



Moisture Sorption on Commercial Humic Acids

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In this work a Dynamic Vapour Sorption (DVS) system is used to study the water sorption by HA to better understand the possible complexation of water by HA. The differences between batches and the effect of humidity perturbations were also studied and the need to use any alkali solution for dissolving HA will be discussed.

Introduction

The sorption properties of Humic Acids (HA) are nowadays important, intensively studied and well established in the literature. This is especially true for some examples we are reporting here: the association of triorganotin with dissolved HA [1]; the sorption characteristics of $^{241}\text{Am(III)}$ and Eu(III) bound by Humic Substances (HS) chemically immobilised on silica gel [2]; the phenanthrene binding and sorption to dissolved and to mineral-associated HA [3]; the sorption of non-ionic organ solutes to HA-mineral complexes [4] and the sorption of heavy metals by mineral-HA substances [5]. Furthermore, HA also play an important role in the sorption of different compounds in soils [6], organo-clays [7], kaolinite [8], montmorillonite [9], and even to silica [10]. Finally, HA are themselves sorbed onto inorganic/mineral surfaces which allow the studies of the mitigation of facilitated pollutant transport processes [11] and of their role in contaminant binding [12]. Nevertheless, HA sorption properties still need to be intensively studied. Surprisingly, nobody in the literature is yet studying the moisture uptake of HA or their salt forms, humate.

Method

Commercial HA were purchased from both Aldrich (Aldrich 1: Lot. No 61700-096 and Aldrich 2: Lot. No 16308-078), Steinheim, Germany and Fluka (Fluka 1: Analysis No 38537/1 293 and Fluka 2: Analysis No 38537/1 594), Buchs, Switzerland.

The samples were run on a DVS automated moisture sorption analyser at 25°C with a sample size between 15 and 25 mg. The powder was spread around the inside of a glass pan. The instrument has a working humidity range of 0-98% RH with a sensitivity of $0.1\ \mu\text{g}$.



Results

Figure 1 below, shows gravimetric the moisture sorption kinetics for two batches of two commercial HA at 25°C.

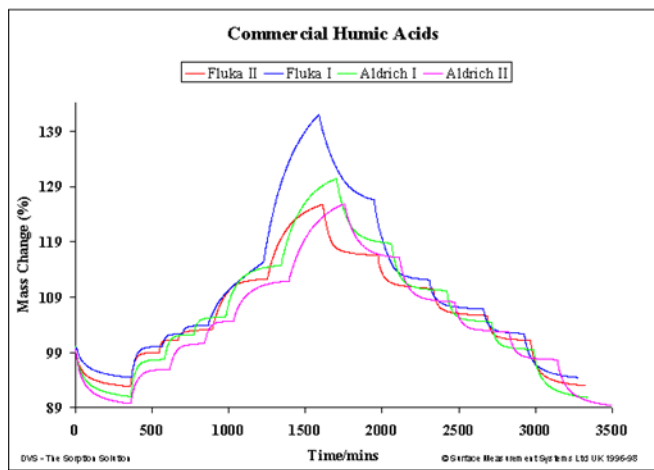


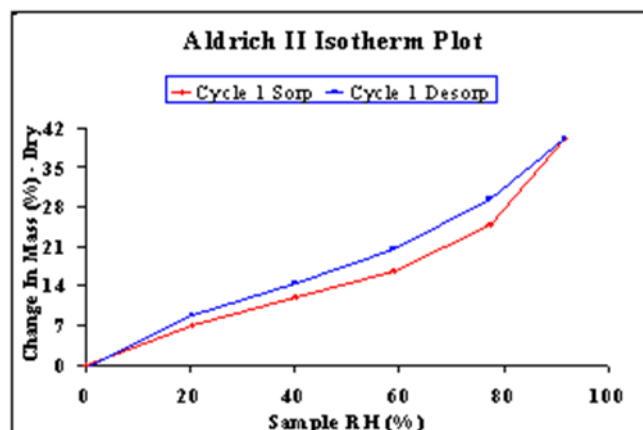
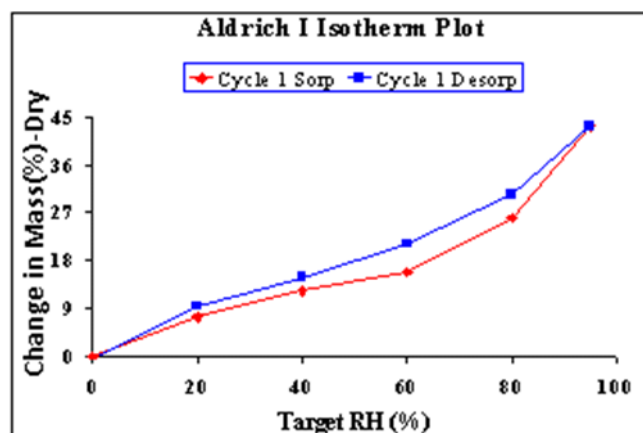
Figure 1. Effect of relative humidity on commercial HA; samples weight (mg): Fluka I = 24.07; Fluka II = 15.34; Aldrich I = 23.50; Aldrich II = 24.71

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 which was of 15% RH. The isotherm data are plotted in Figure 2 for both sorption and desorption cycles.

The data in Figure 1 shows an 11% mass decrease for Aldrich II, 10% for Aldrich I, 7.5% for Fluka II and 6.5% for Fluka I during the first drying (0% RH) step. Then for the three next steps at 20, 40 and 60% RH, all samples follow simple adsorption kinetics with each step tending towards equilibrium sorption. The last two steps at 80 and 95% RH do not reach equilibrium and show a steady increase of the mass over the time period measured. The highest increase was

observed for Fluka I HA. The desorption behaviour shows a product which remains stable and reaches equilibrium rapidly. The cumulative sorption at the end of the 95% RH step is 51% moisture content for Fluka I, 44% for Aldrich I, 40% for Aldrich II and 36% for Fluka II. The differences in cumulative water uptake between two humic acids batches for studied HA are in the range of 4 to 15% moisture content. A long-term study of 100 consecutive commercial HA batches might bring new aspects concerning the whole HA behaviour and their development in the soil.

Consequently, the isotherm plots of Figure 2 show differences between the sorption/desorption of the two types of commercial HA. The water sorption for Fluka HA is slower up to 60% RH than the water sorption for Aldrich HA. Over 60% RH, the contrary is observed. The desorption step is very similar for all HA within the experimental errors except for Fluka I HA for which a quick water desorption is observed up to 60% RH.



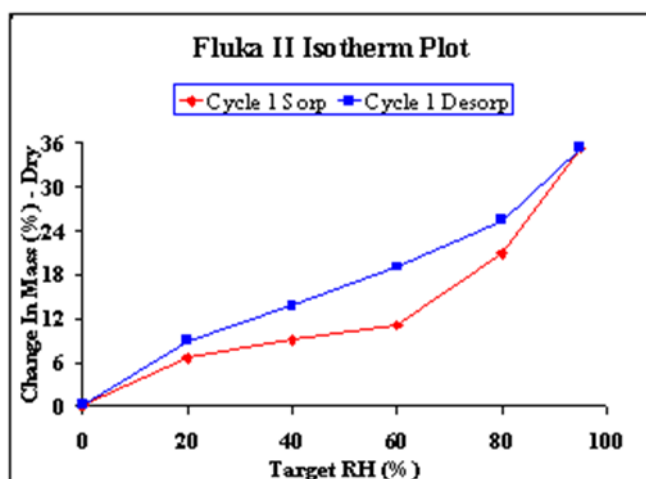
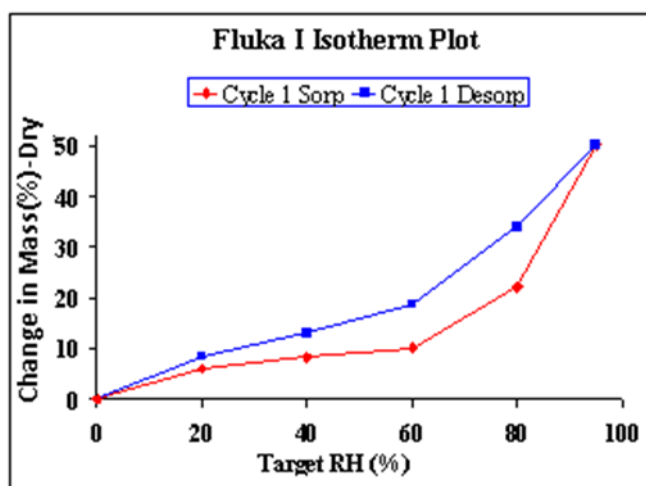


Figure 2. Sorption/Desorption Isotherms of HA at 25 °C; samples weight (mg): same as in Figure 1

An interesting alternative is to examine the stability of the powder to relative humidity modulation. This is an interesting feature of DVS performance and is useful for illustrating the effects of behaviour changes of HA due to relative humidity fluctuations. Humidities were chosen that would span a sufficient range to severely challenge the HA. As shown in Figure 3, the humidities selected were 0% and 95% RH and the ramp rate was 47.5% RH per hour for the first five cycles. Then, after again reaching the 95% RH maximum value, some modulation steps were performed with three desorption/sorption between 80 and 95% RH. Each of these modulation steps was fixed for a period of 30 minutes. Finally, using a constant fixed time (30 min), the desorption was

performed until the sample was completely dried. It is clear that the powder gains more moisture as a result of each relative humidity cycle.

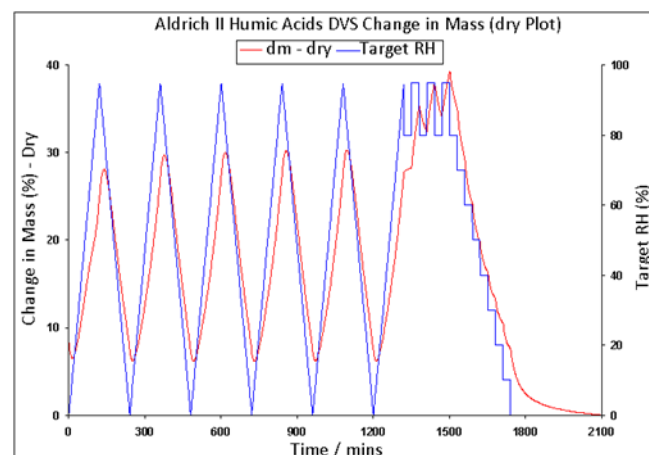


Figure 3. Water pickup during relative humidity modulation for Aldrich II HA; Sample weight: 18.75 mg.

The data in Figure 3 shows a sloping 2% mass decrease during the first RH ramping step before HA takes up moisture. Up to 95% RH the rate of moisture uptake is constant except around 90 minutes into the measurement when a slight shoulder on the adsorption kinetics is observed. This might be due to either some morphological or some conformational changes of HA. The desorption behaviour shows a product which remains stable and follows a constant decrease in moisture content. The cumulative sorption at the end of the 95% RH is 21.57% moisture content for cycle 1, 23.88% for cycle 2, 24.03% for cycle 3, 24.10% for cycle 4 and 24.12% for cycle 5. The cumulative water uptake increases for repeated cycles until the sample reaches a limiting maximum moisture content. However, when performing humidity modulations at high RH levels between 80 and 95% RH, the apparent maximum moisture content can be exceeded. The data indicates the upper level of change in mass that will be reached when performing about six additional small modulations will stabilise around 43%.

From above results, it is obvious that HA are not directly soluble in water as their moisture uptake is limited. The humate form of HA is dissolves more easily. Thus alkali solutions as



NaOH, ammonium vapours and LiOH are used to dissolve HA. In fact, the data suggests HA are more likely to complex water molecules into their structure by up to 51% of their own dried mass. Considering that the average molar milli-equivalent per gram of HA is 9 [13], it can be estimated that each mole of HA is complexing 2 to 5 moles of water.

Conclusion

The flexibility of the DVS software enables measurements to be undertaken easily for following differences between humic acids. In addition, it permits the measurement of the quality of different batches of commercial samples. Relative humidity modulation measurements are also of interest to find out the moisture uptake upper limit for constant repeated cycles. Moreover, some morphological or conformational changes were observed for the first time on HA during its moisture uptake. Finally, the complexation of water by HA can be estimated.

Acknowledgement:

SMS thanks Mr. David Fetsch for his contributions to the Application note.

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