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Communication

Water Adsorption Dynamics into Active Carbon Probed by Terahertz Spectroscopy

Honglei Zhan,[1,3,‡] Shixiang Wu,[2] Rima Bao,[1,3,‡] Kun Zhao,[1,3,4,*] Lizhi Xiao,[1] Lina Ge[1] and Hongjie Shi[1]

It is vital to characterize the adsorption dynamics in oil-gas reservoirs and pollution control industry. Terahertz (THz) spectroscopy was used to study the adsorption of the water molecules into active carbons. The absorbance at selected
10 **frequencies and the first principal component scores over the whole THz range were related to the corresponding time lengths. The collective tendency expressly tracked the dynamics of water adsorbed into active carbon pores. Therefore, THz technique can be used as a promising tool to**
15 **monitor the adsorption issue in petroleum and environment fields.**

The adsorption phenomenon plays a significant role in many fields, such as oil-gas reservoirs and wastewater treatments.[1,2] Shale gases, which is an unconventional natural gas hidden in the
20 strata or mudstone layers in a free or an adsorbed state, is becoming an important force in the world market. The research regarding the oil-gas' adsorption in tight reservoir has important practical significance.[3,4] Some studies were related to the adsorption as well as absorption of organic molecules or ions
25 from water or other solutions, along with the interaction between the adsorbed substances and porous materials.[5-12] The discussion regarding the dynamic adsorption process will be a key issue and active carbon is used to adsorb water molecules in this study to simulate the adsorption dynamics in the current oil-gas reservoirs
30 and environment pollution industry. Scanning electron microscope (SEM) and atomic force microscope (AFM) are appropriate ways to describe the holes' surface and structure, but the dynamics process cannot be observed clearly by SEM and AFM. Firstly, active carbon with liquid water was not appropriate
35 during the SEM measurement because a vacuum environment is necessary when measuring and liquid water is not allowed in case it volatilizes and harms the SEM setup. Secondly, the vacuum environment will greatly affect the adsorption dynamics because of the very large water concentration gradient between sample
40 and vacuum environment. Thirdly, the vacuum, an extreme condition, is not normal in actual petroleum industry so that the experiment is not appropriate to simulate the true adsorption dynamics. Finally, the water molecules cannot be obviously observed because of its nanometer-scope size, which cannot be
45 clearly distinguished by SEM. In addition, although AFM has a very large resolution of atom, its scanning velocity is very small

and the time length is very long. AFM is also not a suitably online method to monitor the adsorption dynamics because the adsorption length is less than twenty minutes.[13]

50 Terahertz time-domain spectroscopy (THz-TDS), a technique to bridge the gap between the microwave and the infrared spectra, has been developed rapidly over the last few decades.[14-16] This method can provide rich information about the inter-molecular and the intra-molecular vibration modes and also simultaneously
55 give the amplitude and phase information. The hydrogen-bond collective network formed by water molecules changes on a picosecond (ps) time, thereby causing the THz spectrum to be sensitive to the fluctuations of the water dipole moments.[17,18] THz technique is an appropriate method for the process monitoring
60 because of the online property and the simple measurement condition when detecting, which is necessary for the rapid identification of adsorption dynamics in the actual industry. Moreover, THz provides an indirect method for the adsorption dynamics characterization depending on the absorption effect in
65 THz frequency range. In this study, the THz measurements of water drops adhering onto active carbons at various time frames have been discussed. The research focuses on the process observation that the water molecules gradually move into the active carbon. First, the absorption spectra of sample were
70 calculated over the range of 0.1 to 1.45 THz. Second, the principal component analysis (PCA) was adopted to build a relationship between the THz adsorption and the time frames. Finally, the THz absorbance at 0.5, 0.8, 1.0, 1.1, 1.2, 1.3, and 1.4 THz were extracted along with the first principal component
75 scores over the whole range, and were associated with the corresponding time frames. The results showed that THz technique identified the different stages, especially the adsorption process of the water molecules into the pores of the active carbon.

Fig. 1 shows the THz field amplitude as a function of time
80 after the transmission of the THz pulses through the sample with different time frames. The hydrogen-bond network, which is a special inter-molecular or intra-molecular inter-reaction and a type of strong molecule link, was formed with the mode of O-H⋯O in the water molecules. The ceaselessly forming and
85 breaking of hydrogen-bonds on the ps time grade, which is connected to the reorientation dynamics of the water molecules, were detected due to the sensitivity of the THz-TDS. In this research, air environment was selected in that it is the commonest condition. A relatively normal adsorption condition is better to

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simulate the adsorption phenomenon in actual petroleum and environment industry. After employing the fast Fourier transform to THz-TDS in Fig. 1, the THz frequency-domain spectra (THz-FDS) was obtained. The absorbance (A) spectra of sample was

5 then calculated by $-\log(Amp_{Sam.}/Amp_{Ref.})$, where $Amp_{Sam.}$ and $Amp_{Ref.}$ are the THz-FDS amplitudes of samples and reference (air). The samples' absorbance spectra only reflect the absorption effect of ACFC with or without water in THz range. Fig. 2 illustrates the frequency dependent absorbance as the water

10 adhered to the active carbons at various time frames over the range of 0.1 to 1.45 THz and there is no characteristic peak because liquid was used in this experiment, which is consistent with the statement of liquid water absorption in THz range in a previous report.[19] The results indicated the changes in the THz

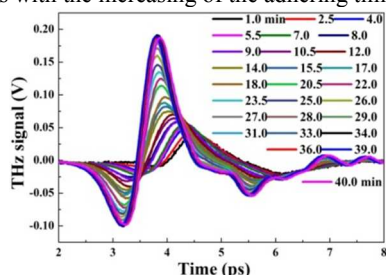15 optical constants with the increasing of the adhering time.

Fig. 1. THz-TDS of the sample with different time frames from 1.0 to 40.0 minutes.
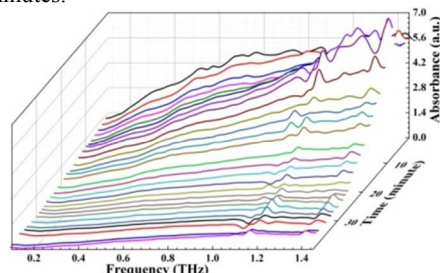

20   Fig. 2. The frequency dependence of absorbance. The x-axis, y-axis and z-axis indicate the frequency range (0.1 to 1.45 THz), the adhering time of water drop onto the active carbons, and the absorbance, respectively.

   The dependence of adsorption process on the adhering time

25 was evaluated in detail at randomly selected frequencies. The corresponding results are displayed in Fig. 3, which shows the absorbance as a function of the adhered time after the transmission of the THz pulses. The absorbance basically remained unchanged in the 0-10.5 minutes range; then decreased

30 in the 10.5-29.0 minutes range; and remained invariant in the 29.0-40 minutes range. The nonlinear dynamics on the basis of collective tendency was brought into correspondence with each other at 0.5, 0.8, 1.0, 1.1, 1.2, 1.3 and 1.4 THz, indicating a special rule wherein there existed a certain response of the water

35 molecules which adhered onto and into the active carbon in the THz range.
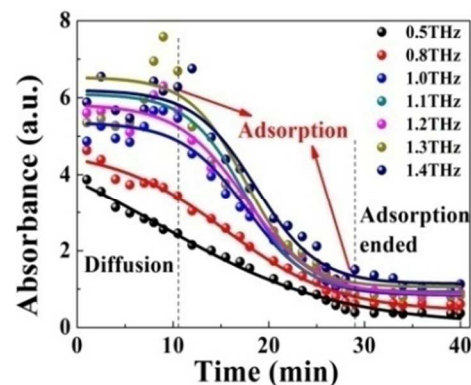

Fig. 3 The time dependence of absorbance at selected frequencies.

   The observed changes of the THz absorbance were very

40 significant during the adhering process. As mentioned above, the whole process can be divided into three stages: 1-10.5, 10.5-29.0 and 29.0-40 minutes, in accordance with the adhered time, as shown in Fig. 3. In the first stage, the water drop adhered onto the superficies of the active carbons and diffused to the surrounding

45 area according to the concentration gradient of the water molecules. This diffusion process was divided into two parts: the surface motion and the depth diffusion. The two processes were carried out simultaneously and their competing actions made the THz absorbance change only slightly. In this stage, the quantity

50 and intensity of hydrogen bonds do not change because water molecules are not adsorbed. However, during the second stage, the THz absorbance gradually decreased with the water drop's adhered time. This stage was homologous with the water molecules' adsorption process. The active carbon, which was a

55 type of material with a very large specific surface area, adsorbed the water molecules into the voids. In the adsorption stage, with the increasing molecules adsorbed into active carbon, the water molecules were scattered in different holes, especially in inner ducts, so that the intra-molecular vibration changed and the THz

60 response was weaker and weaker. Consequently, the THz absorbance spectra can achieve the tracing of the motion that water molecules were gradually adsorbed into the voids of active carbon. In the third stage, when the adsorption ends, the intra-molecular vibration remained unchanged so that the absorbance

65 values of the samples with different time frames kept unchanged in that the adsorption process ended and the water molecules were adsorbed in a stable state in the carbon's pores. To highlight the difference between the non-adsorbed and adsorbed samples, a contrast of the THz frequency-domain spectra (THz-FDS)

70 amplitude, phase, which are calculated by fast Fourier transform of THz-TDS and optical parameters including refractive index (n) and absorbance (A) of the active carbons with water drop adsorbed at 40 minute and without water was illustrated in Fig. 4. Although several peaks are found in Fig. 4 (a), they are resulted

75 from the vapor in air, which is selected as the measurement condition. The absorbance spectra in Fig. 4 (d) do not have any characteristic peaks because of the calculation of $-\log(Amp_{Sam.}/Amp_{Ref.})$ and is consistent with the spectra in Fig. 2. The significant differences existed between the samples within

80 the range of 0.1 to 1.45 THz, thereby indicating that the water molecules were adsorbed into the active carbon rather than volatilized into air.
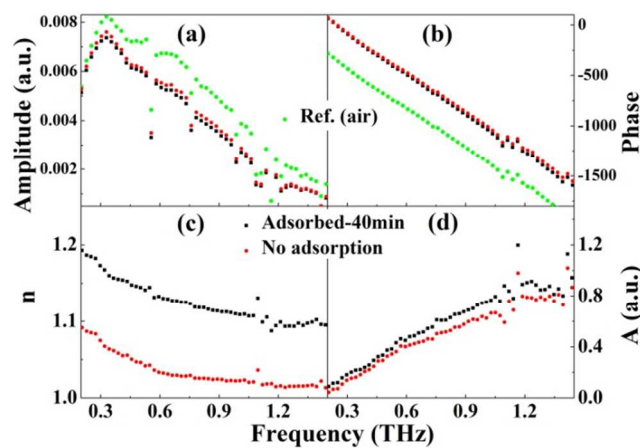
Fig. 4 THz-FDS amplitude (a), phase (b) and optical parameters including refractive index n (c) and absorbance A (d) of the active carbons with water at 40 minutes and without water drop.

5   In this study, PCR method was used, which was able to narrow multiple variables a few principal components (PCs) with dimension reduction technology, to analyze the motion process with the input of the THz absorbance spectra of the samples in the 0.1 to 1.45 THz range; however, none of the spectral
10 pretreatments were used.[20] As shown in Fig. 5, the x-axis and the y-axis indicate the first and the second PC scores, of which the contribution rates are 97.5% and 2.0%, respectively. Therefore, the first two PCs, particularly PC1, represent the majority of sample information. The sample occupies different positions in
15 the coordinate system with different adhered time. In regards to the adhered time, the sample had similar PC1 scores and different PC2 scores in 1.0-10.5 minute, different PC1 and PC2 scores in 10.5-29.0 minute, and same PC1 and PC2 scores in 29.0-40.0 minute. The adsorption process with different adhered time
20 frames reflected different PC scores; consequently it can be classified as having three stages.
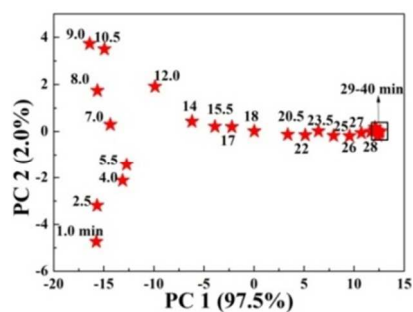

Fig. 5. PC1 versus PC2 for absorbance data over the range of 0.1-1.45 THz.
25   Since PC1 represented the most information of the original variables in the system due to its high contribution rate (97.5%), the PC1 scores were extracted and were associated with the corresponding time as shown in Fig. 6. An analogous trend was obtained and its time. of transition points was similar to that
30 shown in Fig. 3. Each time interval was evident. Thus, based on the regular curves from Figs. 3 and 6, a conclusion was drawn that the THz technique can be used as an effective and promising tool to track the adsorption process of the fluid adsorbed into the pore structure.
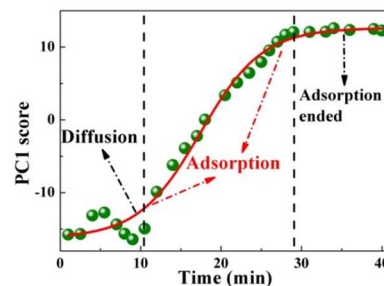

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Fig. 6 The time dependence of PC1 scores in PCA system.

    In order to test and verify the repeatability and accuracy of the above conclusion, another similar experiment was performed where three drops were used and the PCA was also used to
40 calculate the PC scores. Only the PC1 scores were extracted due to its high contribution rate (96.33%) and associated with the corresponding time frames, as shown in Fig. 7. Although the time of the transition points seemed different, the three stages were obviously distinguished and the second stage was the adsorption
45 process over the time of 11 to 42 minutes. The longer adsorption time was resulted from the increase in the quantity of the water molecules. These results showed that the adsorption process was evident and accurately expressed by the THz technique.
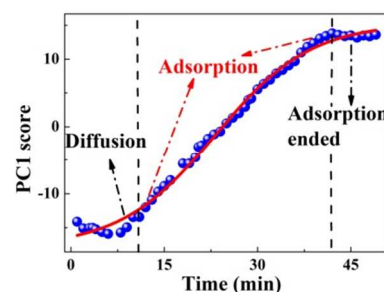

50 Fig. 7. PC1 score's dependence on the corresponding time of three-drop-water experiment.

Conclusions

In summary, the adsorption process of water into active carbon was monitored using THz-TDS. The absorbance at any frequency
55 reflected the water adsorption dynamics into active carbon and the adsorption process was then validated by PCA calculation with the absorbance over the whole THz range. Therefore, THz-TDS represents a promising technique to monitor the adsorption dynamics so that THz technique will be greatly popularized in
60 petroleum and environment industry in the future.

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Notes and references

[1] *State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China*

[5] [2] *Petroleum Exploration and Production Research Institute, China Petroleum and Chemical Corporation, Beijing 100083, China*
[3] *Beijing Key Laboratory of Optical Detection Technology for Oil and Gas, China University of Petroleum, Beijing 102249, China*
[4] *Key Laboratory of Oil and Gas Terahertz Spectroscopy and*
[10] *Photoelectric Detection, China Petroleum and Chemical Industry Federation (CPCIF), Beijing 100723, China*

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*Corresponding author: ainiphoto@163.com
‡These authors contributed equally.

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