A THEORETICAL APPROACH TOWARDS THE DESCRIPTION OF PHENOL REMOVAL BY NOVEL ACTIVATED CARBONS

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Aim

The adsorption of phenol for the removal of this toxic compound has been investigated in many experimental studies whereas the simulation studies are scarce, especially comparisons with experimental data.

This work aims to give deeper insight into the adsorption of phenol using GCMC and MD simulation. Carbon black is used as a reference material and comparison with experimental data for the carbon black and activated carbon data was done.

Models

Models for the carbon materials

Carbon black was modelled as a large slit pore of 75 Å (Fig. 1a). The influence of surface irregularities has been investigated by removing up to 30 % of the carbon atoms in the inner layers in patches with a radius of twice the C-C bond length (Fig. 1 b,c). Activated carbon was modelled by a pore size distribution of slit pores.

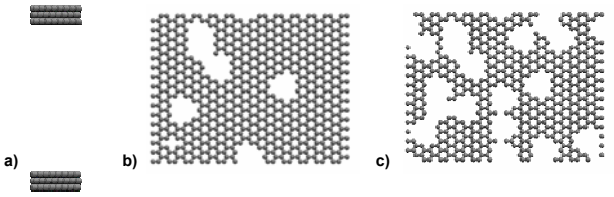

Fig. 1: a) slit pore model, b) 10 % of carbon atoms removed, c) 30 % removed

Nitrogen adsorption

Carbon black

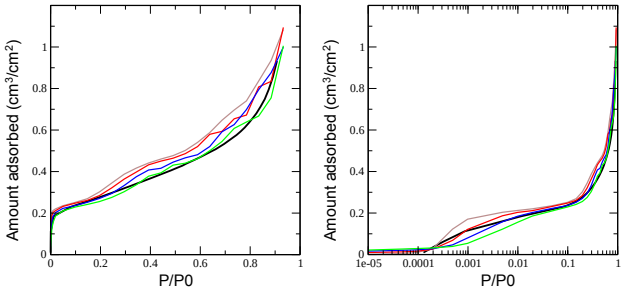

Fig. 2: Influence of surface heterogeneity on the adsorption of nitrogen for models of carbon black. Black: experimental data [1], grey: unmodified model, red: 10 % removed, blue: 20 % removed, green: 30 % removed.

Activated carbon

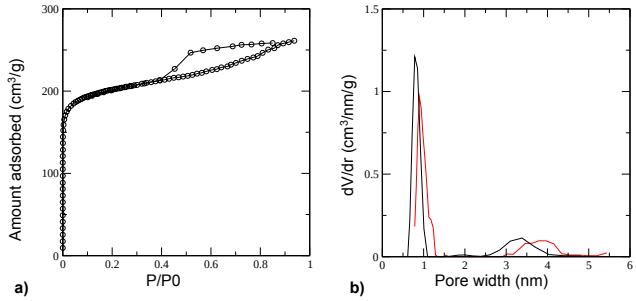

**Fig. 3: a) Experimental nitrogen isotherm [2];
b) resulting pore size distributions. Red line: NLDFT, black line: QSDFT.**

Phenol adsorption

Without water

Grand canonical Monte Carlo simulations

Grand canonical Monte Carlo (GCMC) simulations with the MUSIC simulation code were used to study the adsorption of phenol without the solvent effect. Therefore, phenol adsorption of the corresponding gas phase was investigated (without water). The potential parameters were taken from the OPLS-UA force field. For carbon black, the model with 10 % of surface atoms removed was chosen. For activated carbon, slit pore models with the pore size distributions shown in Fig. 3 b were used.

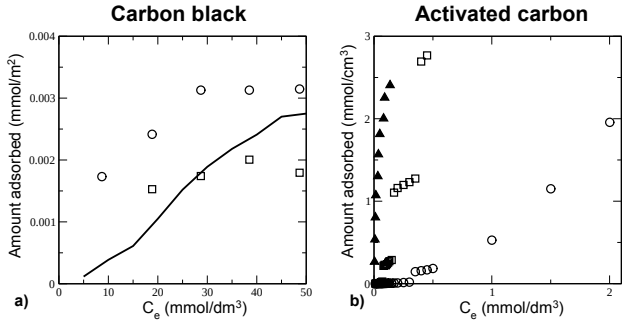

**Fig. 4: Phenol adsorption. a) ○: sample N339, □: sample N375 [1], line: sim 10 %
b) ▲: sample C738 [2], □: sim (QSDFT), ○: sim (NLDFT)**

With water

Molecular dynamics simulations

For the molecular dynamics simulations, the GROMACS simulation code was used. The potential parameters for phenol were taken from the OPLS force field, and the TIP4P model was taken to model water. As for the GCMC simulations, the unmodified model was chosen. The phenol concentration ranged from 45 to 55 molecules per unit cell, which were all adsorbed on the surface. Simulations were run for 27,000 ps and the analysis was done for the last 4,000 ps. For comparison, one simulation without water was run with 55 molecules.

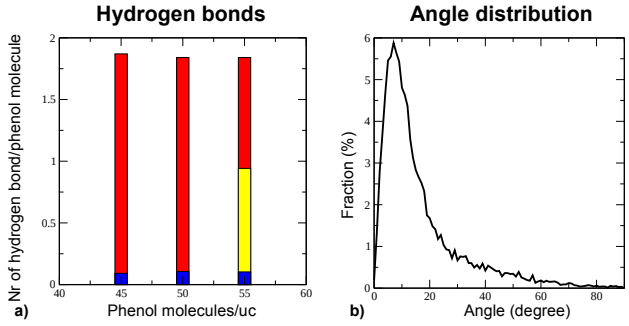

Fig. 5: a) hydrogen bonds. blue: phenol-phenol; red: phenol water; yellow: phenol-phenol (no water present) b) angle distribution between phenol and the carbon surface

Summary

The nitrogen adsorption isotherms (Figure 2b) show that the model with 10 % of the surface atoms removed give good results at low loading. Also, the GCMC simulation of phenol (Figure 4a) shows a very good fit. With the QSDFT method, a better agreement was obtained for the phenol adsorption on activated carbon than with NLDFT.

The MD simulations give further insight into the orientation of the adsorbed molecules. The hydrogen bonds between phenol atoms are reduced in the presence of water where the water-phenol hydrogen bonds are dominant. The angle between the phenol molecules and the carbon surface in solution is very low (phenol nearly flat on the carbon) with a maximum at 7 degree.

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References:

[1] Carrott *et al.* (2008), *Ads. Science and Techn.*, 26, 827
[2] Nabais *et al.* (2009), *Journal of hazardous materials*, 167, 904