

Electronic Supplementary Information

Ionosilicas as efficient adsorbents for the separation of diclofenac and sulindac from aqueous media

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Results

1. Characterization of material A

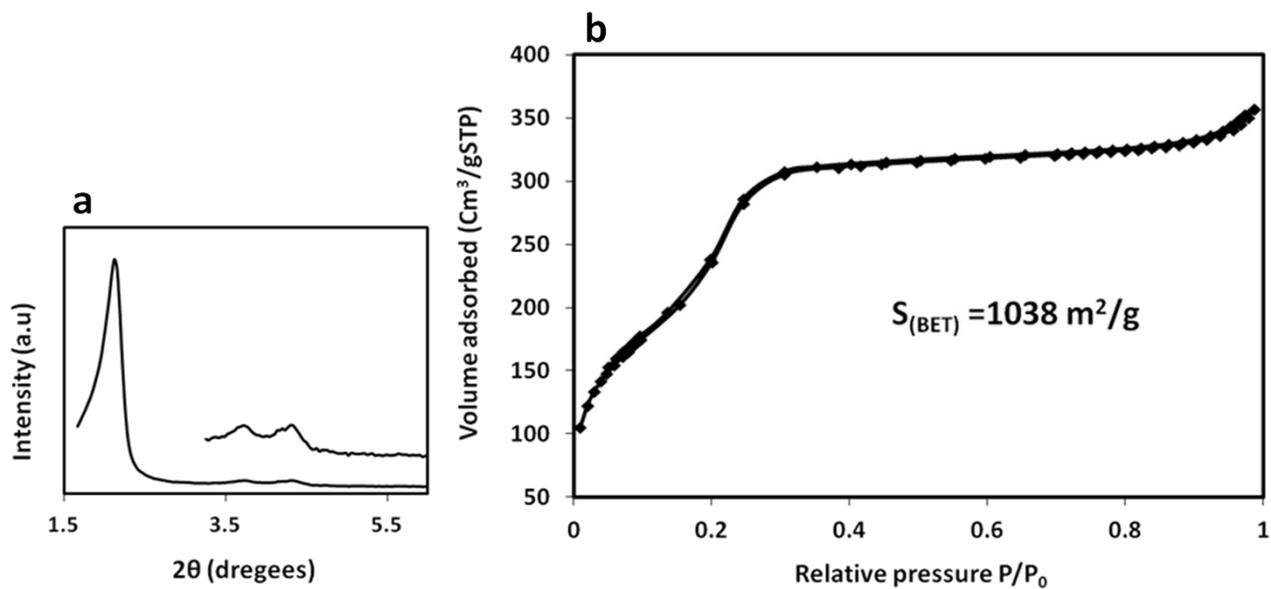


Figure S1: a) X-ray diffraction pattern of Material A, b) Nitrogen sorption isotherm of material A

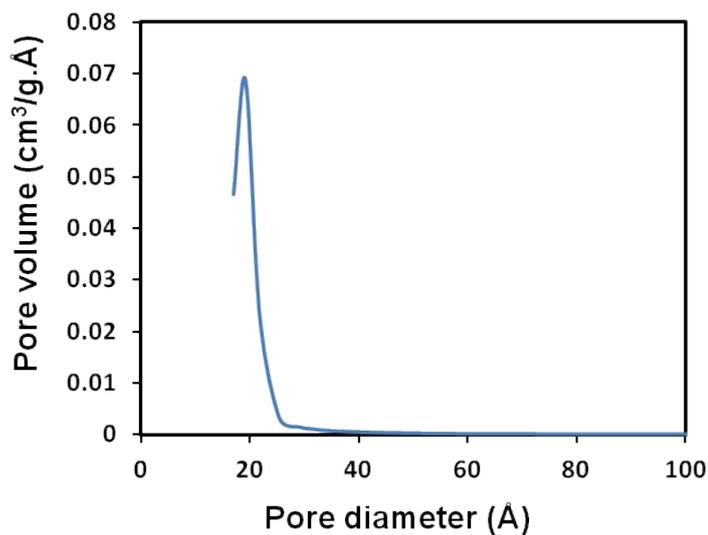


Figure S2. BJH pore size distribution of material A

2. Detailed FTIR characterization of diclofenac sodium salt–

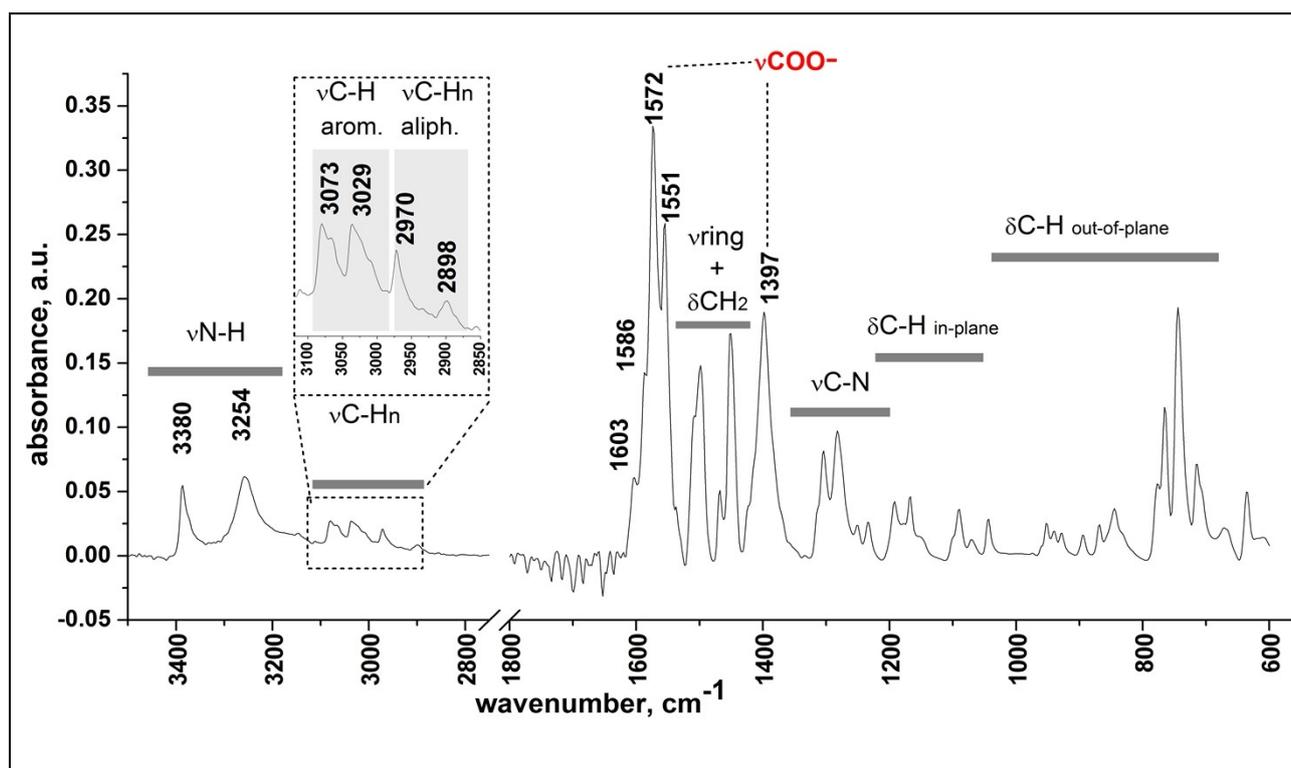


Figure S3. FTIR spectrum of diclofenac sodium salt

In the high frequencies range signals due to N-H stretching can be found at 3380 and 3254 cm⁻¹, furthermore signals due to C-H stretching in the aromatic and aliphatic part of the molecule are present in the 3100-2850 cm⁻¹ range. In particular, signals at 3073 and 3029 cm⁻¹ can be assigned to the stretching mode of aromatic CH groups, whilst signals at 2970 and 2898 cm⁻¹ are ascribable to $\nu_{as}CH_2$ and ν_sCH_2 respectively.

In the low frequencies range antisymmetric and symmetric stretching signals of carboxylate group can be found at 1572 and 1397 cm⁻¹ respectively. NH deformation modes and ring stretching modes are responsible of the signals at 1603-1586 cm⁻¹; furthermore, ring stretching modes and deformation modes of the methylene group contribute to the complex pattern of signals in the 1520-1420 cm⁻¹ range. Typical deformation frequencies of methylene groups are lowered to 1430-1420 cm⁻¹ when the methylene group is adjacent to a carbonyl group. The signals at lower frequencies are ascribable to C-N stretching modes (1300-1200 cm⁻¹), in plane (1200-1000 cm⁻¹) and out of plane (900-690 cm⁻¹) CH deformation.

3. FT IR study of sulindac/ionosilica and sulindac sodium salt/ionosilica complexes

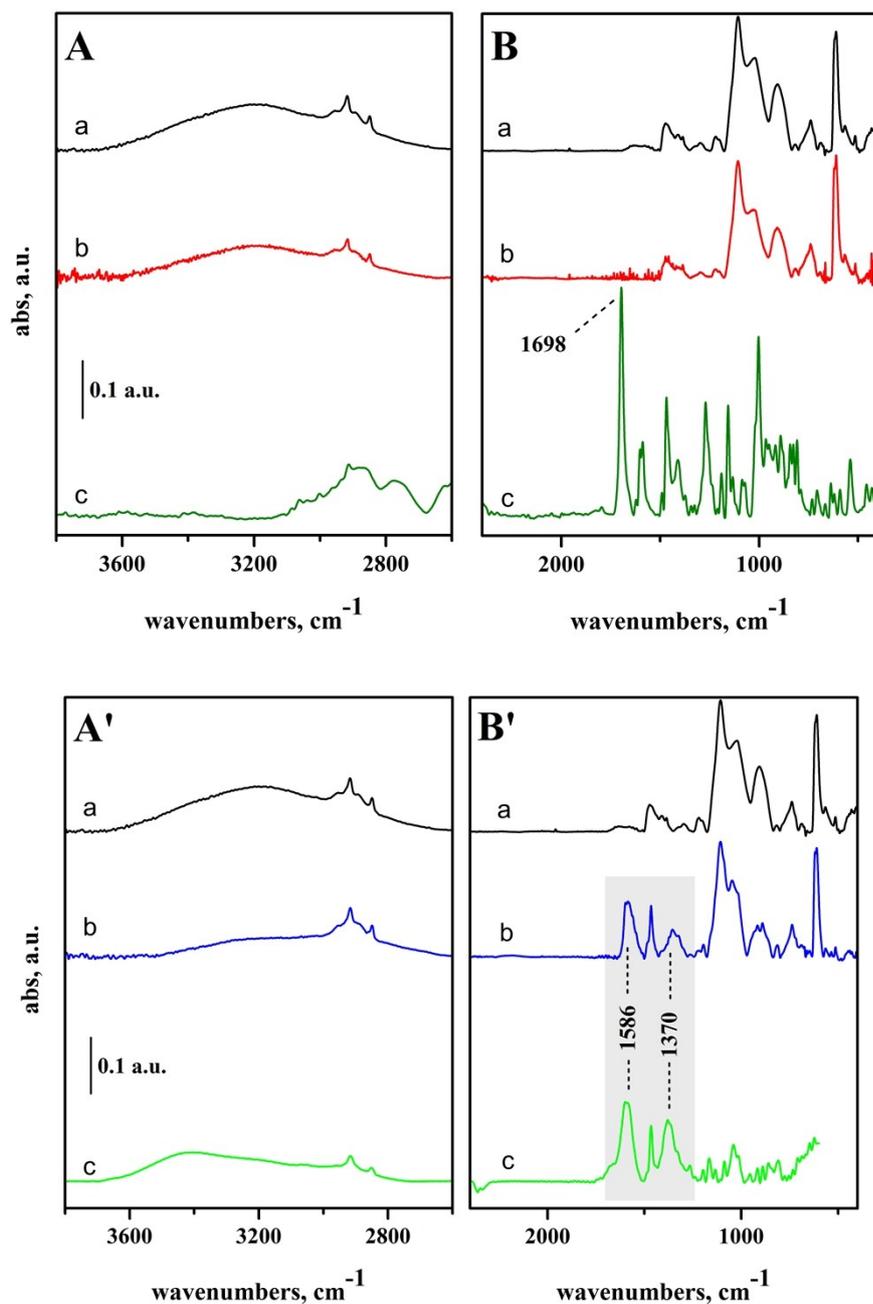


Figure S4. A, B. FTIR spectra of Material A (curve a), A-SUL/HC (curve b) and SUL in solid form (curve c); **A',B'**: FTIR spectra of Material A (curve a), A-SUL-Na/HC (curve b) and SUL-Na in solid form (curve c)

In figure S4, panel A and B FTIR spectra of Material A, sulindac and of the corresponding hybrid system A-SUL/HC are reported. The spectral profile of A-SUL/HC is coincident with the spectra of Material A; no signals ascribable to Sulindac molecule are present. On the contrary, in the case of sample A-SUL-Na/HC, in which Sulindac Sodium salt was adsorbed, typical signals ascribable to

carboxylate moieties of SUL-Na molecules are clearly observable, confirming the successful incorporation of the drug in Material A.

4. Solid and liquid NMR spectroscopy

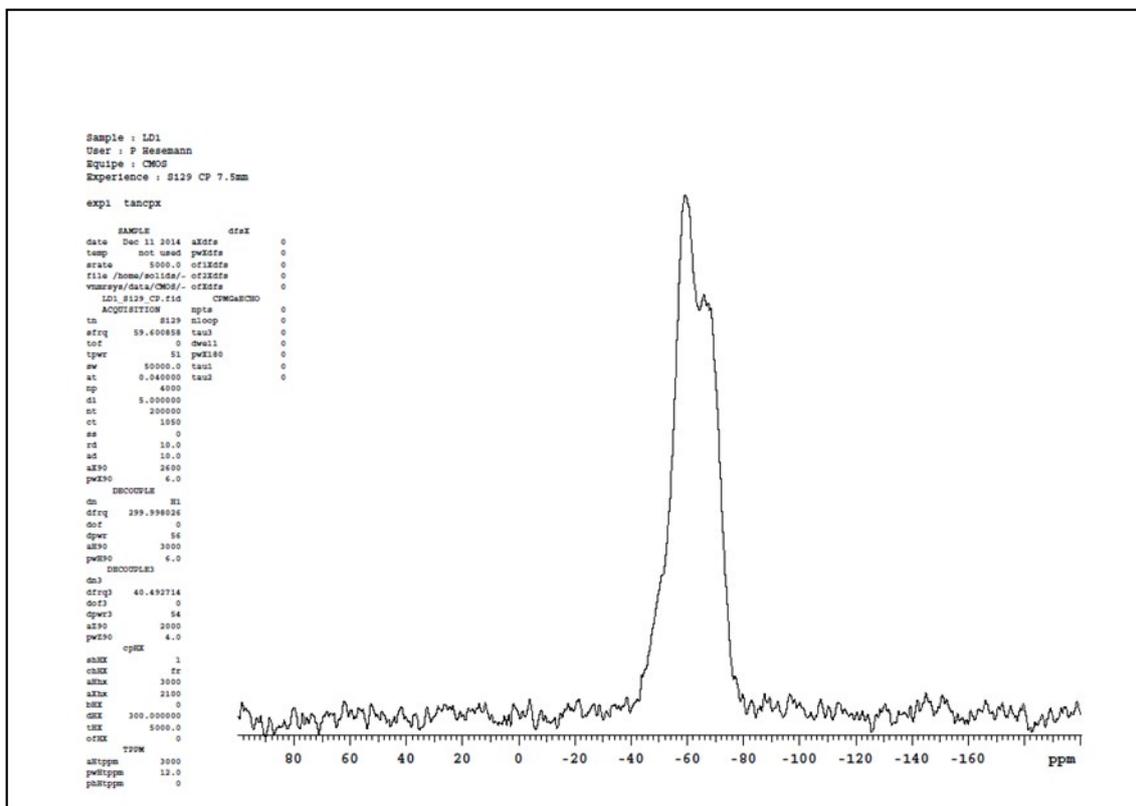


Figure S5. Solid state NMR ^{29}Si of DCF-Na/HC sample

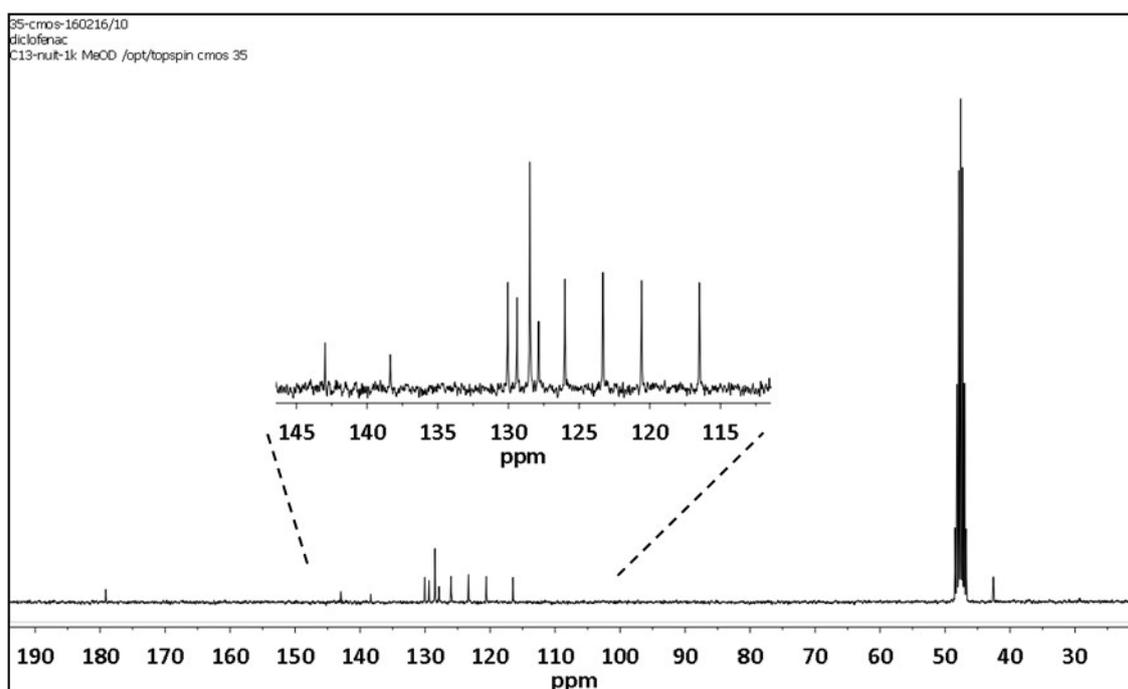


Figure S 6. ^{13}C liquid NMR spectra of diclofenac DCF-Na (solvent: MeOD)

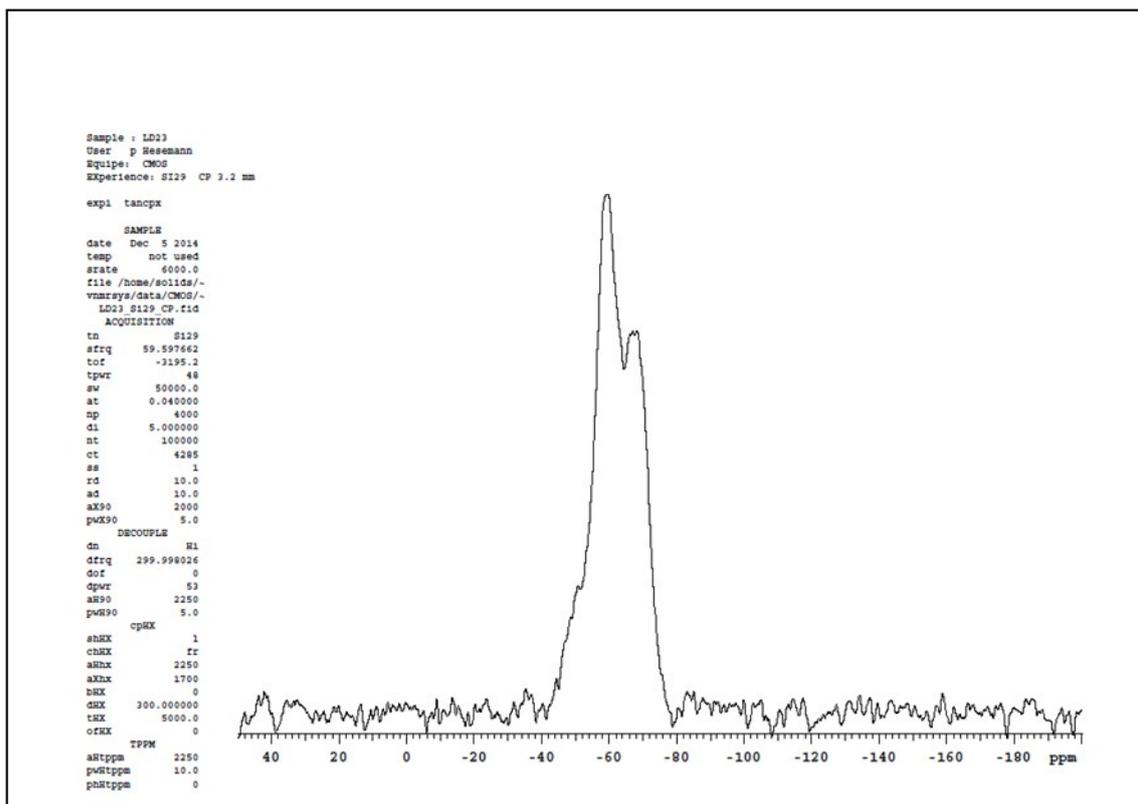


Figure S7. Solid state NMR ^{29}Si of SUL-Na/HC sample

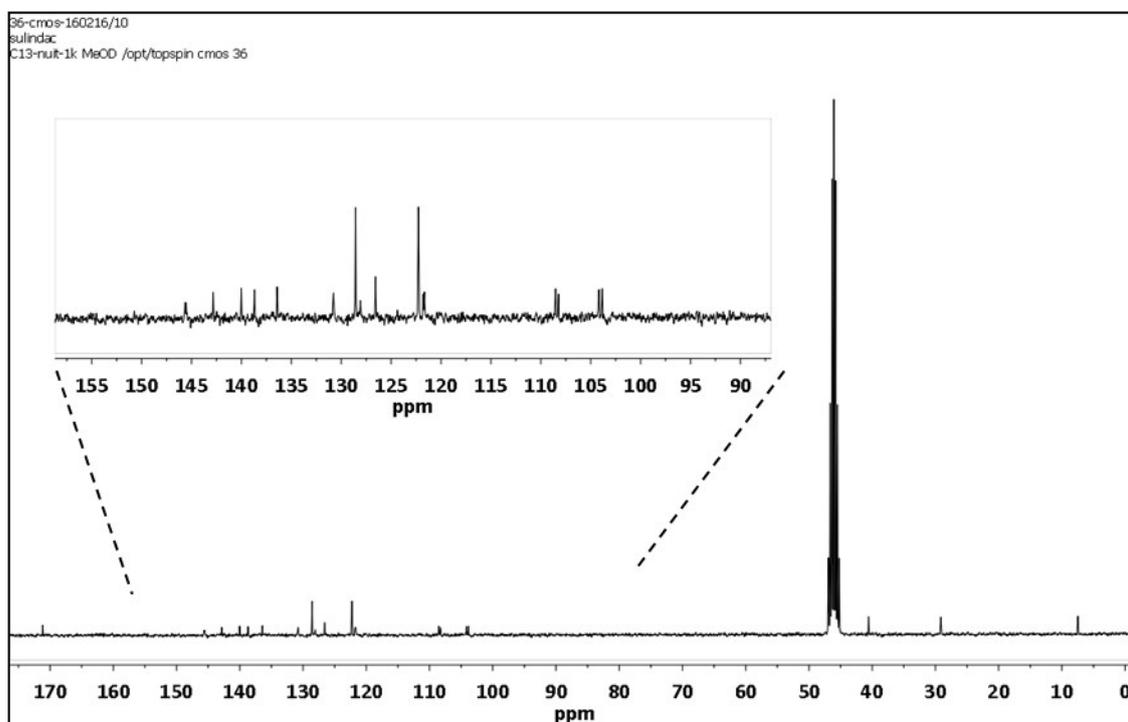


Figure S8. ^{13}C liquid NMR spectra of sulindac SUL (solvent:MeOD).

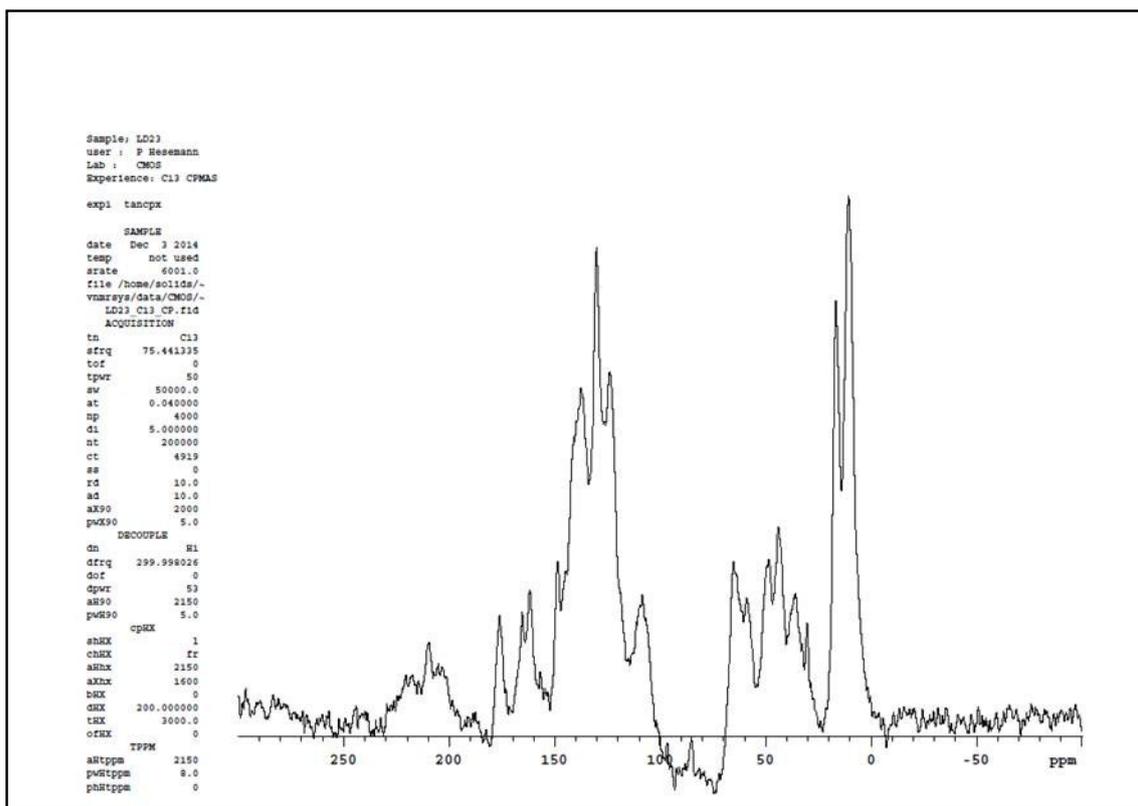


Figure S9. Solid state NMR ^{13}C CP mass of SUL-Na/HC sample

5. Nitrogen adsorption-desorption (BET)

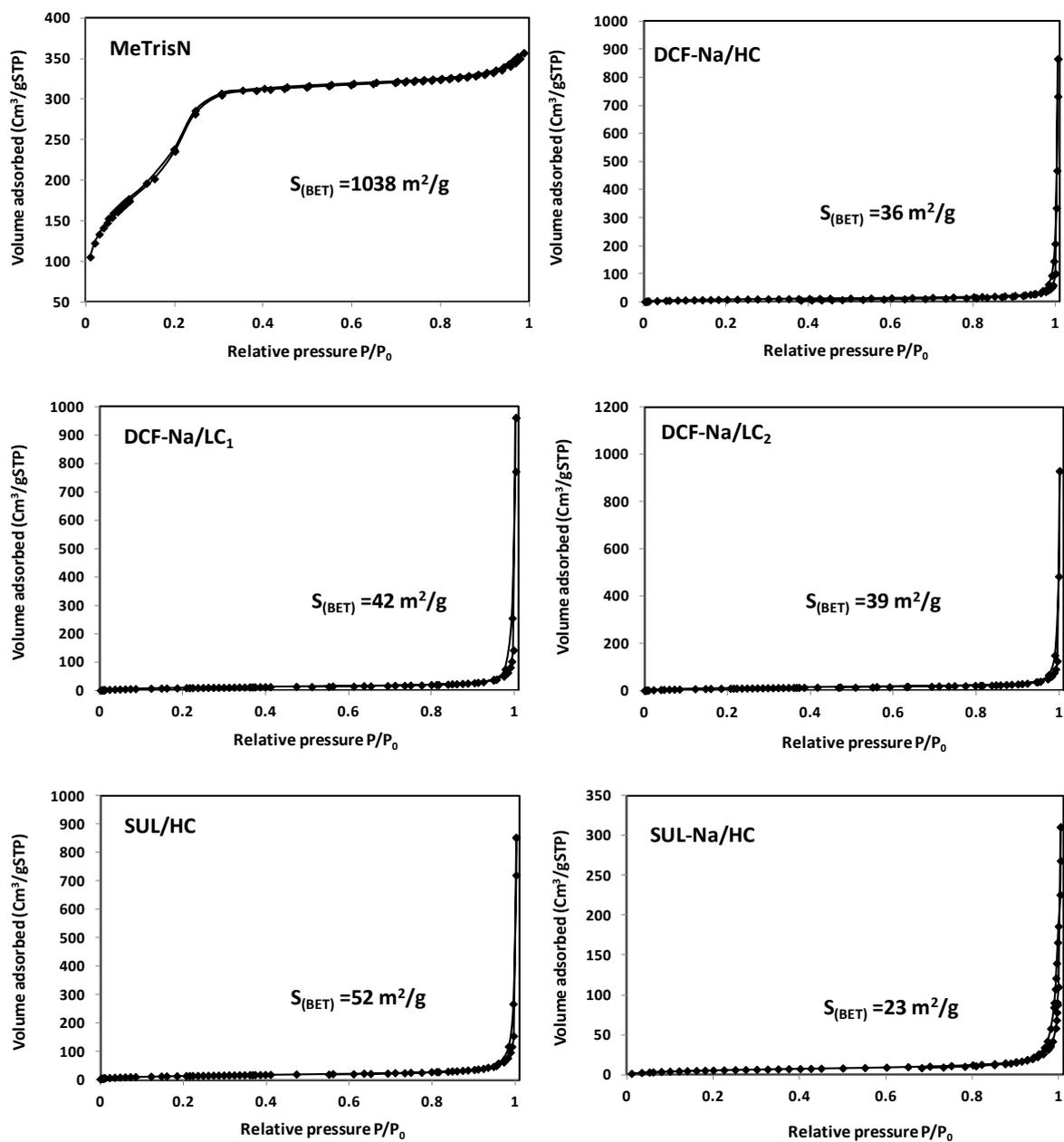


Figure S10. Nitrogen sorption isotherms of Material A and drug/silica complexes.

6. Loading of diclofenac on silica material type MCM41

The diclofenac loading on MCM-41 type material was performed in deionized water. Prior 0.3 g of diclofenac was dissolved in deionized water at concentration of 0.03 M, and then 0.3 g of MCM-41 material was added under stirring at RT. After 24 h the solid material was filtered and washed with water followed by drying in vacuum at 60°C, the complex diclofenac-silica material was called **MCM-41-DCF-Na**.

7. Thermogravimetric analysis

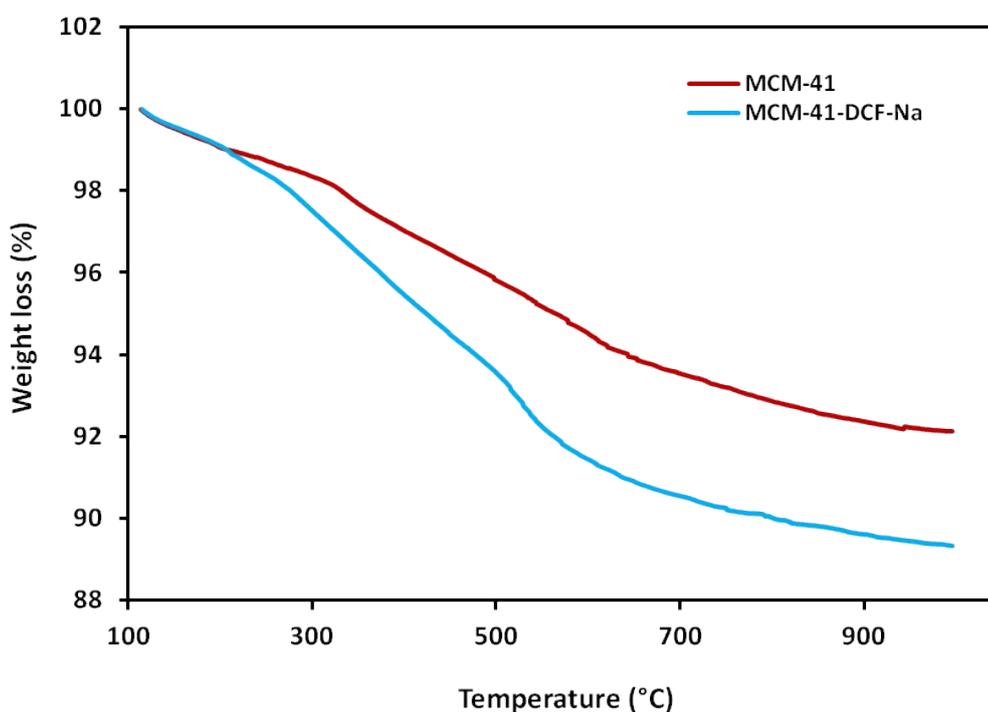


Figure S11. Thermogravimetric analysis: silica material (red curve), **DCF/silica** complex (blue curve).

8. Adsorption capacity of silica

Table S1: Adsorption capacity Q of silica measured by different techniques.

entry	Sample	UV/Vis Supernatant analysis ^a	Thermogravimetric analysis ^b
		Q (mmol/g) ^c	Q (mmol/g) ^c
1	MCM-41-DCF-Na	0.156	0.088

$Q_{(uv)} = (C_{init} - C_{final}) / \text{weight of the material}$

where C_{init} is the initial diclofenac concentration, while C_{final} is the diclofenac concentration after 24 h exchange with the material.

$Q_{(ATG)} = [(\text{weight loss of MCM-41}) - (\text{weight loss of MCM-41-DCF-Na})] / [(\text{mass molar of DCF-Na}) * (\text{weight of the material})]$

9. Release Test

Figures S12 and figure S13 show the release efficiency of drug as a function of time of the loaded sample (DCF-Na) in powder form and pellet form respectively in deionized water medium. With powder form the release was constant and the quantity was very small less than 4%, in the case of pellet the release efficiency was around 0.5% and stop after 6 hours. We also obtained a same results in acidic medium pH=3 the release was less than 2%.

According to these results, ionosilica material are strongly adsorbing and retaining the negatively charged Diclofenac molecule, this is supported by the collapse of material's mesoporosity observed with the results obtained from the nitrogen adsorption-desorption (BET),so we could say that ionosilca are a useful traps for sequestration and they have potential for drug removal from wastewater.

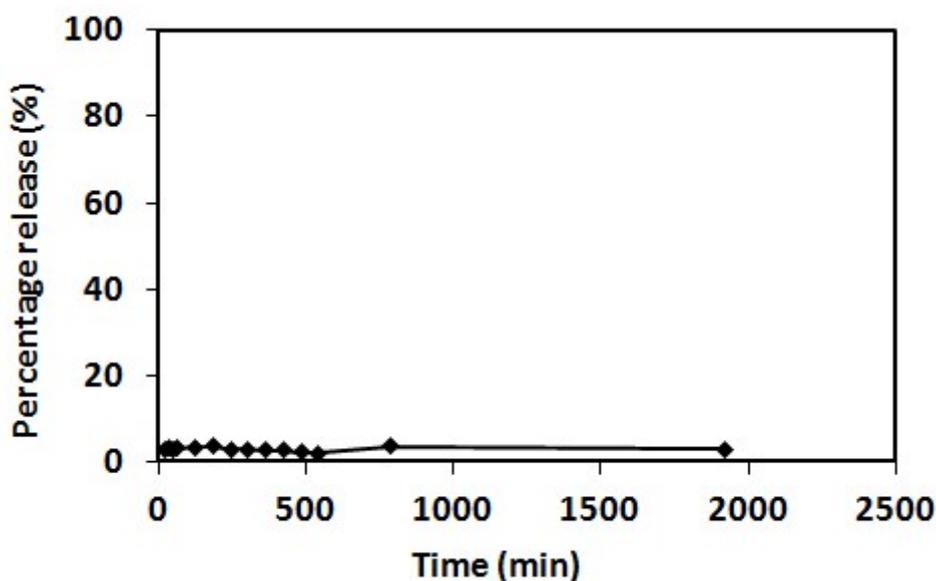


Figure S12. Release test with powder sample.

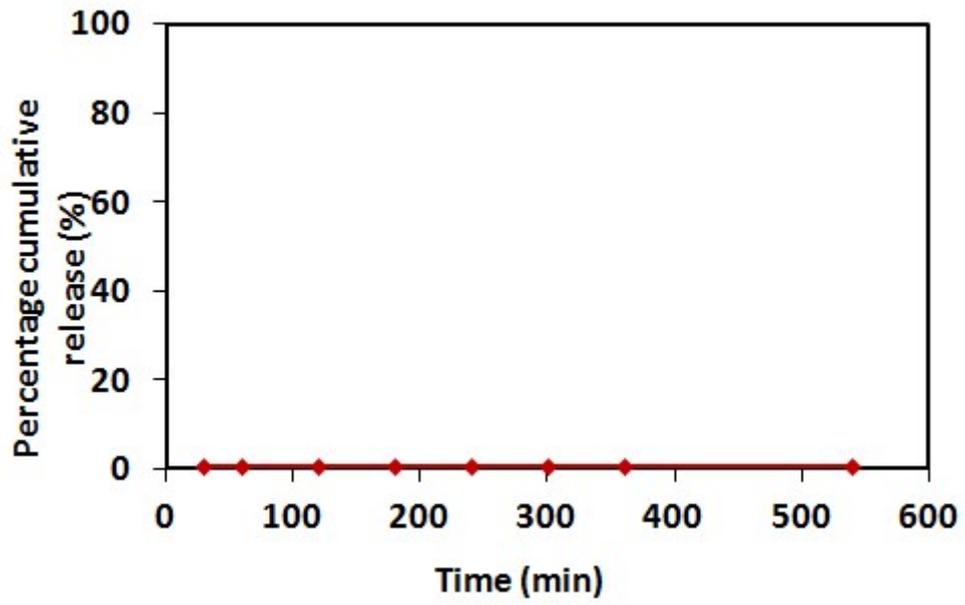


Figure S13. Release test with pellet sample.