

Insights on the mechanisms of H₂S retention at low concentration on impregnated carbons

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S1. CHARACTERIZATION OF THE IMPREGNATED PHASES

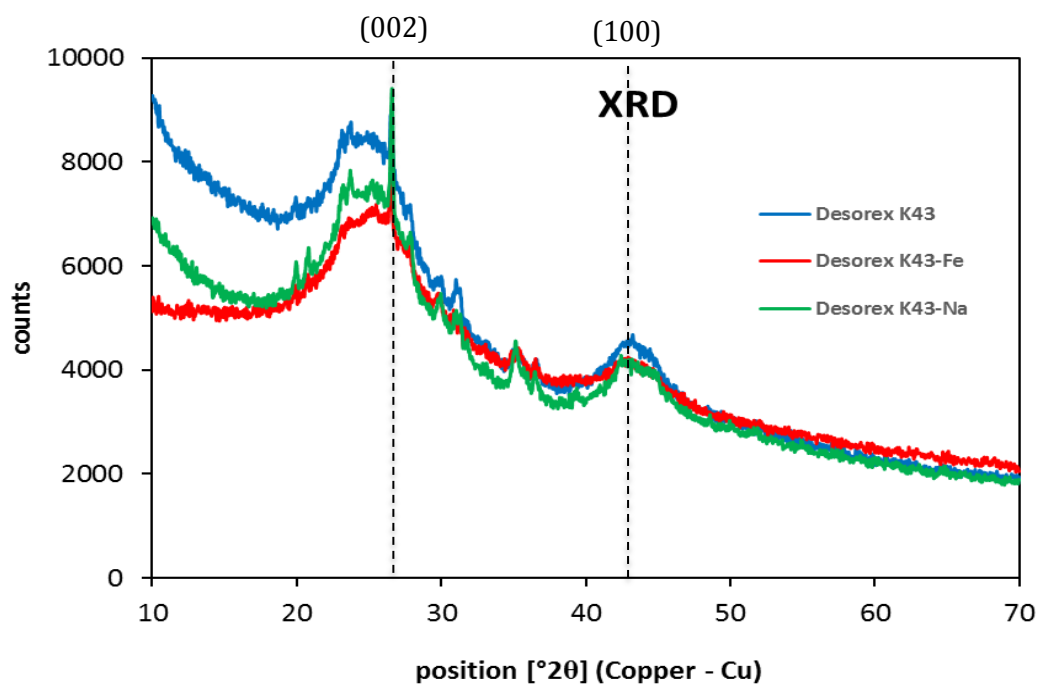


Figure S1 – X-Ray diffractograms of the samples K43, K43-Fe and K43-Na.

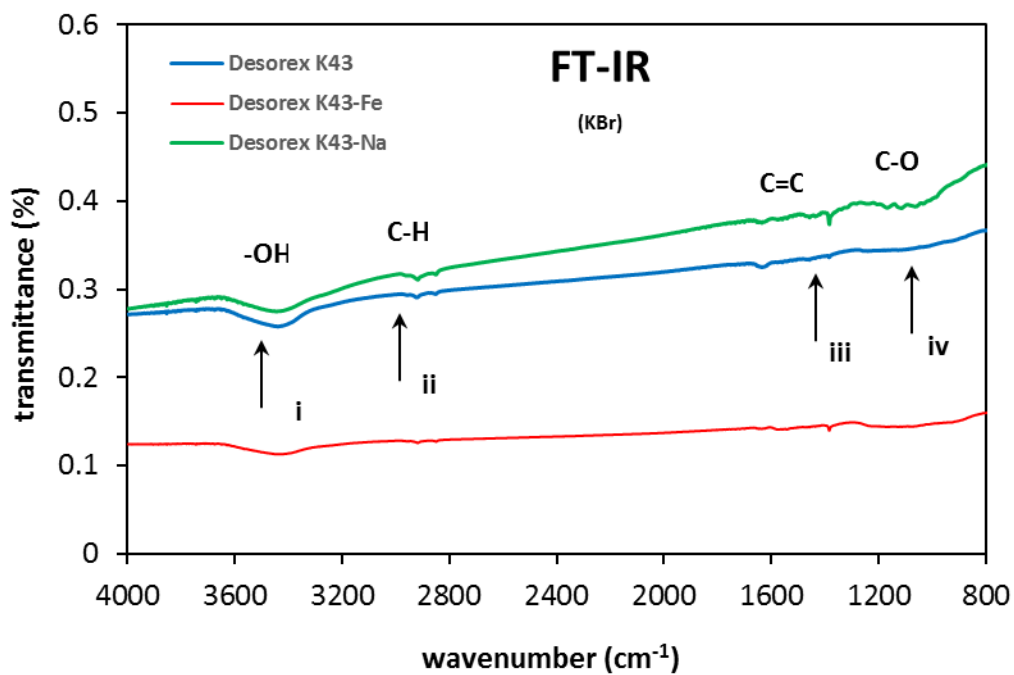


Figure S2 – FTIR spectra of the samples K43, K43-Fe and K43-Na.

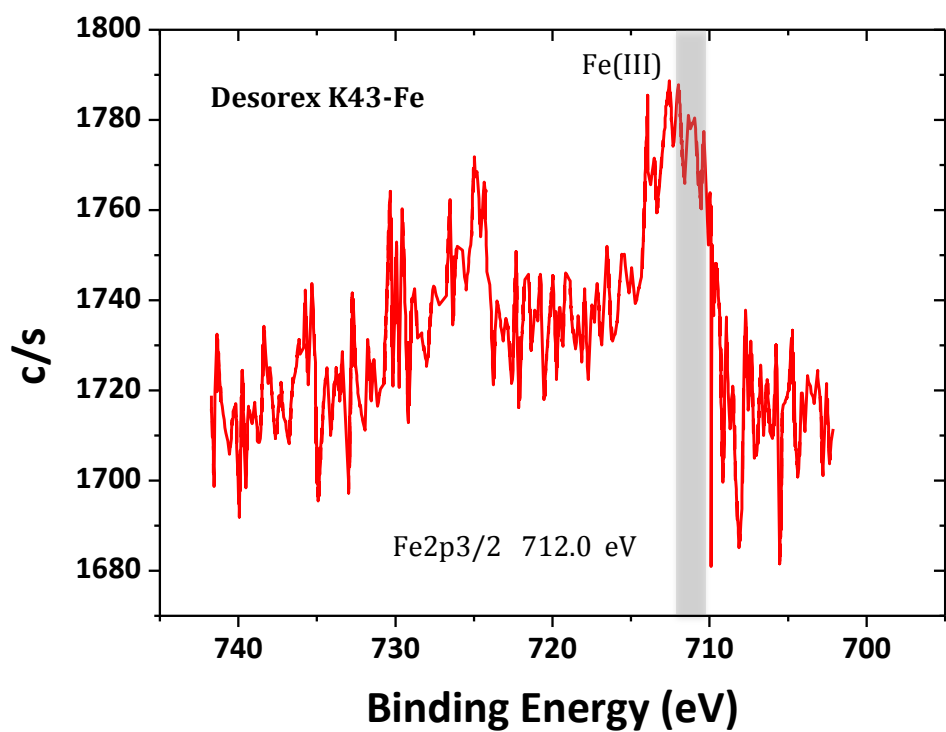


Figure S3 – XPS spectrum of Fe_{2p3/2} for the sample K43-Fe.

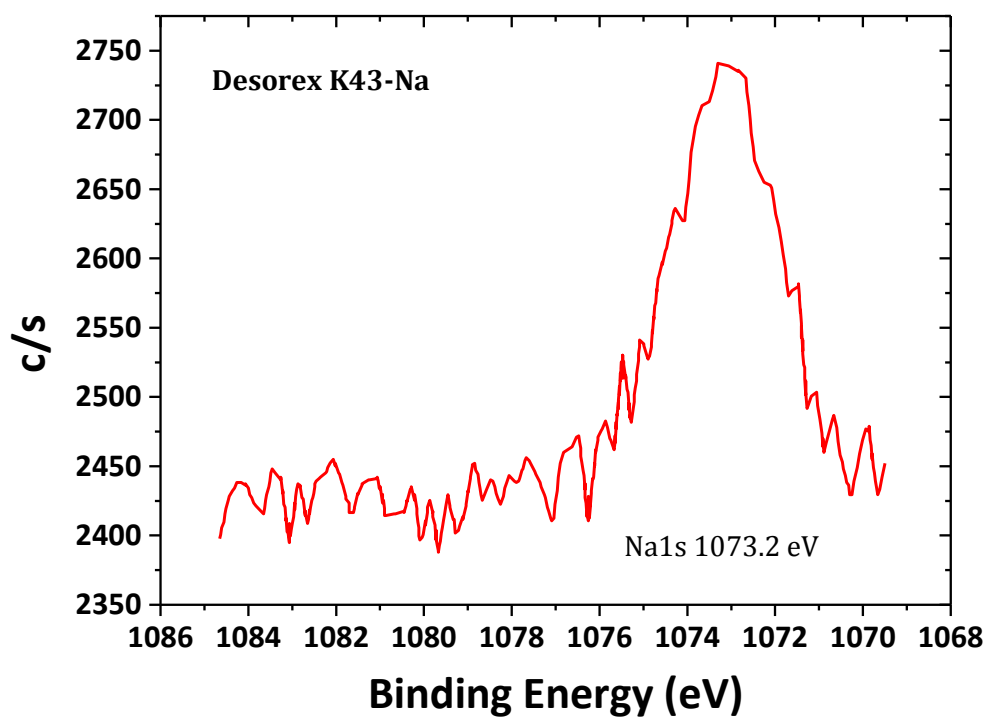


Figure S4 – XPS spectrum of Na_{1s} for the sample K43-Na.

Table S1 - Atomic concentration table results from XPS.

Sample/Species	C1s	O1s	Na1s	Al2p	Si2p	Fe2p
Desorex K43	91.72	6.82	0.01	0.51	0.82	0.13
Desorex K43-Fe	90.59	7.10	0.18	0.68	1.15	0.30
Desorex K43-Na	85.21	10.49	0.59	1.26	2.22	0.23

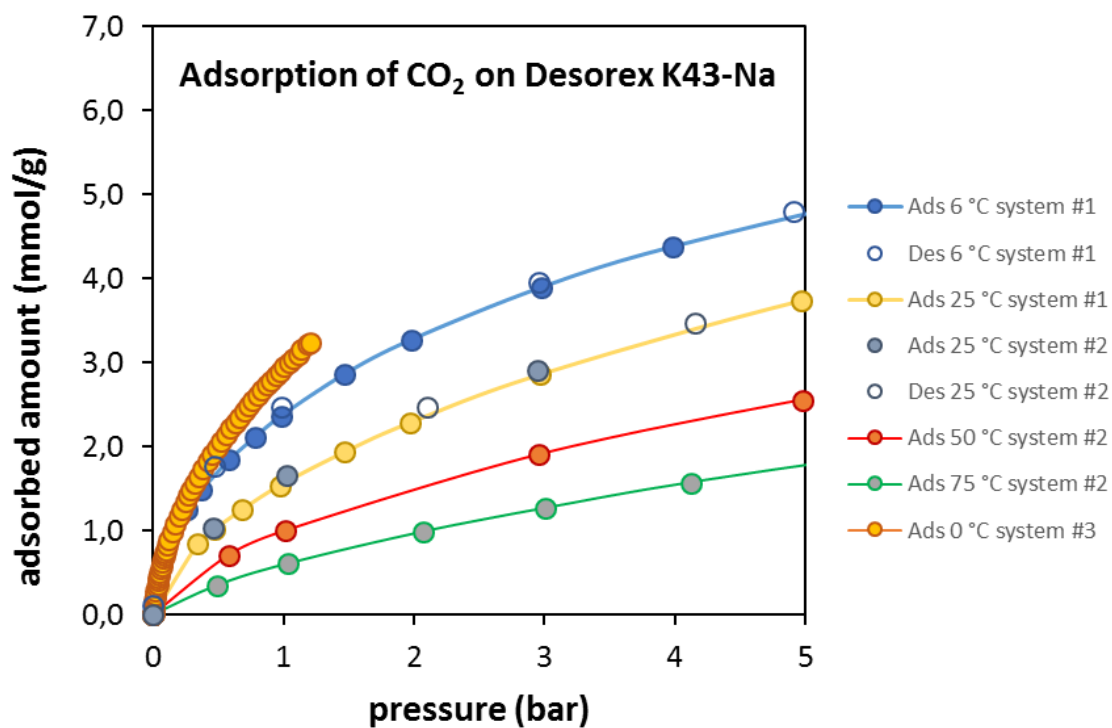


Figure S5 – Adsorption isotherms of CO₂ at 0, 6, 25, 50 and 75 °C and pressures up to 5 bar were obtained with three different experimental systems.

S2. MOLECULAR SIMULATION DETAILS

There is no experimental data of H₂S adsorption heat on graphite surface, thus the reference used to calculate the carbon-H₂S interaction parameter was the experimental adsorption heat of 40 kJ/mol obtained at infinite dilution on Westvaco's WVA 1100 activated carbon (Bagreev et al. ¹). Instead of a graphite surface, the calculation was done in a pore of 7 Å center-to-center (approximately equal to an effective pore of 4 Å) assuming that the experimental value at infinite dilution corresponds to the heat released during the filling of the smaller (more energetic) pores of the WVA 1100 carbon. For $\epsilon_{\text{solid-solid}} = 36.4$ K, the value of 40 kJ/mol is obtained at the same concentration of 500 ppm H₂S used in the experiment. Therefore the Lennard-Jones parameters used were: carbon with $\sigma = 3.4$ Å (Steele) and a new $\epsilon_{\text{s-s}} = 36.4$ K (this work). Molecule of H₂S: model of Kristof and Liszi ².

With the corrected epsilon value we calculated the adsorbed amounts of H₂S from 0 to 4000 ppm (0 to 400 Pa) in the center-to-center pores of 7 and 8.9 Å (approximately 4 and 6 Å effective) (Figure S6). An important aspect in the isotherms of figure S6 is the abrupt drop in the adsorption capacity between the pores of 7 and 8.9 Å.

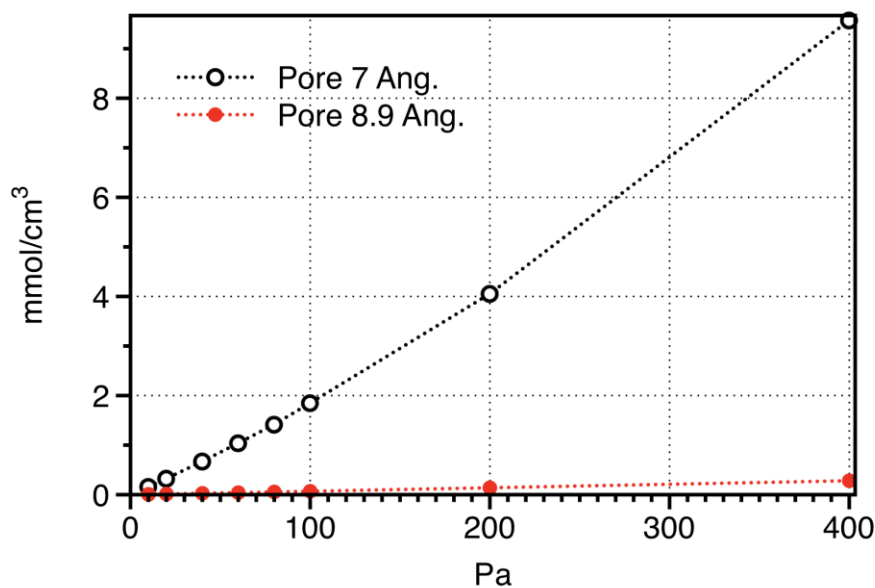


Figure S6 – Simulated adsorption isotherms of H₂S at 298 K on slit pores of 7 and 8.9 Å.

According to the methodology used previously (Lucena et al. ³), from the isotherms simulated in the individual pores it is possible to predict the adsorption isotherm in activated carbons. The total gas uptake (Q_{total}) for a carbon is determined by the sum of the products of the total volume of each pore (V_{pt}) by the simulated uptake (q_{pore}) in each pore:

$$Q_{total} = \sum_{m=1}^M V_{pt_m} q_{pore_m}$$

We observed that the PSDs of the carbons K43, K43-Na and K43-Fe can be approximated by two pores of 7 and 8.9 Å (approximately 4 and 6 Å effective) without significant loss of precision. Thus, every volume determined by the CO₂ isotherm at 273 was attributed to the pore of 7 Å and every volume of N₂ at 77 K to the pore of 8.9 Å.

The final physical adsorption values of H₂S at 298 K and 100 ppm are 0.2, 0.18 and 0.3 mg/g on the activated carbons K43, K43-Fe and K43-Na respectively (Table S2)

Table S2 – Simulated total uptake of H₂S (Q_{total}) on the activated carbons at 298 K and 100 ppm (10 Pa).

	K43		K43-Fe		K43-Na	
	V _p CO ₂ (cm ³ /g)	V _p N ₂ (cm ³ /g)	V _p CO ₂ (cm ³ /g)	V _p N ₂ (cm ³ /g)	V _p CO ₂ (cm ³ /g)	V _p N ₂ (cm ³ /g)
	0.0207	0.37	0.0177	0.36	0.0426	0.3
	Pores					
	7 Å	8.9 Å	7 Å	8.9 Å	7 Å	8.9 Å
Theoretical H ₂ S Adsorbed (mmol/cm ³)	0.1621	0.0068	0.1621	0.0068	0.1621	0.0068
q_{pore} (mmol/g)	0.0033	0.0025	0.0025	0.0024	0.0069	0.0020
Q_{total} (mg/g)	0.2		0.18		0.3	

The force field was validated for a complete H₂S isotherm on the Norit RB4 activated carbon (experimental data extracted from Cruz et al. ⁴). Unlike the carbons K43-Fe and K43-Na, the activated carbon Norit RB4 has no impregnating material. It has an area of 1320 m²/g and a wider PSD, reason for which it is better represented by 3 pores with center-to-center sizes of 7, 8.9 and 18.5 Å (approximately 4, 6 and 15.5 Å effective). Based on the RB4 PSD, the determined pore volumes are 0.0178, 0.166 and 0.389 cm³/g for the pores of 7, 8.9 and 18.5 Å, respectively. The experimental and simulated H₂S isotherms at 298 K are compared in Figure S7, showing a very good match between both curves.

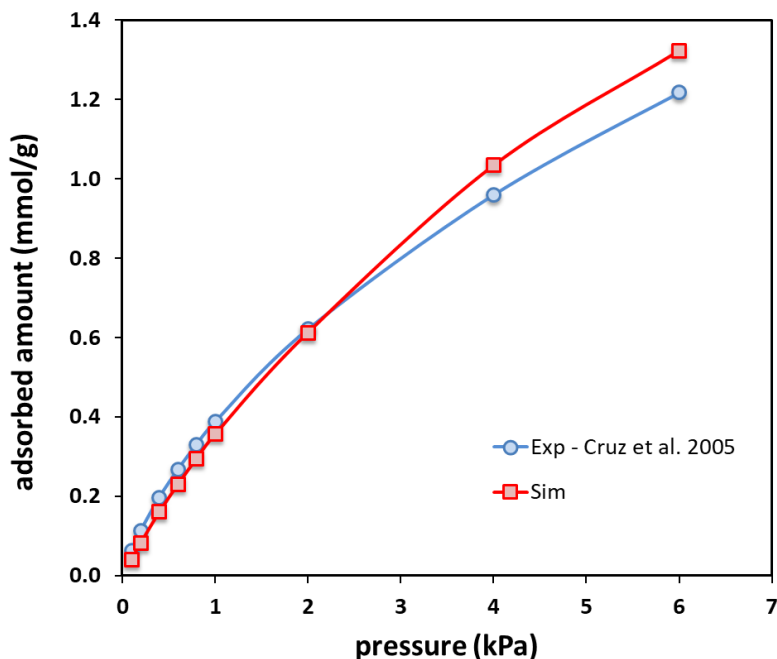


Figure S7 – Comparison between simulated and experimental data for H₂S adsorption on carbon Norit RB4 – Model validation.

References

- (1) Bagreev, A.; Adib, F.; Bandosz, T. J., Initial heats of H₂S adsorption on activated carbons: Effect of surface features. *Journal of Colloid and Interface Science*, **1999**, 219, 327–332.
- (2) Kristof, T.; Liszi, J., Effective intermolecular potential for fluid hydrogen sulfide. *J. Phys. Chem. B*, **1997**, 101, 5480–5483.
- (3) Lucena, S. M. P.; Gomes, V. A.; Gonçalves, D. V.; Mileo, P. G. M.; Silvino, P. F. G., Molecular simulation of the accumulation of alkanes from natural gas in carbonaceous materials. *Carbon*, **2013**, 61, 624 –632.
- (4) Cruz, A.J.; Pires, J.; Carvalho, A.P.; de Carvalho, M.B., Physical adsorption of H₂S related to the conservation of works of art: The role of the pore structure at low relative pressure. *Adsorption*, **2005**, 11, 569–576.