Moisture Sorption on Bohemian Brown Coal Humic Acids

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In this work a Dynamic Vapour Sorption (DVS) system was used to study the water sorption by HA of Bohemian brown coal origin to follow the possible complexation of water by HA.

Introduction

The water sorption properties of Humic Acids (HA) were recently studied for commercial samples [1,2,3]. The effect of humidity modulations were also studied. These results will be discussed in regard to previous work [1].

Method

Czech originated HA were obtained from VUAnCh, Usti nad Labem, Czech Republic and have been characterised elsewhere [4,5]: 193 MAR, oxyhumolite (young brown coal) origin from Bilina (Czech Republic); 316 MAR, peat soil origin from Vrsany (Czech Republic); 317 MAR, oxyhumolite origin from Vrsany (Czech Republic) and 346 MAR, tschernozem origin from Chotesov (Czech Republic).

Results

Figure 1 shows gravimetric data for HA at 25°C. The sample was a fine powder and equilibrated at 0%RH for five minutes before the experiment was started. Samples were initially dried under a continuous flow of dry air (< 0.1% RH) to establish the dry weight. The instrument was run in dm/dt mode to decide when equilibrium was reached, with a dm/dt set at 0.002% min⁻¹. When

the percentage change in mass falls consistently below this threshold, the DVS software automatically moves on to the next programmed humidity. The humidity range chosen for these experiments was 0-95% RH in steps of 20% RH, except for the last one which was 15% RH. The isotherm data are plotted in Figure 2 for both sorption and desorption cycles. All sample weights were between 20 and 25 mg.
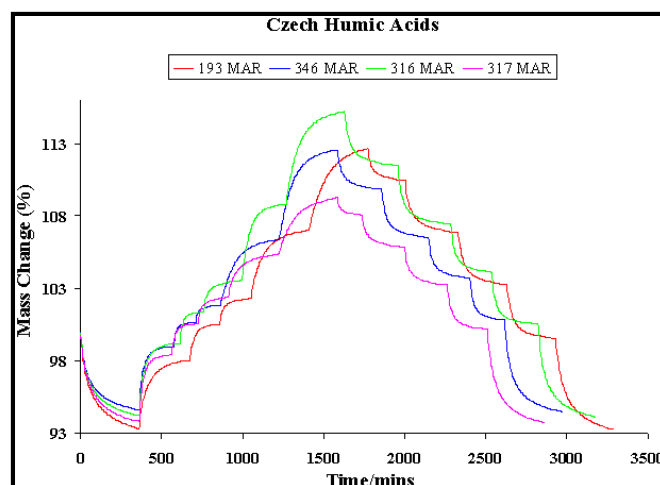

Figure 1. Effect of relative humidity on Czech HA.

The data in Figure 1 shows a sloping 7.6% mass decrease for 193 MAR, 6.9% for 317 MAR, 6.5% for 316 MAR and 6% for 346 MAR during the first

0% RH step. These results show that the initial moisture content is following the order oxyhumolite (193 MAR and 317 MAR) > peat > tschernozem for studied HA. Then for the three next steps at 20, 40 and 60% RH, all samples follow simple adsorption kinetics and each step tends to equilibrium sorption. The last two steps at 80 and 95% RH do not completely tend towards equilibrium, showing a constant slight increase of the mass with time. The highest increase was observed for peat soil HA (316 MAR). The desorption behaviour shows products which remain stable and reach equilibrium rapidly. The cumulative sorption at the end of the 95% RH step is 25.1% moisture content for 316 MAR, 22.8% for 193 MAR, 21.4% for 346 MAR and 18.4% for 317 MAR. For Czech humic acids the cumulative water uptake is in the range of 18 to 25% moisture content at 95%RH. Peat soil HA (316 MAR) has a better ability to adsorb moisture than oxyhumolite HA (193 MAR).
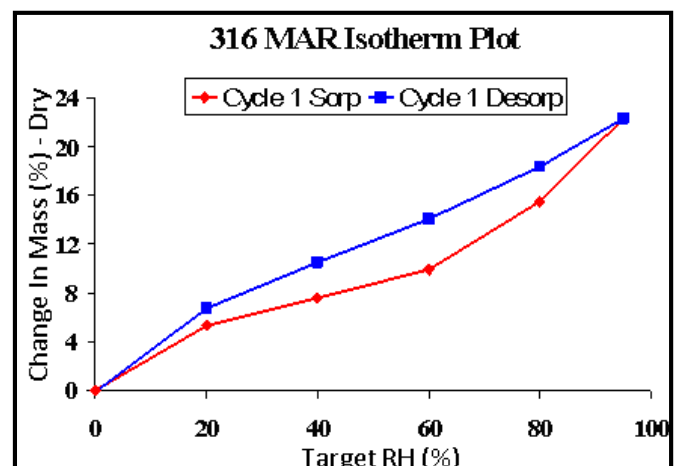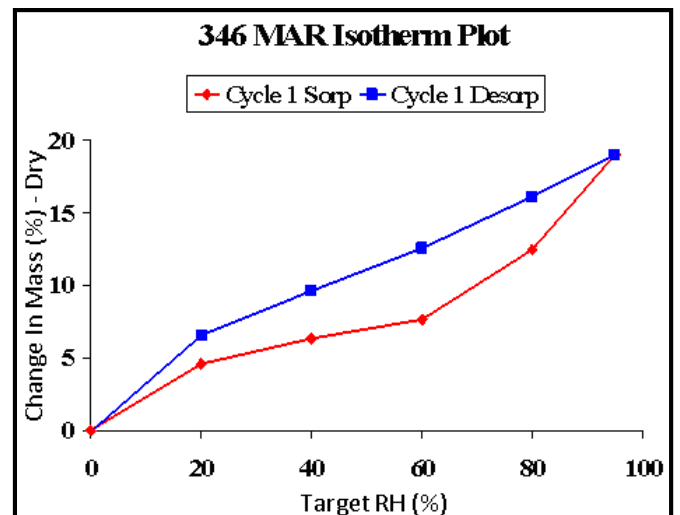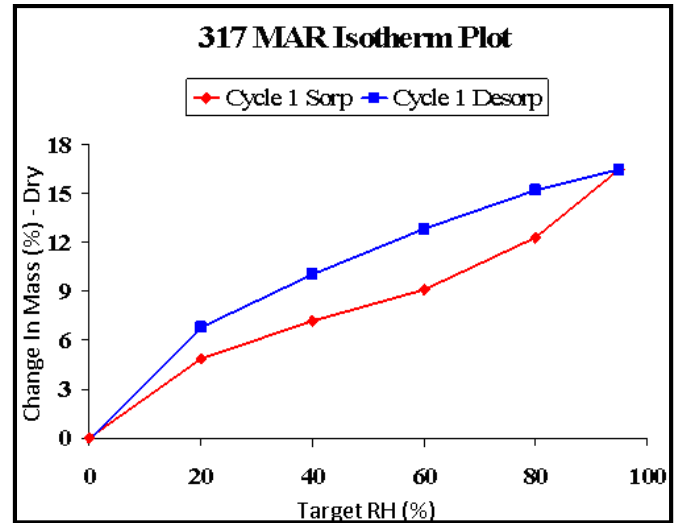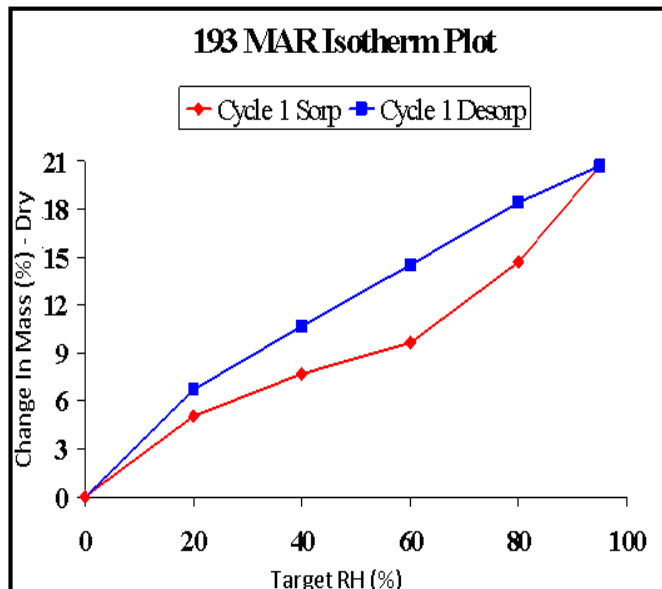

Figure 2 Sorption/Desorption Isotherms of HA at 25°C.

Consequently, the isotherm plots of Figure 2 show differences between the sorption/desorption of studied HA. The water sorption for all HA is fast up to 20% RH leading to a 5% change in mass of each samples. Then some changes occur. Both

oxyhumolite HA samples (193 and 317 MAR) present a very similar sorption shape. The water uptake is a little slower for peat (316 MAR) and tschernozem (346 MAR) HA up to 60% RH. This is followed by a quicker increase of moisture uptake. The desorption step is very similar for both oxyhumolites HA within the experimental errors. It is interesting to observe that peat (316 MAR) and tschernozem (346 MAR) HA present a similar behaviour of their desorption step.
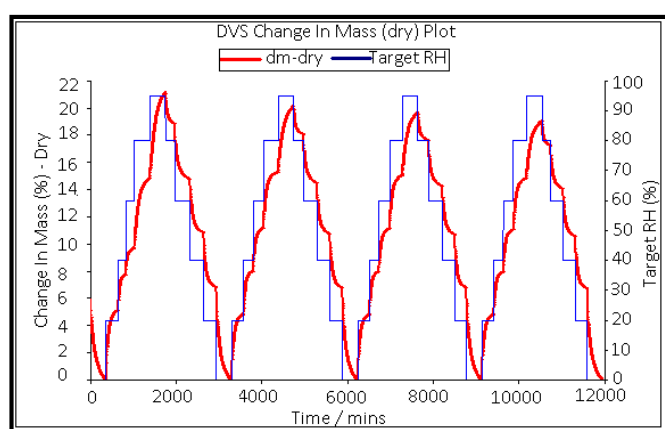

Figure 3. Multiple measurement for 37.3 mg 193 MAR HA.

Figure 3 shows a continuous and repeated measurement for four sorption/desorption cycles. The experiment was performed as previously except that the HA powder was equilibrated at 0% RH for ten minutes. Comparing the different cycles, we observed that cycles 1 and 2 take the same time of measurement ($\approx$ 2950 minutes) while cycle 3 is 100 minutes shorter and cycle 4 is 200 minutes shorter. The main differences in the sorption shapes between cycles occur for relative humidities higher than 60% RH. Furthermore, the cumulative sorption at the end of the 95% RH is decreasing after each cycle, presenting a 21.6% moisture content for cycle 1, 20.6% moisture content for cycle 2, 20.0% moisture content for cycle 3 and 19.5% moisture content for cycle 4.
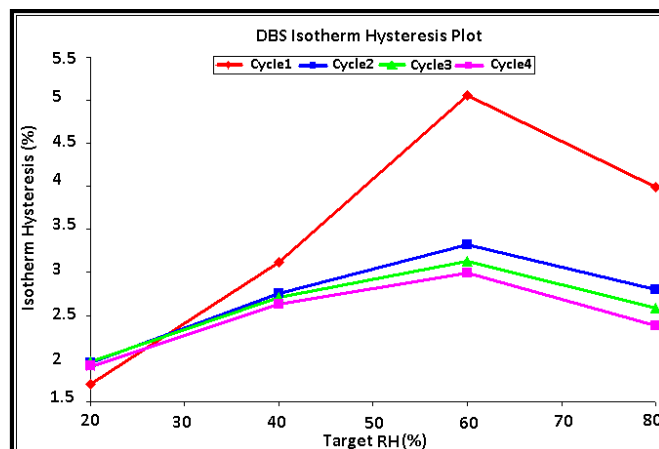

Figure 4. Hysteresis phenomenon for 37.3 mg 193 MAR HA.

Figure 4 presents an interesting alternative for viewing the stability of the powder against repeated humidity cycles. This analysis is an interesting feature of DVS performance and is useful for illustrating that HA, even as a powder (solid form), is a dynamic system. This is illustrated by observed wide isotherm hysteresis due to a decrease (from cycle to cycle) of HA's ability to pick up water. This might be explained by some conformational changes in HA's molecules during the desorption steps.
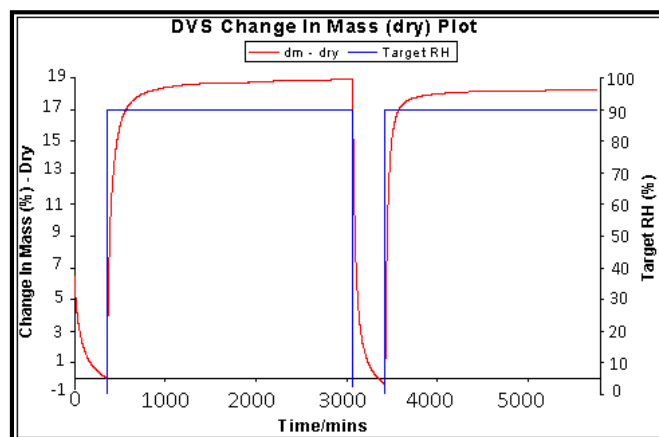

Figure 5. Water pickup stability for 193 MAR HA; sample weight (mg): 31.0.

Another attractive way to study this effect is presented in Figure 5 where successive 90% RH steps separated by a 0% RH drying step show that HA are not able to recover the same amount of water they picked up previously. The difference observed is of 1.5% change in mass.Finally, 193

MAR HA was studied on Figure 6 to follow the effect of modulation steps from 80 to 95%RH after a quick sorption/desorption cycle. This might be similar to soil conditions encountered in autumn or spring in England. Ten modulation steps were completed (shown in blue) and the response of the sample is shown in red. It is clear that the powder gains more moisture as a result of each relative humidity modulation. This means that the water uptake limit of HA can be overcome. Supplementary adsorbed water represents a 0.22 mg increase in overall mass or a 0.5% change in mass.

Figure 6. Water pickup during relative humidity modulation for 193 MAR HA; sample weight (mg): 44.4.

The obtained results allow the determination of the amount of water, which is most likely complexed by humic acids. Thus, the following values were obtained making the assumption that the average molar milli-equivalent per gramme of HA is 9.

1 mole of 316 MAR HA (peat soil) is complexing 1.73 mole of water

1 mole of 193 MAR HA (oxyhumolite) is complexing 1.43 mole of water

1 mole of 346 MAR HA (tschernozem) is complexing 1.32 mole of water

1 mole of 317 MAR HA (oxyhumolite) is complexing 1.14 mole of water

These results show that Czech HA from various origins are two to three times less complexing water than commercial HA [1]. The most likely explanation is that commercial samples present a much higher content of humate (salt form of HA) than Czech humic acids. This might be due to both their geographical origin and the extraction procedure.
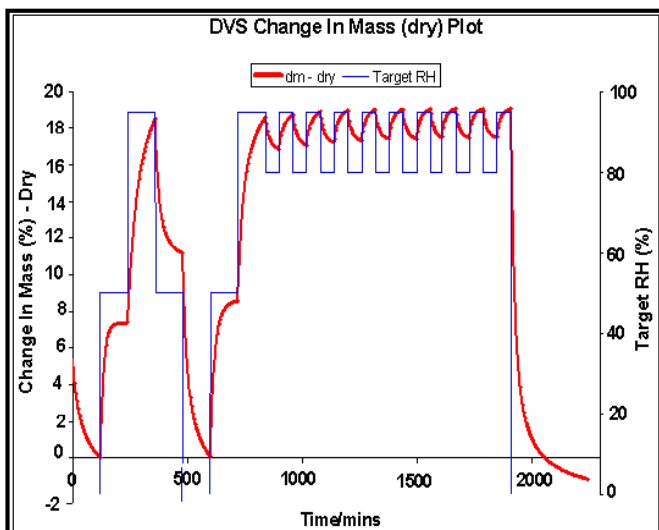
Conclusion

In this work, the HA's water pickup limits were shown. Furthermore, the Dynamic Vapour Sorption technique allows us to more likely explain the basic differences observed between samples and to quantify them. It was shown that Czech humic acids are complexing two to three times less water molecules than commercial samples. This is mainly due to their lower humate form content. It is planned to perform similar measurement on samples prepared on the same way and from different origin.

Acknowledgement:

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References

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