University of South Bohemia in České Budějovice

Faculty of Science

COMPUTATIONAL STUDY OF GREENHOUSE GAS ADSORPTION ON BIOCHAR

Bachelor thesis

Ivan Khodonovych

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BACHELOR THESIS

COMPUTATIONAL STUDY OF GREENHOUSE GAS ADSORPTION ON BIOCHAR

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ANNOTATION

Thesis is focused on the adsorption mechanism of greenhouse gas such as N2O, CH4, and CO2 at the surface of biochar by classical molecular dynamics (MD) simulations. For each gas, adsorption efficiency, molecules capturing by biochar were studied at equal range of concentrations for each gas.

DECLARATION

I hereby declare that I have worked on my bachelor's thesis independently and used only the sources listed in the bibliography. I hereby declare that, in accordance with Article 47b of Act No. 111/1998 in the valid wording, I agree with the publication of my bachelor thesis, in full to be kept in the Faculty of Science archive, in electronic form in publicly accessible part of the STAG database operated by the University of South Bohemia in České Budějovice accessible through its web pages. Further, I agree to the electronic publication of the comments of my supervisor and thesis opponents and the record of the proceedings and results of the thesis defense in accordance with aforementioned Act No. 111/1998. I also agree to the comparison of the text of my thesis with the Theses.cz thesis database operated by the National Registry of University Theses and a plagiarism detection system.

České Budějovice, 2.12.2019

Ivan Khodonovych

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I wish to express my sincere gratitude to Babak Minofar, Mgr., PhD and patience during this project. I also so thankful to my parents that they could make possible to take part in this cross border program. That is great opportunity to follow my dreams and goals.

TABLE OF CONTENTS

1. INTRODUCTION

Our planet is made livable by consisting of different gases, which play an important role from creation period of Earth up until today. Nowadays, a lot of processes of nature and circulation of substances come out of control. One of the main problems of the 21st century is “greenhouse” effect, which caused by an excess of water vapour, CO_2, N_2O, CH_4 and so on. These gases get our planet warmer due to trapping of longwave radiation emanated from the Earth’s surface and reflect back, necessitating more heat, than it is necessary [1]. Meanwhile, we can see the phenomenal progress of developing “clean” sources of energy, such as Hydropower, Wind and Geothermal in the last 50 years. The best option for us today is comparing together all power of renewable energy strategies, which can actually decrease of emission of bad gases (but it cannot change the situation in the opposite positive, to reverse “greenhouse” effect). While low-temperature pyrolysis for producing biochar can decrease the amount of greenhouse in the atmosphere. This combination may change the graph of mean temperature on our planet and finally lead us to a better future [2].

Pyrolysis technology relies on thermal decomposition by heating to temperature over 400°C of biomass such as wood or even waste with low access to oxygen. Biochar is a major product of that and has remarkable environmental properties. But, during reactions yield a lots co-products: syngas, liquid bio-oils, a difference of organic compounds with hydroxyl, carboxyl, and ester groups [2].

Net withdrawing of CO_2, N_2O, and CH_4 from the air is the result of efficient sticking together pyrolysis and application of biochar to the soil. For example, due to photosynthesis, CO_2 is assimilated and producing by plants, being involved in the energy cycle of this planet while the biochar can retain gases on its surface in the soil for a long time. If new carbon dioxide is fixed by plants, the biochar burial becomes a net sink of carbon [3]. In soil, it was shown

as one of the best and keep cations of better than other kinds of substances. Comparing biochar to other carbon forms in soil or even salts, it is not ideal and with time can decompose cations and release gases such as methane or carbon dioxide, but this timescale of this reaction will take so long [3, 4]. Due to that, it will be also useful to apply biochar technology in places with high atmospheric concentration of CH_4, as gas station, factories, peat fields to prevent bad incident (forest fires, gas explosions and so on).

Preliminary results of different experimental methods indicate that biochar can not only adsorb CO_2, but that the application of biochar may decrease emissions of two even more worse greenhouse gases, nitrous oxide and methane (due to experiments, level of N_2O emission was reduced by 80%) [5]. So, biochar has impact on the natural nitrogen cycle by absorbing of nitrous oxide on his surface for further transformations. It was also discovered that adsorption of NH_3 can happen on the surface of biochar therefore it is easier for plants to uptake NH_3 for their metabolism. On the other hand, the fact of absorbing of NH_3 under industrial condition needs to be studied by adding carbon dioxide and water under pressure and temperature [6-13].

Volatilization of ammonia from agricultural systems is one of the major anthropogenic sources of atmospheric NH_3 (10–30% from fertilizers and animal excreta) [14]. We can state on low efficiency of fertilizers or even manure to stay in soil for increasing voluminosity. Based on it, applying technology of biochar in the soil may not only decrease amount, such “dangerous” Ammonia which can easily be converted to ammonium, but increases productivity on the agriculture fields. As noted before, the bad side of Ammonia is influencing on the human health and changing the transferring of terrestrial and atmospheric radiation as well. Also, atmospheric NH_3 can easily be oxidized to nitrogen oxides and placed back on earth acidified water and environment, in total to cause irreparable harm biodiversity of our planet. Comparing even to CO_2, this

gas is hundreds of times more dangerous for global planet warming and has much bigger contribution to “green-house” effect. Research showed soft option for decreasing overage of N by capturing ammonia and stimulating better use fertilizer. So, overall process is based on absorbing certain concentration of nitrogen oxides on biochar for farther transforming in ammonium, which simply increase N uptake by plants and yield [15-17].

OBJECTIVE

The objective of the present thesis is to understand the adsorption mechanism of greenhouse gas such as N_2O, CH_4 and CO_2 at the surface of biochar by classical molecular dynamics (MD) simulations. Several factors can affect the adsorption process and many interactions are involved in adsorption process thus molecular modelling will help to understand the nature of interactions in molecular level. This work is going to address several questions concerning the adsorption of greenhouse gas on surface of biochar which are not revealed theoretically such as:

How hydrophobic character of biochar molecules can influence the adsorption of greenhouse gas on the surface of biochar?

Which kind of interactions are involved in adsorption process of greenhouse gas on the surface of biochar?

How pyrolysis temperature and functional groups on the surface of biochar molecules can influence the adsorption of greenhouse gas?

2. MATERIALS AND METHODS

The main task of present thesis is to investigate different properties which can influence the adsorption of greenhouse gases on biochar in molecular level therefore classical molecular dynamics (MD) simulation method has been used. This method has been used in many scientific disciplines, particularly in material science physic, chemistry and biochemistry, where we can explore and investigate the structure and function of different biomolecules such as enzymes, proteins, DNA and RNA. Meanwhile, MD simulation has been used in much bigger scales in such as cosmology and astronomy to discover interaction between space dust particles. It can be named as a bridge between micro particles (molecules, atoms) and macro world – planets and galaxies. It helps us to predict many physical and chemical properties of many systems which are going under experimental conditions therefore to be compared with experimental findings. It is possible to predict how chemical system will be performed in this exactly case under particular physical and chemical properties, so that computational modelling can be called as virtual experiment which is based on certain level of approximation.

2.1. Introduction

Biochar is produced due to the heating of biomass (such the most important organic source of carbon) over 400 °C in a low oxygen environment. Besides solid char, there are supplementary producing gaseous syngas and many bio-oils as well.

Biochar itself is stable carbon-rich coal-like material, which is applied in the soil for higher plant productivity. The molecule of this component has neutral to alkaline pH, which is useful for acidic soils. High carbon content and specificity

of functional groups makes these molecules suitable for application in other areas, so not only in soil improvement. For example, waste management, climate change mitigation and energy production.

The structure of biochar has a direct impact of the chemical composition of primary biomass and physical conditions such as temperature and pressure. For example, at a temperature of approximately 150 °C, organic matter starts to degrade, losing chemical bounds composition complexity. At 200°C to 260°C hemicelluloses are decomposed, cellulose below 350°C, and lignin at 260°C to 500°C. [27] By controlling these factors, it is possible to yield necessary molecules with specific Nitrogen and Oxygen-containing functional groups. In addition, physical properties depend not only upon starting biomass but also upon carbonization, pyrolysis processing conditions, what makes a different degree of alteration of the original structures of the biomass, the formation of cracks in final structure due to microstructural reformation.

Biochar as object of research is produced with pyrolysis technology and has many unique characteristics, what can give us distinguished impact on final result. These molecules formed at different temperatures can contain of oxygen, hydrogen, and nitrogen containing functional groups on surface. Previous research shows reducing of Oxygen and Hydrogen functional groups by dehydration and decarboxylation at high temperature pyrolysis production; however, there can be observed increased abundance of nitrogenous groups (wave number, ~2000–2400) around 600 C degrees [24]. In general, due to hard controlling of temperature procedure, there can be identified many others groups in different proportions and formed sometimes accidentally such as amine, sulfur, ester groups (1195), alkane (2910), and cyclic alkene (1570) groups with strong peak. In case of this work, used biochar samples contain of carboxylic acid, ether, phenol, aldehyde groups with two sizes: small one with 7 benzene (Fig.1) rings in structure and larger one with 17 benzene rings (Fig. 2). That can

give us opportunity to have more proper and wide results having different kinds of functional groups each specifically attracted according to gases. So, specification of applied areas prove expectation about effectiveness of adsorption.

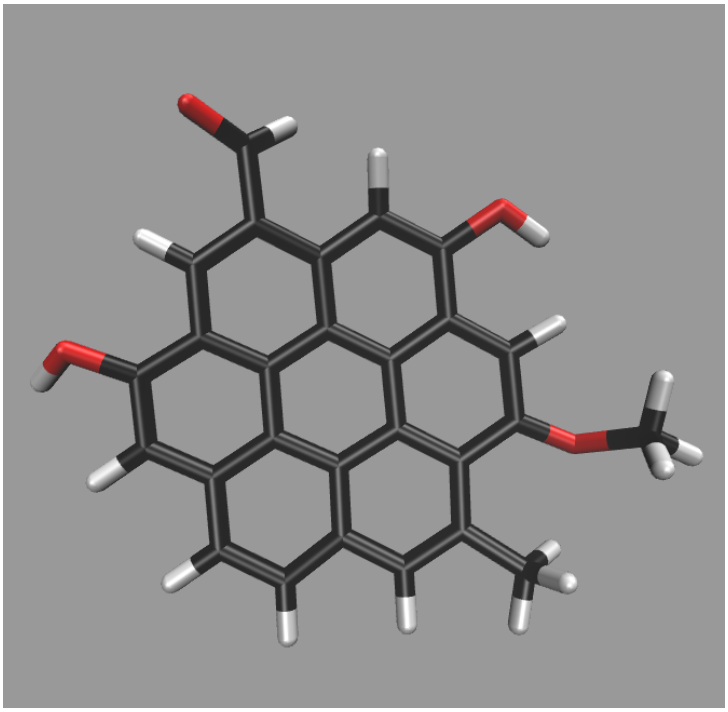

Figure 1 Structure of Biochar with 7 benzene rings.
There are ether, aldehyde and two alcohol functional groups.

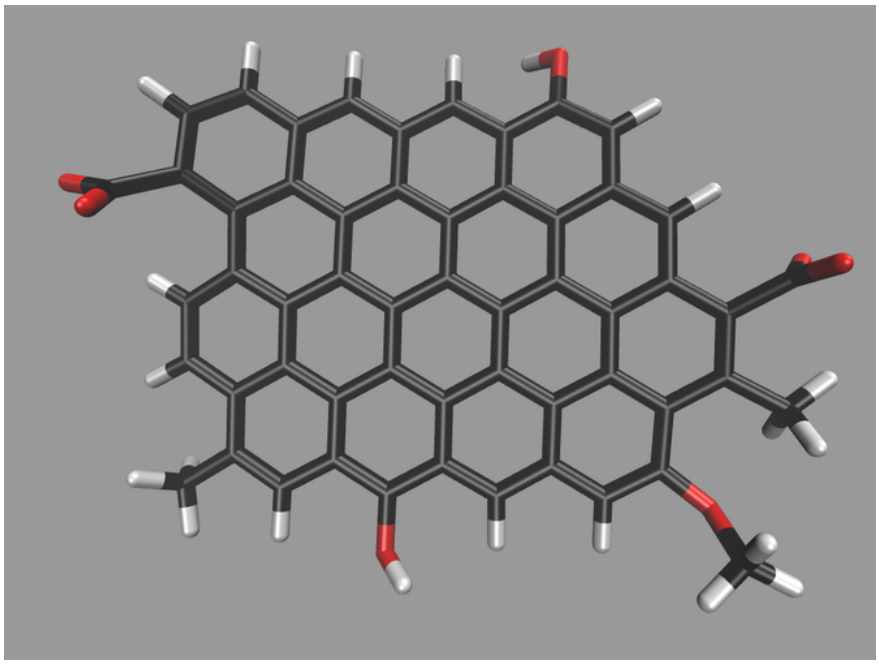

Figure 2 Structure of Biochar with 17 benzene rings.
There are two carboxyl, one methoxy and two alcohol functional groups

2.2. Molecular Mechanics

In order to calculate the energies in molecular level two main computational methods have been used which are a) quantum mechanics method and molecular mechanics method. In quantum mechanical approach the system treated quantum mechanically in which molecules are containing nuclei and electrons. In molecular mechanics the atoms of the molecules feel forces and the energy is related to these forces. Moreover, electrons are not explicitly included in calculation therefor the energy of system is calculated as a function of nuclear position.

For solving task or problems, it is necessary to understand the basic level of the chemical reciprocal actions or influence atoms, molecules on each other. Meanwhile, if using of all modern technologies of analyzing on the microscopic-level, does not possible to get full picture of the molecular-level world [18]. Even trying apply specialized nanomicroscopes to get pictures of atomic structure, on microscopic level we cannot answer questions about interactions. But, in such case MD can be used for this purpose to perform simulation on molecular scale and in in a short period of time. Because, mathematical representations that is used in MD simulations is actually represent scales of real atoms, molecules and connections between them in nature. Applying model forces between units in molecular models are gotten partially from theoretical part of classical mechanics [18].

2.3. Molecular dynamics

Molecular dynamics is based on the principles of molecular mechanics, characterized by the idea of atoms as solid spherical bodies with a van der Waals radius (which approximates the size of an atom) and a point charge at its center. Mutual interactions between atoms are represented by the linked bodies (atoms) harmonic springs (bonds).

This simulation method provides numerical data received from analyzing intra- and intermolecular forces between all units in whole system [20]. All these forces are simply rated from the mechanical model will be mentioned in the previous chapter. The force acted on the system is calculated by applying Newton's equations of motion [20].

$$F = m\frac{d\boldsymbol{v}}{dt} = m\boldsymbol{a},$$

Where **F** is a force on object; **a** – acceleration and **v** is a velocity of object, while **m** – masa of object, which is constant [21]. There are two main aspects when describing the laws of motion: dynamics and kinematics. Dynamics generalizes such concepts as, moment, force and energy of particles that are taken into account. In that case, sometimes within this framework they resort to the differential equations that the system satisfies, and to the solution of these equations. However, kinematics is simpler, because it considers only the variables associated with the position of the object and the time, which greatly simplify in conditions of steady acceleration. Multiple solving the Newton equation for a system of interacting particles can determine trajectories of units [18,19]. This represent all path of modelling in time - variance in positions and velocities of particles [20].

2.4. Periodic boundary conditions

The main part of MD simulations is to obtain information of small systems containing of particles. Using modern technologies and methods it possible to analysis around hundreds to millions of atoms. However, the representing picture is still not clear. To solve this task, we should occasionally apply such a free boundary, rigid boundaries, periodic or mixed boundary conditions.

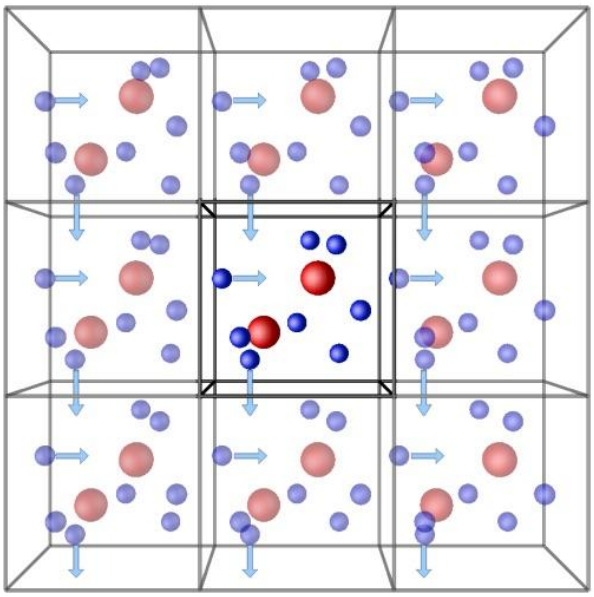

Figure 3 Representation of periodic boundary conditions [27].

Periodic boundary condition is one of the most popular kind of boundary conditions. It is appropriate to use for simulating the small part for big system. Each particle within the cell is interacting not just with alternative particles within the computational box, however with their images within the adjacent boxes as well. All Particles in the computational cell are periodically multiplied to create an infinite lattice.

2.5. Slab geometry simulations

While MD simulations are best fitted to the study of a system that may be thought-about to increase infinitely in different directions, most vital chemical

and biological processes take place at interfaces. For practical reasons, useful to apply slab geometry simulation, however the calculations of the long-range interactions between particles is one of the problems. The basic idea of this method is to put simulating system in cell with certain volume, which can be extended in different sides. In this particular case, cubic unit was used cell which such a multiple along z-axis, when x- and y-axis stay the same. As a result of such replication of the simulation box, extended slab area is up to 2 interfaces. So, it should to use unique approximation for calculations including air/water interfaces [20].

In this work, we represent process of gas-absorbing in system filled with water. When considered rate of exhaled molecules of gas on one interface, cleavage them from the cell and involving back others from opposite side, whereas keep concentration of molecules balanced (Fig. 3).

2.6 Interactions at the surface of biochar

There are two types of adsorption can occur on biochar surface with different interactions: physisorption and chemisorption. In physical adsorption, there is often observed Van der Waals, dipolar or dispersion interactions, which are not stabile and fragile by nature. There is releasing of energy during adsorption, but molecules remain in initial non-modified form which means no chemical reaction take place in physisorption while in chemisorption chemical reaction occurs. When chemical adsorption take place changing of particles and reaction proceed with emitting energy (exothermic reaction). The molecules of gas stacked to surface of Biochar by chemical bonds – covalent and so much hydrogen bonds (between oxygen functional groups and molecules of gas) (Fig. 4) Due to such interactions, distance of adsorbent accommodated on the surface is shorter in chemisorption than in physisorption. As MD simulation is based on classical mechanics therefore no chemical reaction can be studied by it therefore

the physisorption process in which non-covalent interactions are involved is the aim of this study.

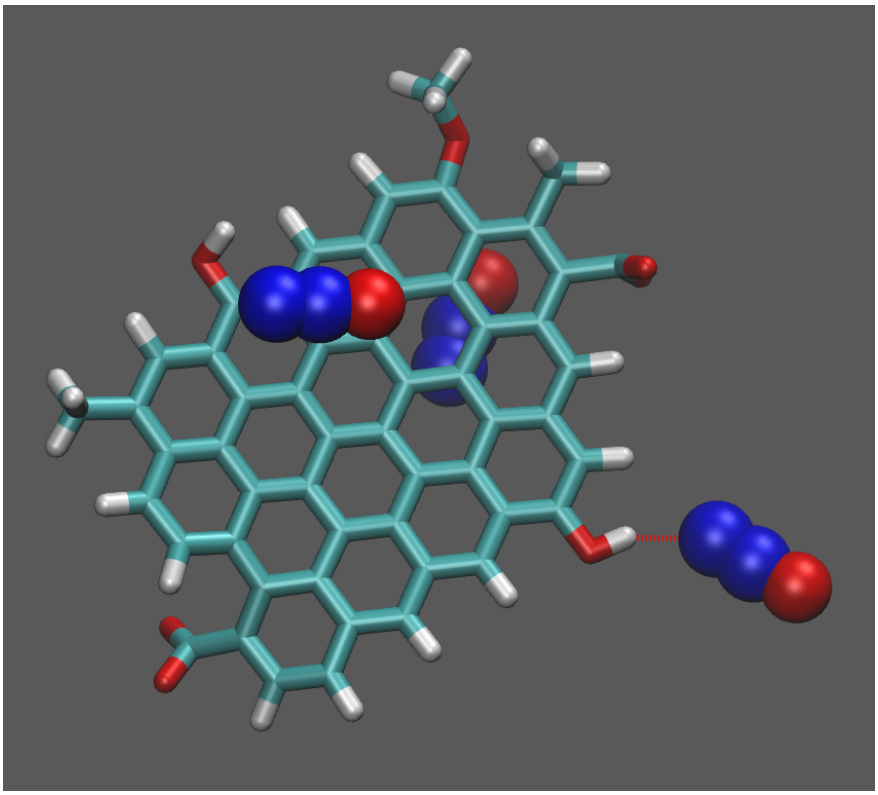

Figure 4 Formation of Hydrogen bond between N2O and Oxygen functional group of Biochar

3. METHODOLOGY

As part of my bachelor thesis, after registration at *https://metavo.metacentrum.cz* I got access to the development of data storage and computational resources. I have connected to Czech super computer facilities with the name of Metacentrum through the SSH client on Linux operating system based personal computer. Using the Linux OS command line, I prepared and collected all required files (structural files, topology files, etc.) for biochar simulations on the computer in University of South Bohemia then after preparations of systems the files for running the simulations have been sent to super computer center for performing all necessary calculations. After performing the simulations in Metacentrum the data transferred to local computer in University of South Bohemia and analysis of the data has been performed. Based on the above-described conditions of simulations, GROMACS [21] software package has been used for performing molecular dynamics simulations. For making graphs after the analysis of MD data and visualization of trajectories different Linux based program packages such as Visual Molecular Dynamics (VMD) [25] and Xmgrace [26] have been applied.

3.1. System Preparation Procedure

This chapter describes the preparation of systems consisting of combinations of two different biochar structures with addition of certain concentration of carbon dioxide, nitrous oxide and methane molecules (Fig.5). The whole process is performed based on GROMACS documentation [22]. The table below (Tab. 1 [23]) lists the most common commands for utilities used to prepare systems in the following procedure.

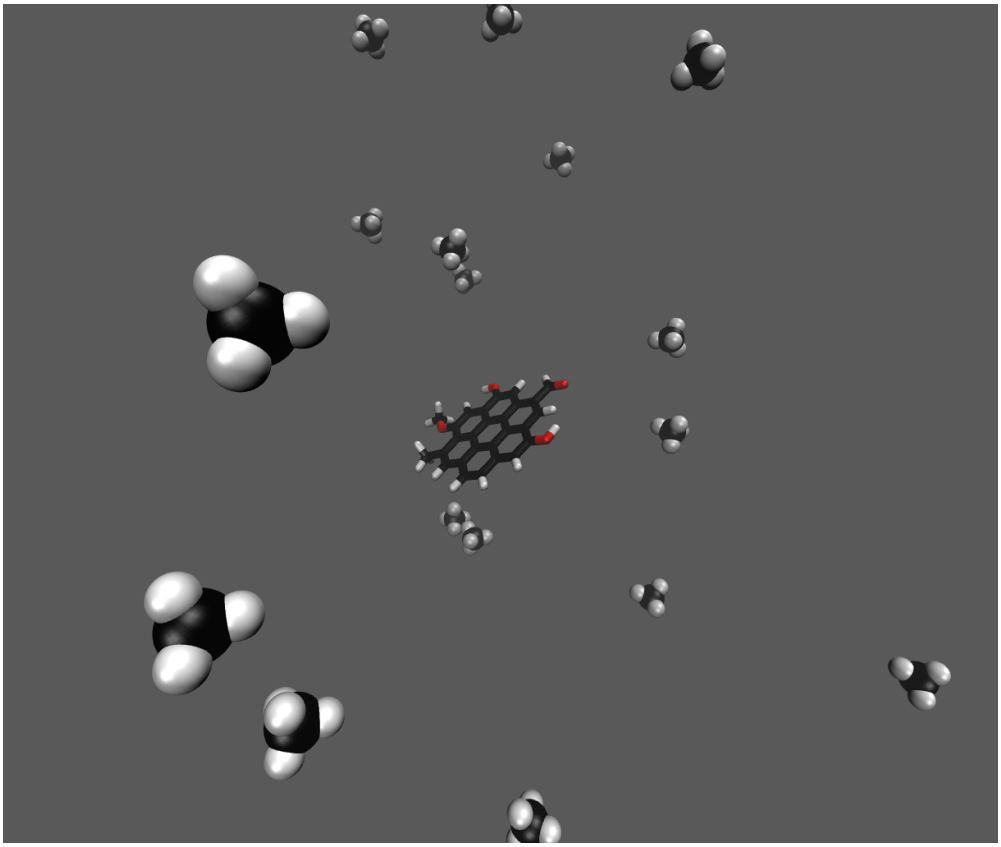

Figure 5 Biochar molecule surrounded with greenhouse gas molecules before performing of simulation

Option	Application
-f	main input file
-o	main output file
-p	topology file (.top)
-n	index file
-c	input coordinates
-s	topology file (.tpr)
-cp	input coordinates of the solute
-cs	solvent coordinate file

Tab.1 Overview of basic options and their applications

1. As we are going to study the adsorption process of greenhouse on the surface of biochar, we need to prepare systems containing biochar molecules, greenhouse gas and water. In order to put molecules in a simulation box in random manner *Packmol* program has been used. *Packmol* is used for making start point for beginning of molecular dynamics simulations which forms a box

with packed molecules based on minimum distance distribution where the molecules can be distributed such a way that short-range repulsive interactions can be neglected therefore minimization of all prepared system by *Packmol* is required [22]. By using *Packmol* 10, 20 , 30 , 40 and 50 molecules of gases randomly added to the cubic box with dimension of 5x5x5 nm and one molecule of biochar either containing 7 or 17 benzene rings, then the boxes were filled with water molecules. All used topology files of biochar and gas molecules had been prepared beforehand by supervisor.

Packmol program produces different structural files which can used by different programs such as TINKER and MOLDY and PDB format which be used in GROMACS.

```
./packmol  <  R17_CO2_50.inp
```

editconf is the function which helps to modify the dimensions of the box of contacting molecules to the size of 5x5x20 box via the -box parameter (Fig.6). All dimensions and coordinates are specified in [nm].

```
editconf_465  -f R17_CO2_50.gro  -box 5 5 20  -o  R17_CO2_50_slab
```

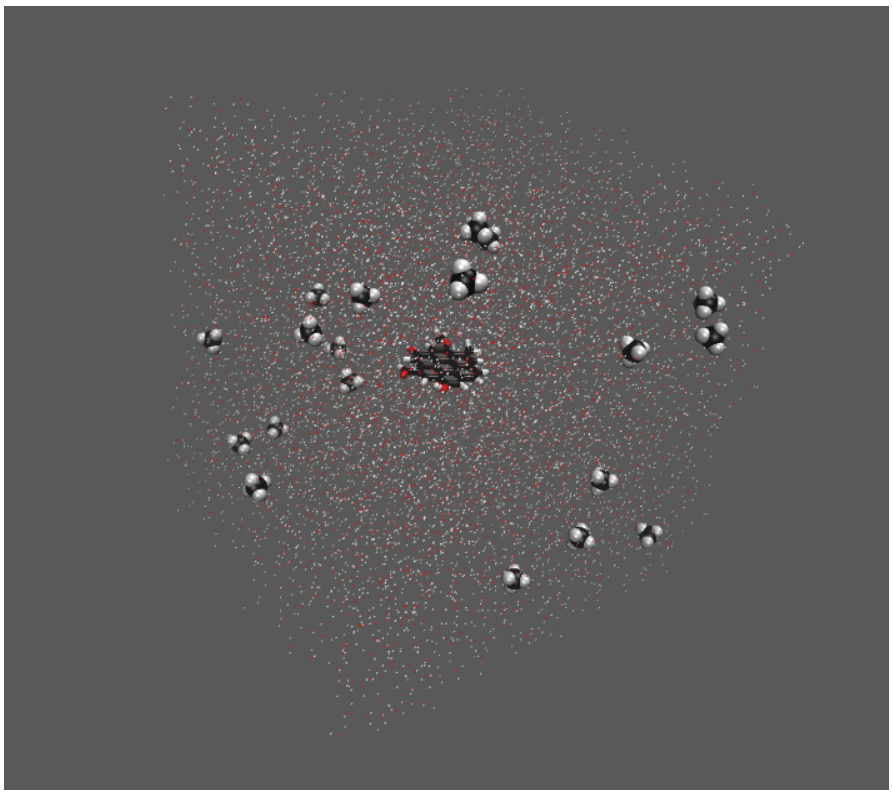

Figure 6 Box with Biochar molecule, greenhouse gas molecules dissolved in water

2. As all systems contain water molecules therefore the box of containing biochar and greenhouse gas molecules was solvated by water molecules via command genbox. In this particular stage, topology file automatically updated by inserting a row with the number of water (solvent) molecules added to the resulting system (Fig.6 and Fig.7).

```
genbox_465 -cs -cp R17_CO2_50.pdb  -p  topology.top  -o  R17_CO2_50_water
```

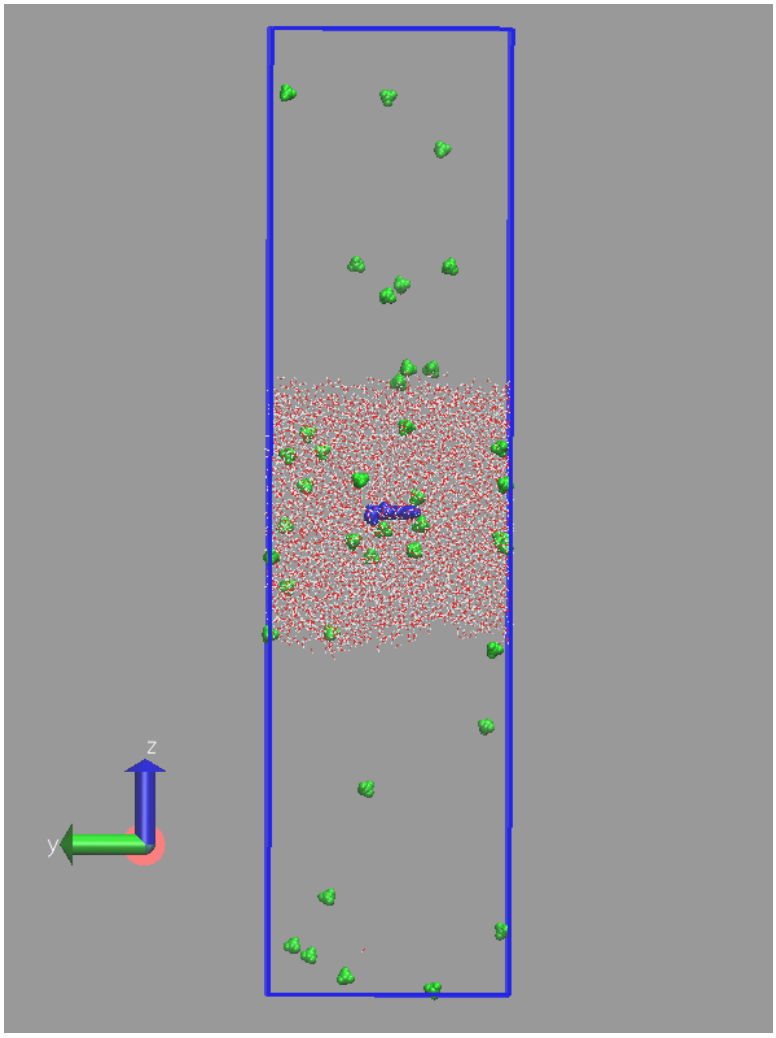

Figure 7 Slab geometry with R7 Biochar molecule in the center and Methane gas molecules (central box dissolved in water)

3. The greenhouse gas, biochar and water molecules are solvated in simulation box randomly therefor the system may not be in minimum potential energy level therefor all systems are need to be energetically minimized. Due to algorithm to change the coordinates, minimizing energy leads to stabilization of system; It is used for reducing the total potential energy by rearrangement and optimizing of geometry in the performing system. In the **.mdp* file is described settings of simulation, what use to generate **.tpr* file. For this kind of energy minimization, *steepest descent* method is applied. After preparation minimization was performed.

```
grompp_465 -f mini_pbc.mdp -c  R17_CO2_50_water.gro -p topology.top -o
R17_CO2_50_min

mdrun_465  -defffnm R17_CO2_50_min  -v
```

4. After energy minimizing the simulation has been done in NVT ensemble for equilibration of each system.

```
grompp_465 -f nvt_dposres.mdp -c R17_CO2_50_min.gro  -p topology.top -o
R17_CO2_50_nvt

mdrun_465  -deffnm R17_CO2_50_nvt  -v
```

Function ***mdrun*** produces these files:

Format .xtc

The *.xtc* file is a compressed version of the *.trr* path containing the coordinates of all atoms in time and box size data. In principle, it is similar to the *.trr* trajectory file but it does not have velocities of atoms. Due to this setting, the coordinates are written to 4 decimal places (as opposed to the default 3) and, as in the default case, the resulting water density graphs do not show undesirable inaccuracies caused by a rounding error [21, 23].

Format .trr

The content of the trajectory depends on the options in the *.mdp* file: the *nstxout* parameter specifies the coordinate write frequency, the particle velocity storage is given by the *nstvout* value and the *nstfout* value by the forces applied. Unless otherwise specified, the coordinates are written to a *.trr* file by default every 100 steps. When saving this type of file, the compression algorithm is not used as is the case with the .xtc trajectory. For this reason, compared to the *.xtc* path, it takes approximately 3 times more disk space [21, 23].

Format .edr

A binary energy file containing all energy, temperature and pressure data stored during simulation at the intervals specified in the *.mdp* file. To get specific values to analyze simulation results, you need to use the *g_energy* tool, which extracts the required data into a *.xvg* text file. This tool allows user to interactively specify all quantities that are contained in the energy file [21, 23].

Format .cpt

The extension of the*.cpt* file is a mobile checkpoint file. The proper simulation position is stored in the checkpoint file, the average information for random n umbers and NMR time. Some decomposition setup data is also stored with dom ain decomposition. [21]

Format .log

The log file gives the final energy of the system. Check to see that the energy is negative. It contains temperature, pressure, energy values, CPU time and MFLOP as build-in information as well. Optionally coordinates can be written to a compressed trajectory file (-x). [21]

5. Furthermore, it is necessary to fix the pressure in the system through NPT equilibration.

```
grompp_465 -f npt_dposres.mdp -c R17_CO2_50_nvt.gro -o R17_CO2_50_npt.tpr
-p topology.top
```

```
mdrun_465 -deffnm R17_CO2_50_npt -v
```

6. If the pressure and temperature values of the system are stabilized we perform long simulations to produce data for analysis of properties we are interested in.

```
grompp_465 -f md2.mdp -c R17_CO2_50_nvt.gro -p topology.top -o
R17_CO2_50_nvt_md
```

```
mdrun_465  -deffnm R17_CO2_50_nvt_md
```

For all longer-running calculations in slab geometry the NVT ensemble has been use and as a good practice is to use a batch file (*R17_CO2_50.sh*) with appropriately modified options instead of direct *mdrun* command in Metacentrum. To run a task, use the command:

```
qsub -q gpu R17_CO2_50.sh
```

The job batch system will queue the job and process it for shared computing resources and system load. More detailed information on batch file content and usage of PBS can be found at: *http://meta.cesnet.cz/wiki/Planner_System_PBS*.

Running gsub in the directory with simulation files (*.tpr topologies) generates the *run_md.qsub* file, which contains all the necessary data to run the task, including the newest *.tpr topology. In the appropriate directory, you need to enter the following two commands to create the batch file and run the simulation:

```
#!/bin/bash
#PBS -j oe
#PBS -l select=1:ncpus=16:ngpus=1:mem=10GB:scratch_local=900gb -l
walltime=24:00:00
#. /packages/run/modules-2.0/init/sh
module add cuda-6.0
module add gromacs-4.6.5
```

```
QTIME=24
cd    /storage/brno7-cerit/home/khodoi00    || exit 1
CPU=16
JOB=R17_CO2_50_nvt_md
export OMP_NUM_THREADS=16
mdrun -v -deffnm $JOB -cpi $JOB.cpt   -nb gpu  -maxh 24
```

When running simulations on the supercomputer, you must first copy the appropriate files from the school machine:

```
scp R17_CO2_50_nvt.tpr khodoi00@skirit.ics.muni.cz:/storage/brno7-
cerit/home/khodoi00
```

7. An important point is to create an index file that is used to define groups of atoms between which the energy contributions are counted, or to remain stationary during the calculation. Additional groups of selected atoms are defined for later analysis. The index file can be produced from *gro* or *tpr* files.

```
make_ndx_465 -f Ring17_CHO_OH2_2COO_1_CO2_50_slab_nvt_md.gro –o index.ndx
```

8. Main function of g_select is write out the result of calculations for selection. -oi option is used as function of time frame for selected residues/molecules/atoms. Use next selection command of necessarily data for analysis.

```
g_select_465 -sf select.dat  -f  R17_CO2_50.xtc -s R17_CO2_50_nvt.tpr -n
R17_CO2_50_nvt.ndx -oi index.dat  -seltype res_com -selrpos atom

awk '{print $2}' index.dat  >  selected_data.dat
```

4. RESULTS

After finishing the long run simulations, systems containing molecules of biochar with 7 Rings (Fig.1) and 17 Rings (Fig.2) with addition of methane, carbon dioxide and nitrous oxide were analyzed. Based on algorithm described in chapter 3. (Methodology part), numbers of adsorbed molecules on the surface of different biochar molecules were calculated. The data received below is for the adsorption of different gas molecules at the surface of biochar which fitted to the Langmuir adsorption isotherm in constant temperature of 300K. Number of gaseous molecules adsorbed on the biochar surface due to applied concentration were visualized using R Studio.

Figure 8 shows the difference in accommodation – polar N_2O, nonpolar CO_2 on biochar with seven benzene rings (*Ring7)*. There is higher total number of N_2O than number of CO_2 (in all concentrations) and area on the sides is more attractive for N_2O, while opposite situation is for CO_2, where central part is significantly more preferable both either for *Ring7* (Fig. 8) or *Ring17* (Fig. 9).

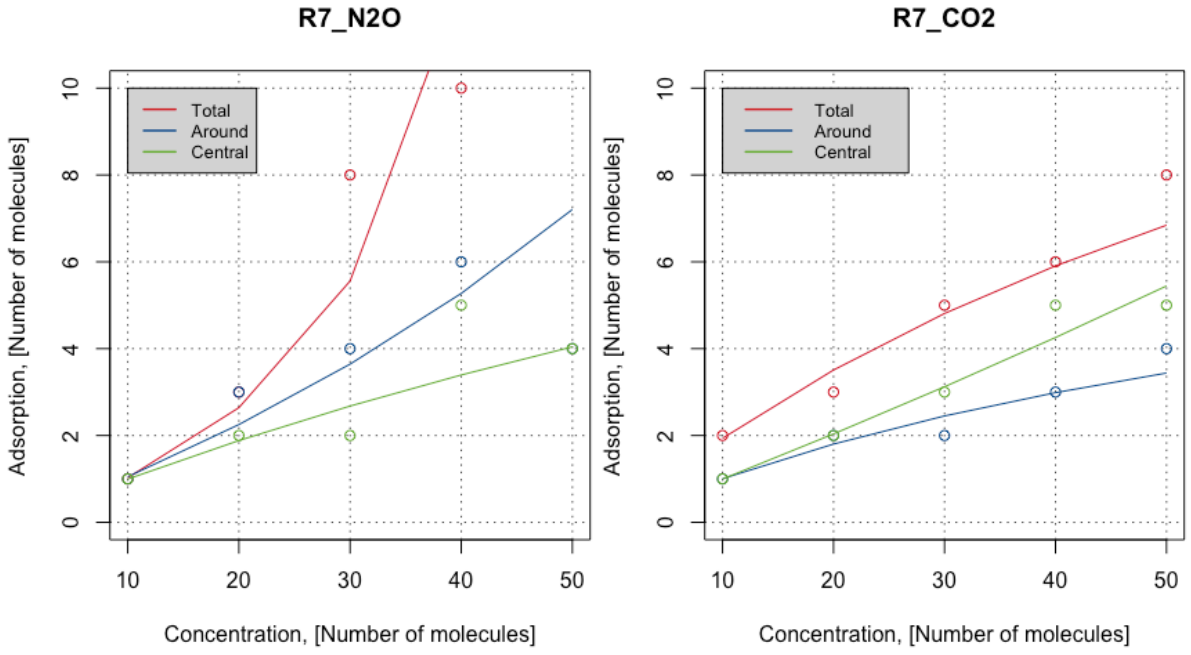

Figure 8 The Langmuir isotherm for adsorption Nitrous oxide and Carbon dioxide on Biochar Ring7

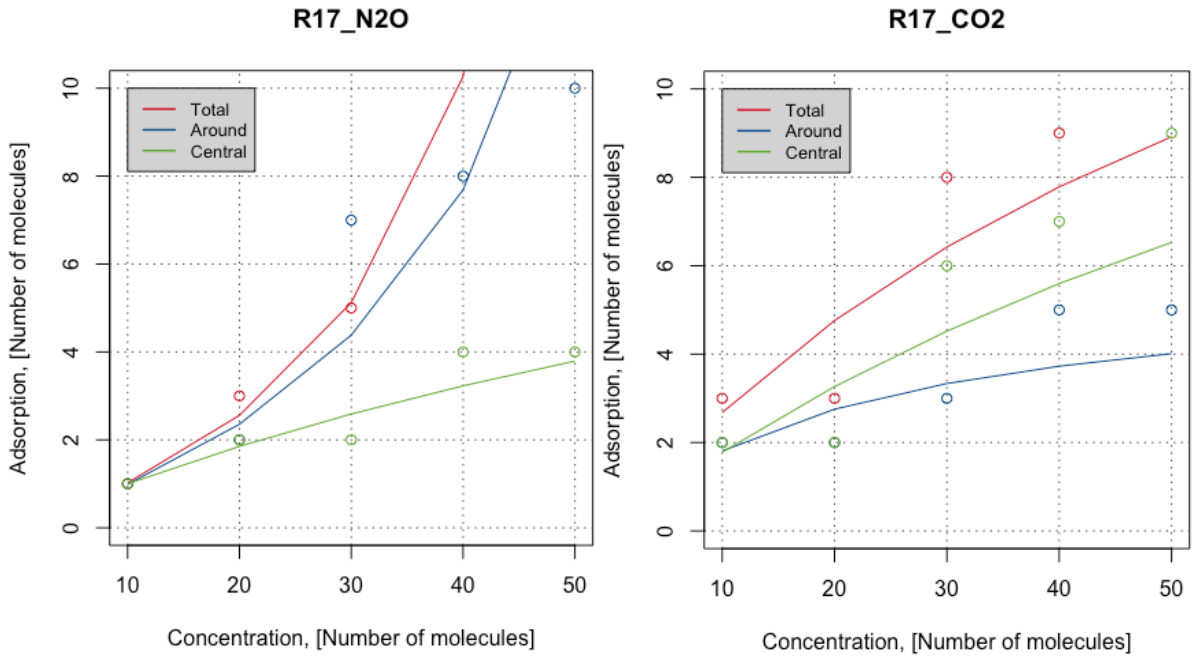

Figure 9 The Langmuir isotherm for adsorption Nitrous oxide and Carbon dioxide on Biochar R17

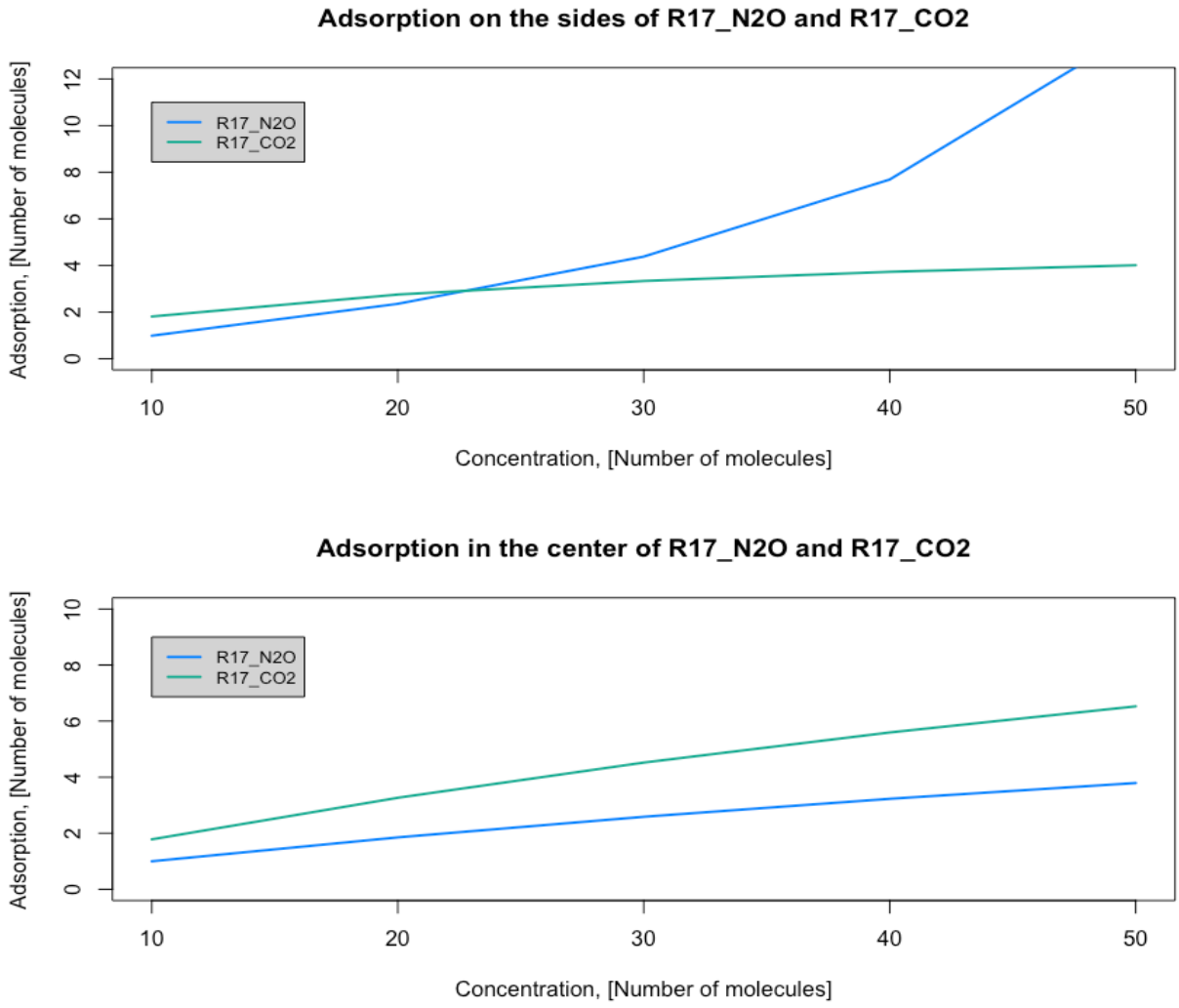

Figure 10 The Langmuir isotherm for adsorption Nitrous oxide and Carbon dioxide on the sides and in the center

Adsorption of two different gasses in case of bigger surface of biochar (Ring7 compared to Ring17) (Fig.10) is bigger and shows in average 7,5% higher adsorption capacity.

The above results demonstrate how strong is the evidence of the attraction of polar molecules of N_2O to the sides of biochar molecules as it is shown in Fig. 6 then to hydrophobic central part of biochar molecules. In the second part of figure 9, CO_2 shows parallel increasing of amount accommodated (stacked) particles with raising concentration. Comparing data of the plot above, possible to predict preferred behavior of nonpolar molecules such as methane at the center of biochar and repulsion from the edges of biochar molecules.

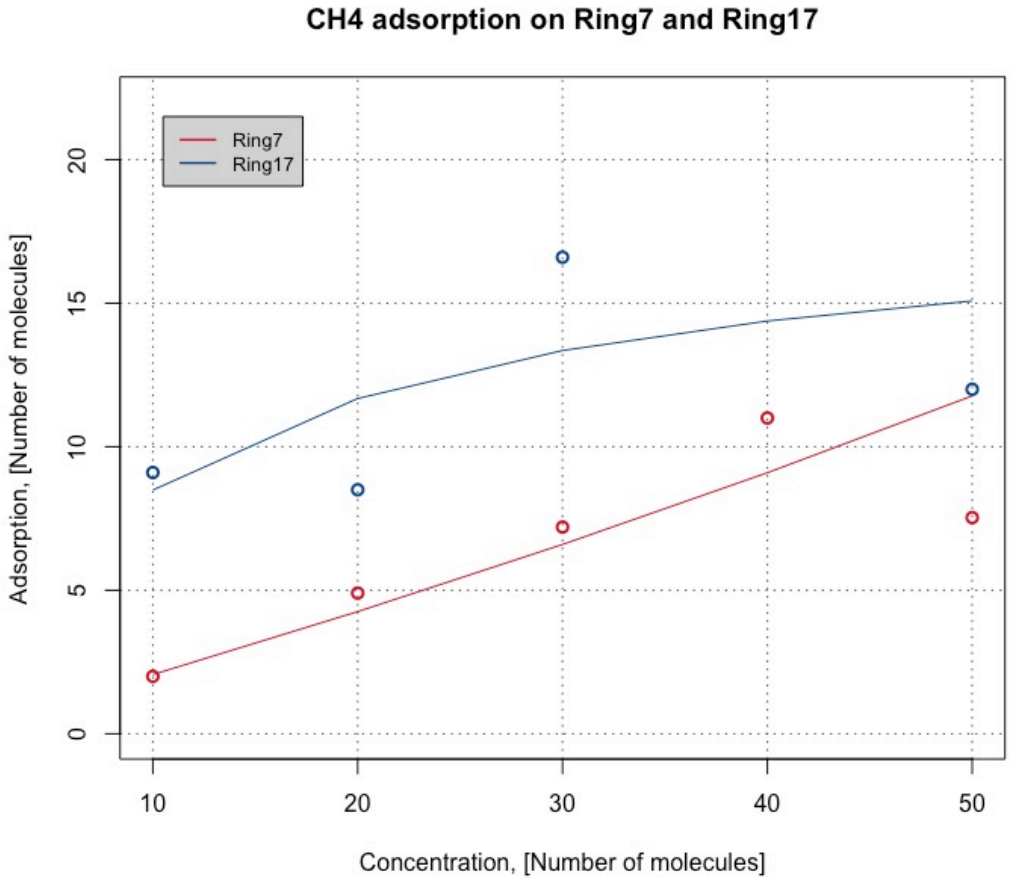

Figure 11 The Langmuir isotherm for adsorption Methane on Biochar distinguished sizes

Figure 11 shows more intensive adsorption of methane molecules at the surface of larger biochar with 17 benzene rings (Ring17) than biochar with 7 benzene rings (Ring7). There is an expected parallel increasing both lines what

indicates similar methane gas stacking on the sides and in the central part of both molecules Ring7 and Ring17 of biochar.

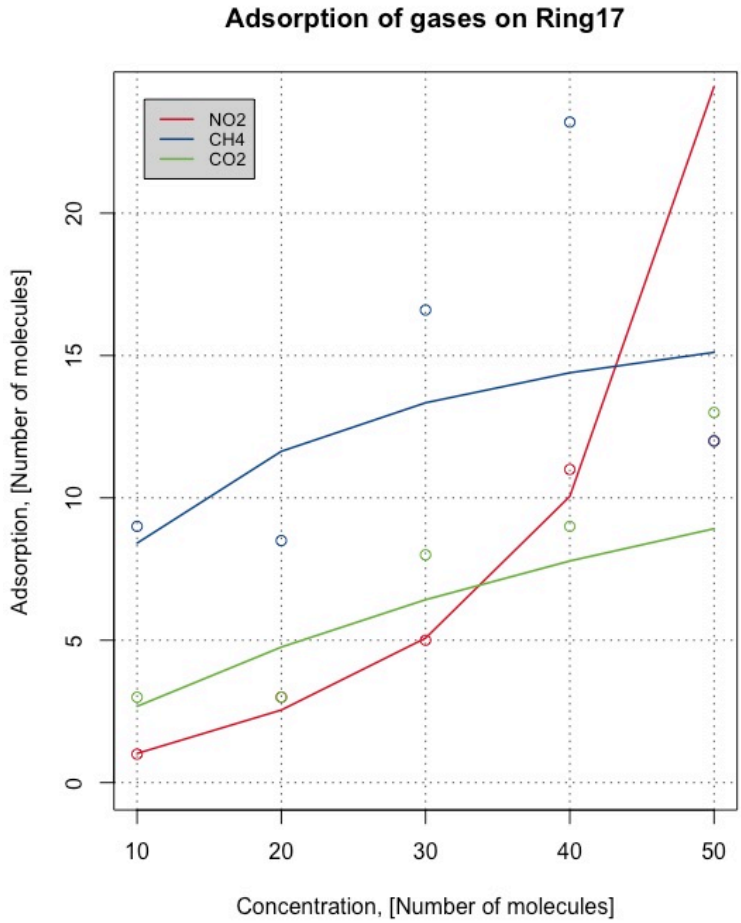

Figure 12 The Langmuir isotherm for adsorption NO2, CH4 and CO2 on Biochar of given form (Ring17)

Results above show similar behavior of methane and carbon dioxide molecules (blue and green lines) in comparison to polar nitrous oxide (Fig.12). The last one increases enormously which means higher attractions and effective adsorption together with increasing of concentration of gases. Under similar conditions (concentrations, size of biochar molecule) methane gas has been approximately 65,7% higher adsorbed at the surface of biochar of Ring17 than carbon dioxide. Adsorption capability of Carbon dioxide is 2,2 times lower than Methane.

DISCUSSION

Biochar such as helpful addition to the soil, looks so attractive for using on a daily basis in agriculture industry. First of all, it is ecological friendly - made from waste urban/agricultural biomass with low energy input during production and will take place in improving soil quality with increasing N uptake efficiency by plants [24]. It is cheap “green-house” gases absorbent, although this scientific field of study is still unclear, but progressively developed in last years.

Studies have shown the importance of specific surface properties of biochar such as porosity which makes it to have excellent ability to capture ions, polar molecules such N2O gas non-polar gases e.g. CH4, CO2. So that it can be concluded that the non-polar gases such as CH4, CO2 can be adsorbed at the surface of biochar by physical adsorption or physisorption [24] while N2O molecule can be adsorbed at the surface of biochar both chemically and physically but in this study due to the nature of MD simulations just physical adsorption taken into account. When adsorbent attached to surface with comparable weak intermolecular forces specifically Van der Waals forces or other non-covalent interactions such as hydrogen bonding. Accordingly to occupation of side-area (negatively charged by oxygen) by polar molecules of water that forms such a cloud of these particular, what work as block and repulsive to the not polar residue; this idea lead to the preferable interactions to carbon atoms (benzene rings) oriented close to the central part of the molecule, so not to the side part.

Although, from the result of simulations with carbon dioxide we can see no significant distinguish in adsorbing on Biochar consist of 7 benzene rings or bigger one with 17 [See Chapter 2.1.]. How it was mentioned above about water cloud around negative molecules, increasing dimensions has no effect so much in case of CO2; what we have no right to say about polar N2O. The last one has dipole moment with polar type of molecule, as the result, form comparable strong

hydrogen bonds be made of O–H···N interactions between carboxylic acid functional group and nitrous oxide; however, we can observe also weak C–H···N hydrogen bonds in the scientific literature. Meanwhile, with extension surface increase proportional number of functional groups around, thus plays important role in capturing of particulars [24].

Studies showed that high temperature pyrolysis produce biochar with larger surface area, but can cause dehydration and decarboxylation of the oxygen and hydrogen containing groups. However, can occur elevation of polar nitrogen containing groups with increasing temperature, which slightly increase curve of the CO2 gas adsorption. Also, addition to surface area and particular interactions of molecules with functional groups of biochar can lead to controlling of adsorption capacity [24].

Findings from previous research works [24] showed that the ability to increase adsorbing effectiveness is due to the extension of surface which we expected from our simulations as well. But biochar with 17 benzene rings molecules “Ring17” had slightly lower curve, so being larger than the “Ring7”. As a consequence, in addition to surface area the presence and type of functional groups is important in regulating the absorption of particles at the surface of biochar. From the analysis, we can see abundance of polar, carboxylic acid groups on the sides of surface help adsorption of different molecules such as CO_2 and CH4 to be adsorbed to the edges of the biochar molecules [20].

With the knowledge that biochar can be applied directly in the soil, shows ability to capture carbon dioxide, methane as the most oppressive pollutants, so that it can be helpful for reducing global warming.

CONCLUSIONS

1. Our computer simulations data of adsorption of gases at the surface of two different size biochar molecules indicated difference between increasing the surface area of biochar and number of particles be adsorbed on the surface can have opposite trend. Other factor which has influence on absorption of gases at the surface of biochar is related to presence of different functional groups situated on sites of biochar. Functional groups such as carboxyl, alcohol, ether, aldehyde group at the surface of biochar for smaller biochar molecule with seven benzene rings (Ring7) (Fig.1) shows larger effective adsorption for gases per unit of area than Ring17 with 17 benzene rings (Fig.2)

2. Significant higher attraction of polar gas molecules of NO2 to the sides of biochar surface due to chemical reactions and physisorption (Van der Waals forces, dispersion and hydrogen bonds). So, clustering of water around the sides (around hydrophilic functional groups, for example carboxyl group) protects against stacking of polar Nitrous oxide particles to functional groups.

3. It was observed difference in absorption of molecules to the surface depending on kind of interactions. CO2 is non-polar molecule, controls by physisorption, what is consisted actually of weak interactions and mostly intermolecular forces between central part of surface. On other hand, N2O as strong polar residue interact mostly with oxygen functional groups or is forming hydrogen bounds.

4. Methane has approximately 40% higher adsorption than carbon dioxide, while two non-polar molecules of CO2 and CH4 have the different number of adsorbed molecules under similar concentrations and size of biochar plate.

5. Approximately 27% higher number of adsorbed polar and non-polar gas particles on larger surface of biochar - Ring17 with 17 benzene rings than smaller Ring7 with 7 benzene rings.

6. High temperature pyrolysis tends to increasing number of nitrogen contains functional groups which are beneficial for capturing ability nonpolar gases such as CO2 or CH4.

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