INTRODUCTION

The adsorption of mixtures of methane and carbon dioxide is a problem of remarkable industrial importance. Adsorptive separation of these mixtures is a vital component of enhanced oil recovery, natural gas production, carbon dioxide capture and enhanced coalbed methane recovery techniques [1, 2]. Since computer simulation is able to provide a convenient route to molecular-level description of adsorption in porous media, adsorption of methane and carbon dioxide on activated carbons has been the subject of numerous simulation studies dealing both with the adsorption of pure components ([3–17], to give just a few examples of these studies) and CO2/CH4 mixture [18–24]. In good agreement with experimental measurements, these studies revealed the key features of CO2/CH4 mixture adsorption, such as the preferential adsorption of carbon dioxide for the majority of carbonaceous adsorbents, and the dependence of adsorption on pore width and gas pressure.

However, the properties of carbonaceous adsorbents can be significantly changed upon addition of water either through adsorption of humid mixtures or due to the wetting of the adsorbent itself, or simply due to atmospheric moisture. Prediction of gas mixture adsorption on wet carbons is severely complicated by the fact that water molecules pre-adsorbed on carbon surface can alter the affinity of the surface to different gases, changing both the capacity and selectivity of the adsorbent.

The potential effects of the presence of water cannot be easily predicted, since gas adsorption experiments do not show a uniform dependence of adsorbent properties on the content of water [25]. Experimental investigations of adsorption at ambient temperatures show that gas capacity in wet coals is lower than in dry ones, and in some cases a different shape of adsorption isotherms is observed [25, 26]. There is a certain controversy concerning the results obtained for adsorption of mixtures in the presence of moisture: evidence of preferential adsorption of both methane and carbon dioxide was found [27, 28]. At temperatures slightly above 0°C, depending on the amount of water in wet carbon samples, adsorption of gases might result both in the increase or decrease of adsorption capacity as compared to dry carbons [29–32], which in the former case is explained by formation of gas hydrates in porous media.

Computer simulation can significantly improve the understanding of molecular-level properties and provide valuable hints for the explanation of complex behavior of gases in wet adsorbents. Therefore, adsorption of gases on wet adsorbents is currently recognized as a potentially promising field for the application of computer simulation methods [33–35]. However, adsorption of pure water and water-containing mixtures proved to be a far more challenging task for computer simulation than adsorption of more common systems such as gas mixtures. The limited number of simulation studies devoted to the behavior of carbonaceous adsorbents in the presence of water can be attributed to the high computational complexity of such systems. While the simulation of water adsorption has attracted considerable attention (see [36] and references cited therein, as well as [37–44]), computational studies of gas adsorption in the presence of water are less abundant [45–52]. Some of
these studies are dealing with competitive water-gas adsorption. It was shown that for water vapor pressures lower than that corresponding to capillary condensation certain amounts of gas can be adsorbed from gas-water mixtures. However, at higher pressures the water molecules fill the porous space and displace the gas molecules from the pore. Non-polar gases can be replaced by water more easily than the polar species with stronger intermolecular interactions (e.g., methane and nitrogen leave the pore more rapidly than carbon dioxide) [45–48]. In [49] the influence of moisture on CO₂ adsorption is discussed. The authors state that stationary bound water molecules do not hinder the access of gas to the pore, but do physically block a part of the micropore volume.

A more convenient approach to modeling adsorption of gases in the presence of pre-adsorbed water was described by Billemont et al. [50], in which the moisture level in the adsorbent was fixed, but the molecules of both water and gases were considered as mobile. The results of Monte Carlo simulation indicated that the mechanisms of adsorption of pure CH₄ and CO₂ are similar to those observed for adsorption in dry carbons, though the presence of water significantly influences the amounts of adsorbed gases. The primary effect of pre-adsorbed water was the observed reduction of maximum gas capacity explained by the shrinkage of accessible pore volume. Increased affinity of the wet carbon to CO₂ was observed in simulations, but this result was not supported by the experimental data obtained in the same study, and the factors controlling the occurrence and extent of the observed phenomenon could not be established without a more detailed investigation. A similar Monte Carlo approach was used by Liu and Bhatia [51] to study the adsorption of CO₂ in carbon nanotubes. The gas adsorption capacity was shown to decrease monotonically with increasing water content, except the low-pressure region, where CO₂ adsorption was enhanced by the presence of water.

In the follow-on study Billemont et al. [52] considered the adsorption of CO₂, CH₄, water and their mixtures in a disordered porous carbon using both experimental measurements and Monte Carlo simulation. As the content of pre-adsorbed water has not been fixed in simulations, adsorbed water was displaced out of the porous space by gases, though in experiments this effect was not observed. Simulation also did not succeed in confirming the supposed formation of gas hydrates for pressures above 3 MPa. Finally, though the realistic model of the disordered carbon succeeded in improving the agreement between simulations and experiment, it could not provide detailed information on the effects of pore size and geometry on coadsorption of gases with water.

In this work we consider the adsorption of pure CO₂ and CH₄ and several mixtures of these gases at different pressures both in dry and wet model carbons. Our primary goal is to obtain a deeper insight into the role of various factors controlling adsorption in the presence of water, addressing some of the problems found in recent simulation studies of gas adsorption in wet carbonaceous materials. Firstly, Billemont et al. [50] and Liu and Bhatia [51] considered three or four different levels of water content, with the maximum amount of pre-adsorbed water being only 0.26 g/cm³. In this work we carry out molecular simulations of adsorption for the whole range of possible amounts of pre-adsorbed water, which can be as high as 0.7 g per cm³ of pore volume, providing up to 10 data points for every model carbon, depending on its pore width.

More importantly, the studies of the effects of pore size have so far been very limited, since in [50] the simulations were carried out for only one slit pore width (1.4 nm), in [51] two carbon nanotubes (1.356 and 2.034 nm) were studied, while in [52] the complexity of the model allowed the authors to address only the overall effects of pore disorder. In this work we present a systematic study of the pore-width effects by carrying out simulations for five slit-pore widths (from 0.8 to 2.0 nm). The effects of other important factors influencing adsorption in wet carbons (e.g., pressure and composition of bulk gas mixtures) will also be outlined in this study.

**SIMULATION DETAILS**

**Molecular Models**

All interactions in the simulated systems were described using the all-atom representation with site-site Lennard-Jones and Coulomb potentials. The three-site SPC/E [53] model was chosen for water; OPLS model of methane [54] and TraPPE model of carbon dioxide [55] were used. The parameters of interaction potentials and molecular geometries are given in Table 1. Test simulations were performed with other sets of models (e.g., using TIP4P/2005 for water or united-atom Lennard-Jones representation for CH₄), yielding very similar results. However, the set of molecular models described above implements a more balanced one-site-per-atom mapping scheme, and was therefore chosen for further work.

The solid carbonaceous adsorbent was modeled in the isolated slit pore approximation and was assumed to possess graphite-like layered structure with slit-shaped pores parallel to the graphene planes. Following the quasi-two-dimensional topology of the slit pore, periodic boundary conditions were applied in the directions parallel to the pore walls, and the nearest image convention was accepted. Though this approach does not account for the connectivity of porous media and the diversity in shapes and sizes of the pores, it is still widely used for simulations of adsorption. This simple and robust model is especially useful for systematic studies in which a high level of structural realism is not required. Moreover, the per-