state temperatures under an electromagnetic field. This athermal effect arises because the energy dissipation into the framework is not effective enough between the host and the guest molecules to completely thermalize the absorbed energy. Nevertheless, we do not believe that such a microscopic effect can affect that much nor the dielectric losses nor the local resulting electric field in the medium. On the opposite at the bed scale, heterogeneity of temperature of a solid bed can occur [16] and interfere with the electric field by creating morphology-dependant resonances. In a previous work, Estel et al. have demonstrated that magnetic transverse modes of propagation appear in a cylindric reactor. Waves propagating thanks to these modes can in some conditions interfere constructively giving rise to strong resonance and the local standing waves are put forth. It is discussed why magnetic TM modes are dominant in cylindrical geometry and how to calculate their position $x_{p,n}$ by explicit asymptotic formulas derived from Mie scattering theory [28]. According to this theory, resonance occurs only when the size parameter ξ_M linked to the diameter of the cylindrical reactor (d, in m), and to the wavelength in the medium (λ_M in m) becomes greater than a mode position $x_{p,n}$ and as long as this mode is unique.

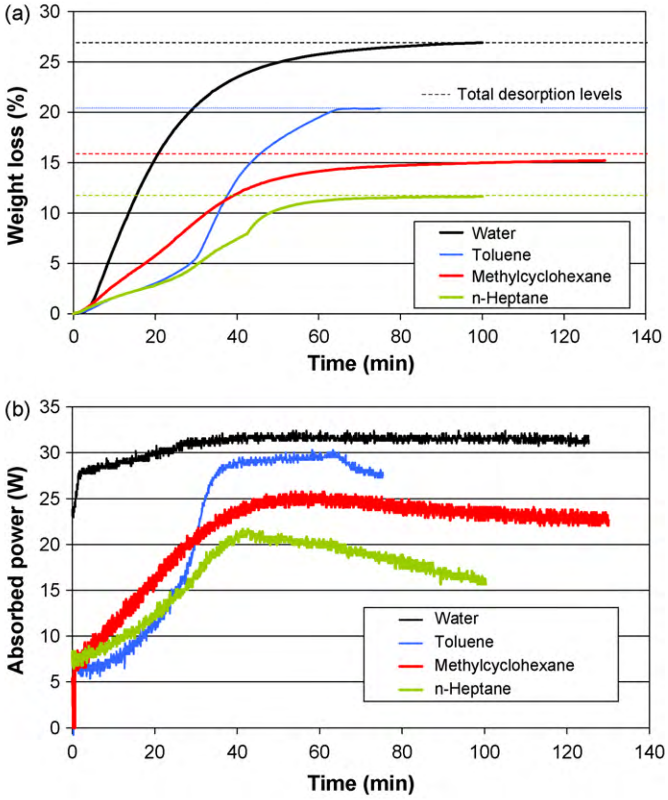

Fig. 7. Desorption of various adsorbates on NaX zeolite – P_incident = 50 W – (a) weight loss (% of dry solid weight) and (b) microwave absorbed power (P_abs) profiles.

$$\xi_\mathrm{M} = \frac{\pi d}{\lambda_\mathrm{M}} \geq x_{p,n}$$

Considering our “dry” NaX permittivities measurements, the size parameter ξ_M has been evaluated and compared to the mode positions $x_{1,1}$ and $x_{1,2}$ corresponding to the two modes $\mathrm{TM}_{1,1}$ and $\mathrm{TM}_{1,2}$ the more likely to appear. Fig. 9 shows that due to the

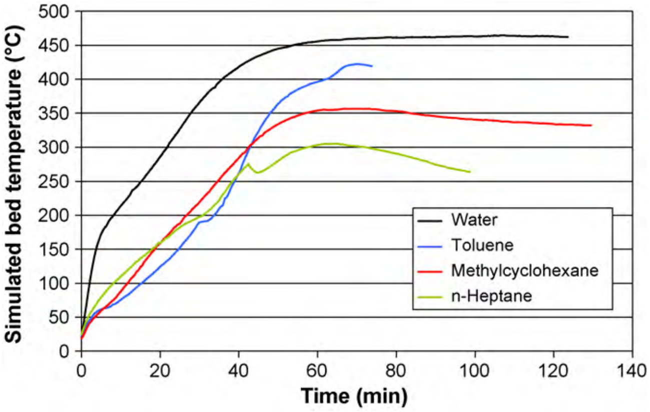

Fig. 8. Simulated bed temperature during desorption under microwaves of various adsorbates.

increasing dielectric permittivities with temperature (Fig. 2), the size parameter increases with the course of the experiment and the $TM_{1,1}$ and $TM_{1,2}$ mode positions decrease. The crossing of $x_{1,1}$ and ξ_M demonstrate that the $TM_{1,1}$ mode can become resonant in an interval of temperature estimated between 110 and 300 °C and as long as the $TM_{1,2}$ is not present in the cylinder. A finer estimation of the temperature of which the phenomenon appears, would not only require a more precise knowledge of the dielectric effective permittivities of the medium but also take into account the glass tube thickness and the reflectance at the air/glass interface. Considering our accelerating absorbed power during VOC desorption, one can think that resonance probably occurred, leading to an important heating of the solid in all VOC cases (Fig. 8). This can even lead to the partial decomposition of the adsorbates.

The behaviour of the three tested VOC is finally quite similar and also suggests that polarity and steric differences between the three hydrocarbons are of less importance compared to the variation of dielectric permittivity of the solid itself with temperature. On the contrary, different behaviours obtained between water and VOC show that the dielectric permittivity of the adsorbate plays a major role in the desorption process. It governs in particular the initial heating of the system and then, temperature and effectiveness levels reached.

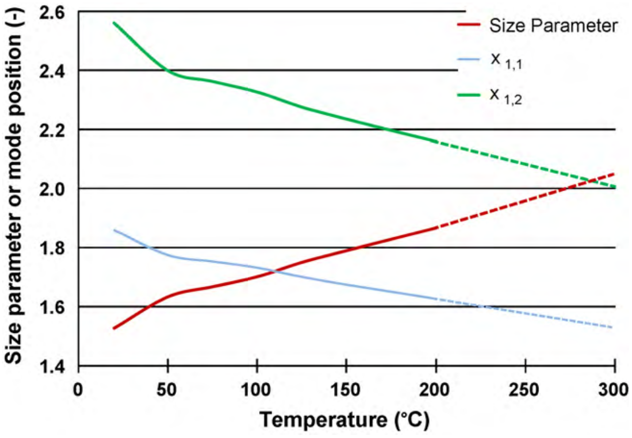

Fig. 9. Size parameter ξ_M and mode positions $x_{1,1}$ and $x_{1,2}$ of the corresponding $TM_{1,1}$ and $TM_{1,2}$ modes during the heating of a "dry" NaX zeolite (water content of 4%) from 20 to 200 °C.

4. Conclusions and recommendations

In our reactor's shape and size, desorption under microwave irradiation is mainly governed by the course of the microwave absorbed power during the process. The porous structure of the solid and the molecular structure of the adsorbates are of less importance compared to the dielectric properties variation of the medium. The adsorbate's nature and more especially its polarity is a factor of prime importance because it governs the initial level of electromagnetic energy conversion. The complex dielectric permittivity of the dry adsorbent and its temperature dependence plays a predominant role as well in the process. On these criteria, the choice of the adsorbent can be optimised for desorption effectiveness at moderate temperatures in the bed. In addition, constructive waves can appear inside the cylinder adding local standing waves obtained by morphologic-dependent resonances. The choice of an optimum reactor diameter can also be of importance. For some particular couples of adsorbent–adsorbate and reactor shapes and sizes, microwave technology appears to be a promising technology for adsorbent regeneration processes.

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