In situ monitoring of water adsorption in active carbon using an oblique-incidence optical reflectance difference method

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H. L. Zhan,[1,2,3,a] K. Zhao,[1,2] H. B. Lü,[4] J. Zhu,[2,3] K. J. Jin,[4] G. Z. Yang,[4] and X. H. Chen[1]

[1]*State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China*
[2]*Beijing Key Laboratory of Optical Detection Technology for Oil and Gas, China University of Petroleum, Beijing 102249, China*
[3]*Department of Material Science and Engineering, China University of Petroleum, Beijing 102249, China*
[4]*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

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The adsorption of water molecules in active carbon in normal condition can be monitored *in situ* with an oblique-incidence polarization-modulated optical reflectance difference technique. The optical response cannot only characterize the time length of adsorption, but reveal the tendency of dielectric properties of active carbon during the adsorption process. Therefore, the whole adsorption can be described by the permittivity obtained by OIRD measurement. Such a technique is also effective under high ambient pressure and temperature because of the optical detection, indicating that the precise measurement carried with this technique can help in building adsorption theory system in some different conditions.
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One of the main issues remaining to be solved in unconventional petro-geology exploration is the adsorption behavior and its dynamics. Shale gas is a common unconventional natural gas hidden in the strata or mudstone layers in a free or an adsorbed state.[1] Adsorption should be physical or chemistry behavior.[2,3] Different reservoirs able to adsorb oil and gas have been studied. However, most articles are related to the adsorption and absorption of organic molecules or ions from water or solutions. In terms of petroleum resources, the adsorption dynamics is a rather more significant issue due to the migration characteristics. Active carbon is a typical adsorbate and is used to adsorb water molecules to simulate the adsorption dynamics.[4,5]

At present, the study about adsorption dynamics focuses on the detection methods and mathematical models.[6–8] Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are appropriate to describe the surface and structure of the holes; however, they can hardly observe the dynamics process and need an extreme condition. Several adsorption kinetic models have been established to understand the adsorption kinetics and the rate-limiting step.[9] Pseudo-first and second-order rate models are often used to quantify the extent of uptake in sorption kinetics. Pseudo-second-order kinetic model investigates the relationship between adsorption and diffusion. These models describe the adsorption dynamics theoretically.[10–12] Therefore, the physical parameters of adsorbates and experimental observation are relatively insufficient and possibly more useful to characterize the adsorption theory.

Permittivity is a basic physical parameter and can be used to determine the polar properties of materials. By monitoring the permittivity change of active carbon, the adsorption and its process can

[a]Author to whom correspondence should be addressed. Electronic mail: zhanhl@cup.edu.cn.

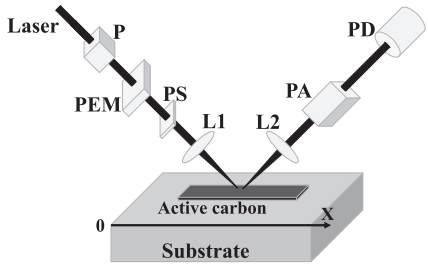


FIG. 1. Sketch of OIRD system for *in situ* monitoring of adsorption process.

be characterized. Oblique-incidence reflectivity difference (OIRD) is sensitive to the interference of subsurface electromagnetic fields. It depends on the dielectric and surface properties because this technique measures the difference in reflectivity between *s*- and *p*-polarized lights.[13–18] In this study, we applied the OIRD method to describe the adsorption information of water molecules in active carbon.

We chose active carbon for this proof-of-principle study because it is a typical porous material whose void radius approximately varied from ~100nm to ~50 μm. The active carbon pellets adhered tightly onto the fiber cloth to form the active carbon fiber cloth.[19] A single drop of water whose volume is 40μL was dropped onto the middle of the active carbon. For the oblique-incidence polarization-modulated optical reflectance difference measurement, we use the OIRD setup in Fig. 1 whose light beam and detection method were described previously by Liu and Zhan et al.[20,21] We fabricated the water adsorption into active carbon for the OIRD measurements using conventional procedure which is used for protein detection as reported previously. This measurement was carried out over the duration of the experiments at room temperature and relative humidity. In order to measure the adsorption process of water molecules in active carbon, the sample was fixed on a chamber in the two dimensional scanning stage of the OIRD system. We detected the real part $\mathrm{Re}\{\Delta_p\text{-}\Delta_s\}$ and the imaginary part $\mathrm{Im}\{\Delta_p\text{-}\Delta_s\}$ signal and took an advantage of the scanning stage with one dimensional shown in Fig. 1. Consequently, we obtained the OIRD signal data of water adsorption with different position and different time length.

Figure 2 illustrates the results obtained from above adsorption performed on the active carbon. We displayed the optical reflectance difference signals over 9 mm of adsorption with the sample at 0 min (No adsorption) and 35 min respectively. As illustrated in the plot, $\mathrm{Re}\{\Delta_p\text{-}\Delta_s\}$ signal intensity are different from sample without water to with water 35 min, even though these active carbons are fixed at the same positions. This indicates that after adsorption the active carbons had differences in optical dielectric constant and the water were adsorbed into the holes of most active carbons. As expected,

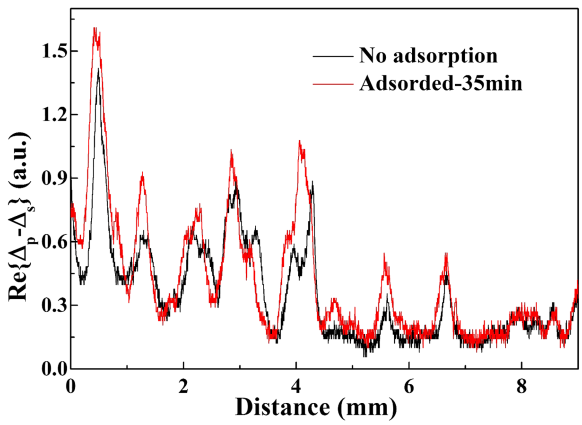


FIG. 2. The analysis of OIRD signal about whether the water is adsorbed in active carbon. The real part $\mathrm{Re}\{\Delta_p\text{-}\Delta_s\}$ signal of active carbon without and with water at 35 minute.

the Re{Δ_p-Δ_s} signal intensities of adsorbed sample are different from that without adsorption in the position range from 0.3 to 6.6 mm. The closer the point is to the middle, the larger difference the phenomenon can be found. In the range of 6.6-9.0 mm, the signal intensities of two measurements are same, representing that the water molecules were not adsorbed by active carbons at these positions which are far from the initial water location.

To further explore the kinetics of the adsorption, we have monitored the process continuously by a constant linear scanning. When the water drop was adhered onto the superficies of active carbon, the water cannot decentralize immediately because of the large tension surface and the OIRD signals have little fluctuation in Fig. 3. During the time frame of >23.7 min, the imaginary Im{Δ_p-Δ_s} signals rapidly increase and keep a high level. This stage was homologous with the adherence time of the water drop. When the adsorption ends, the samples remained unchanged, thus the OIRD signal intensities at different time frames keep unchanged, indicating that the adsorption process ended and the water molecules water adsorbed in a stable state.

According to a widely used formula, OIRD signal intensity is a function of dielectric constant ε_d and effective thickness d.[22] OIRD signal can be analyzed by

$$\begin{cases} \mathrm{Im}\{\Delta_p - \Delta_s\} \propto d \\ \mathrm{Im}\{\Delta_p - \Delta_s\} \propto \varepsilon_d - (\varepsilon_0 + \varepsilon_s) + \dfrac{\varepsilon_0 \varepsilon_s}{\varepsilon_d} \end{cases}$$

where ε_0 and ε_s represent the relative permittivity of the environment and the basement. According to the OIRD response in Fig. 3, when the time length goes to 23.7 min, the water drop adhered onto the superficies of active carbon and diffused to the holes due to the concentration gradient. This diffusion mainly refers to the depth diffusion and experiences a short time frame (0.6 min), thus the depth of water-carbon layer increases rapidly. Then the active carbon which has a very large specific surface area adsorbed the water molecules into the voids. In this stage, with the increasing molecules adsorbed into active carbon, the water molecules were scattered in different holes. The dielectric constants of carbon adsorbing water molecules augment with the time increasing. However, the OIRD signal intensities dwindle after the time exceed amplitude point 24.3 min, indicating the permittivity of carbon-water $\varepsilon_d < \sqrt{\varepsilon_0 \varepsilon_s}$. Consequently, OIRD traced the adsorption process depending on the sensitivity of OIRD to the dielectric properties of sample.

As shown in Fig. 3, the bright scales represent the adsorption dynamics of water molecules in active carbons and have the width of 350 μm. To determine whether the OIRD results are resulted by the structure and properties of the sample, scanning electron microscopy (SEM) was then employed to detect the componential and structural information of active carbon. Spray-gold pretreatment was used for the electric conduction of the sample in the SEM and EDS measurement. Secondary electron (SE) mode was used to obtain new set of images. Fig. 4 (a) shows the SEM images of active carbon

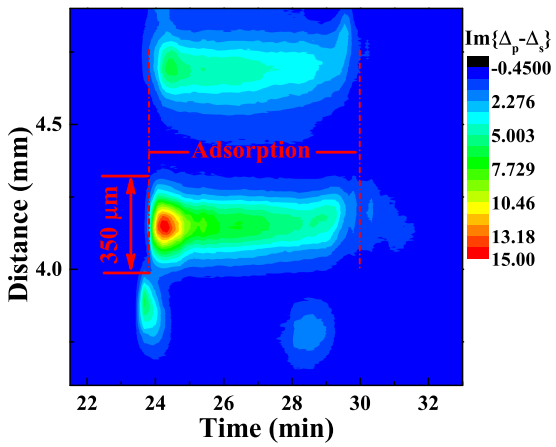
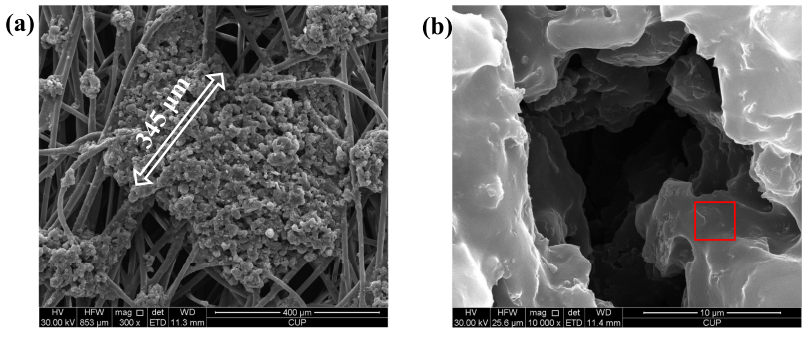


FIG. 3. The measurement results of adsorption dynamics using the OIRD. The color bar represent the Im{Δ_p-Δ_s} signal intensities of samples at different scanning positions and at different time frames.



(d)

Element	Wt%	At%
CK	77.52	91.81
OK	08.03	07.14
AuM	14.44	01.04
Matrix	Correction	ZAF

FIG. 4. SEM-EDS analysis of active carbon sample. (a-b) SE morphology contrast images of active carbon: (b) shows an enlarged view of a selected area in (a). (c-d) Elemental component of active carbon measured by EDS.

adhered on fiber. A single active carbon has a width of ~345 μm, which is close to the width of OIRD signals. Figs. 4 (b–d) illustrate the morphology of the holes and the chemical composition of the active carbon. According to the EDS spectrum, the mass fraction and atom fraction of the chemical element C are 77.52% and 91.81, while those of O are 8.03% and 7.14%. Au was introduced by the spray-gold treatment.

Active carbon is composed of graphene layers and the surface of the carbon is rather large. A hydrogen bond O-H. . . O was formed between the element of the hydroxyl group at the surface of carbon and water molecules. The participation of hydrogen bonding can promote the adsorption behavior and improve the adsorption rate.[23] Besides, the molecules with smaller size are easier to scatter into inner holes and to be adsorbed.[24,25] Due to the adsorption of water molecules, the dielectric properties of active carbon altered gradually. Consequently, OIRD, which reflects the difference between the reflectivity of *s*- and *p*-polarized light, is closely related to the sample's dielectric properties. It is a very promising and practical technology for explore the adsorption theories in the unconventional oil-gas recovery.[26]

In summary, we have monitored the adsorption processes of water into active carbon using OIRD method in a label-free and real-time manner. Based on the OIRD signal intensities, the adsorption time and scale can be obtained. The SEM-EDS analysis about active carbon also validate the OIRD results. The research demonstrated that OIRD offers an approach to monitor adsorption and its process by a non-contact and simple way.

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