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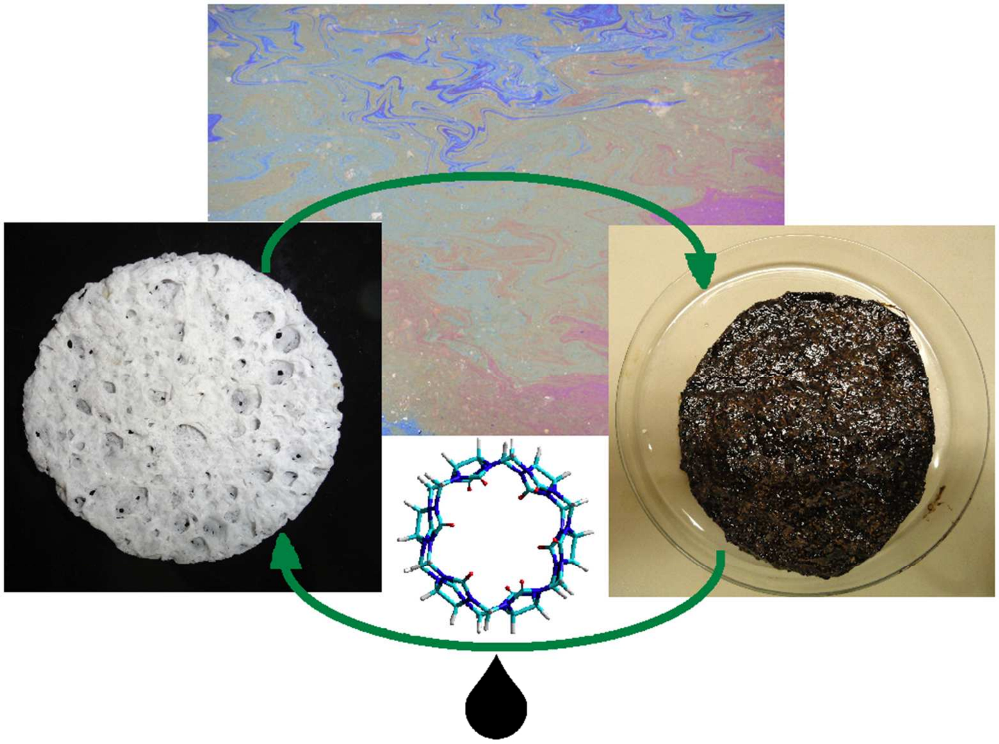

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Reusable cucurbit[6]uril-loaded Poly(urethane) Sponges for Oily Waters Treatment.†

Felipe César Sousa e Silva,[a] Silvânia Marilene de Lima,[a] and Grégoire Jean-François Demets*[a]

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This paper presents the preparation and the absorption characteristics of cucurbit[6]uril/poly(urethane) sponges towards petroleum, Diesel and soy bean oils over fresh and seawater. These sponges are able to absorb more than 3 times their weight in oil in less than 20 minutes. Furthermore, they are reusable and the oil they absorb may be recovered quantitatively for more than ten times, using mechanical pressure . This feature increases their absorption capacity to more than 30 times in weight at least.

Oil leakages are a huge problem for aquatic ecosystems, and unfortunately they are very common. Usually the major part of the oil may be pumped out, but remediation is never quantitative this way. After this process a small quantity of oil is always left behind, forming monolayers or thicker layers, that may impair gaseous exchanges at the air/water interface. Several sorbent materials in different forms such as powders and fibres, are in use today to remove residual oil, as well as chemicals like detergents which drag oil to the aqueous phase, amongst others[1–14]. The research for new materials is constant, because many absorbent materials cannot be used for being too expensive, inefficient or difficult to handle. Others generate bulky waste. Cucurbit[n]urils (**CB[n]**), are toroidal molecules produced by acidic condensation of paraformaldehyde and glycoluril[15]. This synthesis leads to a series of homologues, that contain 5, 6, 7, 8 and 10 glycoluril units (n), altogether with minor amounts of more complex structures as CB[12-14], inverted CBs and CB[5]@CB[10], but CB[6] is its major product[16–19]. CB[6] in particular, has a D_{6h} symmetry and for this fact it is a non-polar molecule. It is insoluble in water but also chemically and biologically inert. Its cavity, (figure 1) is highly hydrophobic, and able to form several inclusion compounds with different organic and inorganic molecules[20,21]. Due to its structure, it has an enormous affinity for non polar structures, such as hydrocarbons for example[22]. It is the ideal molecule to grab oils and similar chemical species from air/water interfaces. In practice, it is better to use monolithic sorbent materials than powders, as they can be easily recovered from the environment, and such monoliths will work better the higher contact area they have with the oils. To prepare monoliths with CB[6] for this application, we have to immobilize it in a solid matrix such as a polymer for example. Making sponges is a very useful way to enhance absorption capacity since their porous structure increases the solid/liquid contact area and reduces their density. Our group recently applied for patents involving cucurbit[6]uril loaded polymers, called Cubions, for a variety of applications, especially water treatment and remediation[23,24]. We describe here CB[6]-loaded poly(urethane) sponges for the specific purpose of removing thin oil stains (petroleum, Diesel and vegetable oil) from freshwater and seawater by simple contact. These sponges are very fast and effective for this task, and may be reused several times, after being squeezed to recover the oil they absorbed.

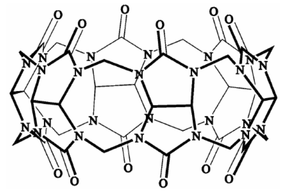

Fig. 1 The cucurbit[6]uril molecule.

Cucurbit[6]uril was prepared and purified following the procedure described by Day and co-workers[16] using glycoluril (Aldrich) and formaldehyde (F. Maia), (MW is 996 g/mol. H^1NMR: δ : 5.75 (s, glycoluril methines); δ : 4.43, 5.97 (d, $|J|_{gem} = 15.6Hz$)[25]. To prepare the sponges, we have dissolved 2.00 g of poly(urethane) or PU (Braskem) in 60 cm^3 tetrahydrofurane (Synth) under stirring for 3h. We added different amounts of cucurbit[6]uril, varying from 35 to 60 % in mass, to the composition at this point. Typically, for a 35 % (m/m) sponge, we would add 1.090 g (1.094 mmol) of very finely grounded CB[6] to the solution to form a suspension, which has to be maintained under stirring for 48 h and becomes very viscous. At this point, we added 8.15 g (49.88 mmol) of trichloroacetic acid (Henrifarma) to the gel that

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[a] *D.Q., Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto. Universidade de São Paulo. Av Bandeirantes 3900 CEP 14040-901, Ribeirão Preto, SP. Brazil. Fax: 55 16 3602 4838; Tel: 55 16 3602 4860; E-mail: greg@usp.br*

maintained its consistency. This suspension is poured over 200 cm^3 of 0.3 $mol.dm^{-3}$ aqueous NH_4HCO_3 (Malinkrodt) in a large Petri dish (18.5 cm diam.). The reaction between NH_4HCO_3 and trichloroacetic acid generates large amounts of carbon dioxide which permeates through the viscous gel, leaving holes and pores in the final polymeric monoliths. These are white very flexible and light-weighted sponges (see figure 2). SEM images (recorded on a Zeiss EVO-50 microscope) show very intricate polymeric networks, and reveal the existence of smaller pores in these structures, measuring from 1 to 5 microns as shown in figure 3 (0.6 m^2/g according to BET) . The sponges are collected with tweezers and rinsed several times in distilled water to remove residual chemicals. The sponges are then dried at 80^oC for 2 hours. We have prepared CB[6]-free sponges exactly the same way, except for the addition of cucurbituril. These sponges could be used as obtained or cut in smaller pieces according to the experimental needs.

Fig. 2 Top and side view of a 54 % CB[6]-PU sponge.

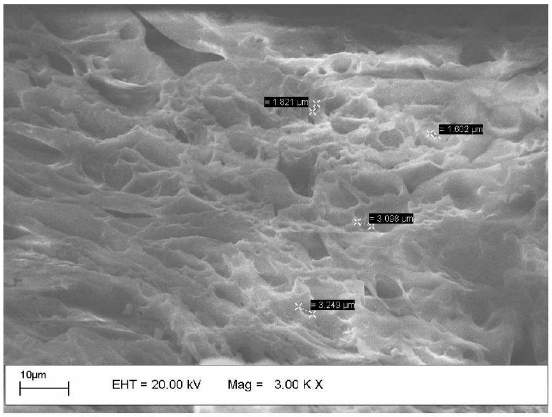

Fig. 3 Scanning electron micrography of a CB[6]/PU sponge (35 %), showing its micro-pores.

To evaluate petroleum absorption capacity and kinetics, we have placed small CB[6]/PU sponge blocks to float over fresh water in beakers (liquid surface = 63 cm^2) and 0.6 cm^3 of crude oil from Espirito Santo basin, Brazil (Petrobras, d= 0.76 $g.cm^{-3}$). We made the same using a pure PU sponge. The sponges were weighed on a a Celtac FA2104 precision balance, at intervals of 1, 5, 10, 15, 20, 30, 60 and 120 min. These experiments were carried out in triplicate. Comparing a CB[6]-free sponge with three others, containing 10, 30 and 60 % CB[6], it is clear that the macrocycle plays a major role in oil absorption. After 20 minutes, the macrocycle-free sponge could absorb no more than 35 % of the oil available. As the CB[6] content in the sponges grows, oil saturation amounts increase linearly from 45, 60 and 95 % for the specimens containing 10, 30 and 60 % CB[6] respectively. All sponges were practically saturated after 40 minutes, as shown in figure 4. This is a clear evidence that oil retention capacity is dependent of CB[6] amount in the polymeric matrix.

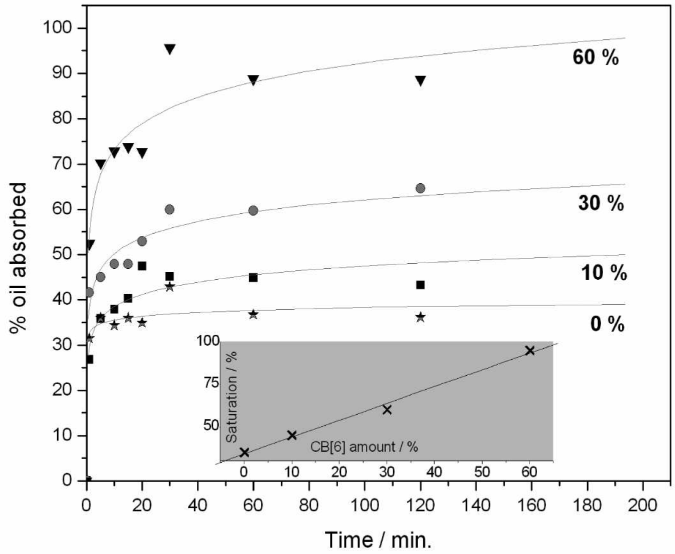

Fig. 4 Absorption test kinetics of petroleum using CB[6]/PU sponges containing 0, 10, 30, and 60% CB[6] in mass. Inset: Oil saturation of the sponges as a function of CB[6] content.

Hard cations may block cucurbit[6]uril portals by complexation, hindering the access of oil components to their cavity. This fact could prevent the formation of caviplexes and reduce their performance in seawater. Such CB[6]/cation complexes could also be leached out from the sponge, since they are more soluble in water than the macrocycle itself[26]. To measure their efficiency in seawater, thin oil stains were produced in beakers (liquid surface = 63 cm^2) placing 0.5 cm^3 of petroleum (the same as above), 0.6 cm^3 soy bean oil (Cargill d= 0.92 $g.cm^{-3}$) or 0.6 cm^3 S10 diesel fuel (Petrobras d=0.83 $g.cm^{-3}$) over 250 cm^3 of natural seawater (Barra da Tijuca, Rio de Janeiro). We have placed small pieces of pure PU sponges and 54 % CB[6]/PU sponges (masses, volumes and results are reported in table1) over the oil stains for two hours at 30^oC. The saturated sponges were weighted on a precision balance and the masses of absorbed oil were calculated by a simple subtraction.

In seawater, the sponges absorption capacity is slightly lowered but CB[6] still plays a major role in absorption. The average recovery efficiency for petroleum was 26.7 % using pure PU sponges and 81.6 % using CB[6]/PU sponges. For soy bean oil, the number is comparable to petroleum (85.1 %). For Diesel fuel, this number rises up to 94.5 %, probably because it contains shorter carbon chains, that interact better with CB[6] cavities[22]. Pure PU sponges may absorb up to 0.2 times its weight of crude oil, while 54% CB[6]/PU sponges do adsorb 2.4 times its weight in petroleum, 2.5 times in soy bean oil, and 3.1 times in Diesel. In terms of area, it means that pure PU sponges would clean a stain if it would cover not less than 12 % of its area, while CB[6]/PU would do the same covering just 3 % of it. Squeezing such sponges, full of oil, in a press (Craver laboratory press, model C 34000/377) we were able to recover what they have absorbed almost quantitatively. Figure 5 reports the recovered oil amounts during 10 successive absorption/squeezing cycles for a single specimen, used as described previously in seawater experiments. After these absorption and squeezing procedures, we were able to recover at least 70 % of the original crude oil. Sponges efficiency is maintained for at least 10 reuse cycles.

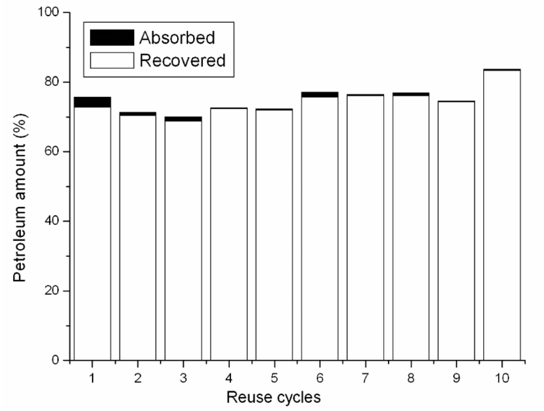

Fig. 5 Total petroleum retained by absorption and recovered by squeezing during absorption/recovery cycles.

In summary, we have demonstrated the sorbent abilities of cucurbit[6]uril immobilised in polymeric sponges towards petroleum, soy bean and Diesel oils. These sponges may absorb up to 3 times their weight in oil, and may be reused up to 10 times for the same purpose, without considerable efficiency loss. These materials are very cheap, and they are excellent alternatives for fresh and seawater remediation after oil spills.

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References

1 F. Moura and R. Lago, *Appl. Catal., B*, 2009, **90**, 436–440.
2 M. Medeiros, M. Sansiviero, M. Araujo and R. Lago, *Appl. Clay Sci.*, 2009, **45**, 213–219.
3 J. Wang, Y. Zheng and A. Wang, *Mar. Pollut. Bull.*, 2013, **69**, 91–96.
4 X. Gui, Z. Zeng, A. Cao, Z. Lin, H. Zeng, R. Xiang, T. Wu, Y. Zhu and Z. Tang, *J. Mater. Chem.*, 2012, **22**, 18300–18305.
5 J. Martins and R. Fernandes, *Water Sci. Technol.*, 1992, **26, 9-11**, 2297–2299.
6 M.-Q. Zhao, J.-Q. Huang, Q. Zhang, W.-L. Luo and F. Wei, *Appl. Clay Sci.*, 2011, **53**, 1–7.
7 P. Calcagnile, D. Fragouli, I. S. Bayer, G. C. Anyfantis, L. Martiradonna, D. P. Cozzoli, R. Cingolani and A. Athanassiou, *ACS Nano*, 2012, **6**, 5413–5419.
8 D. Mowla, G. Karimi and K. Salehi, *Chem. Eng. J.*, 2013, **218**, 116–125.
9 F. D. S. Curbelo, A. I. C. Garnica, E. L. Oliveira and E. L. B. Neto, *Afinidad*, 2006, **63, 521**, 35–39.
10 C. Cojocaru, M. Macoveanu and I. Cretescu, *Colloids Surf., A*, 2011, **384**, 675–684.
11 X. Gui, H. Li, K. Wang, J. Wei, Y. Jia, Z. Li, L. Fan, A. Cao, H. Zhu and D. Wu, *Acta Mater.*, 2011, **59**, 4798–4804.
12 D. Mysore, T. Viraraghavan and Y. C. Jin, *Fresenius Environ. Bull.*, 2004, **13, 6**, 560.
13 D. D. Nguyen, N.-H. Tai, S.-B. Lee and W.-S. Kuo, *Energy Environ. Sci*, 2012, **5**, 7908–7912.
14 J. Wang, Y. Zheng and A. Wang, *Chem. Eng. J.*, 2012, **213**, 1–7.
15 R. Behrend, E. Meyer and F. Rushe, *Justus Liebigs Ann. Chem.*, 1905, **339**, 1–37.
16 A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094–8100.
17 J. Lagona, J. C. Fettinger and L. Isaacs, *J. Org. Chem.*, 2005, **70**, 10381–10392.
18 X.-J. Cheng, L.-L. Liang, K. Chen, N.-N. Ji, X. Xiao, J.-X. Zhang, Y.-Q. Zhang, S.-F. Xue, Q.-J. Zhu, X.-L. Ni and Z. Tao, *Angew. Chem. Int. Ed.*, 2013, **52**, 7252–7255.
19 W.-H. Huang, S. Liu and L. Isaacs, in *Modern Supramolecular Chemistry*, ed. F. Diederich, P. J. Stang and R. R. Tykwinski, WILEY-VCH Verlag, Weinheim, 2008, ch. 4, pp. 113–118.
20 G. Demets, *Quim. Nova*, 2007, **30**, 1313–1322.
21 E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensah and X. Lu, *RSC Adv.*, 2012, **2**, 1213–1247.
22 M. Florea and W. M. Nau, *Angew. Chem. Int. Ed.*, 2011, **50**, 9338–9342.
23 G. Demets, T. Teodosio, H. Correia and T. Cavallini, *Patent application number PI 1.002.556-1*, 2010.

Table 1 Pure PU and 54 % CB[6]/PU sponges absorption tests during two hours using different oils over seawater (63 cm^2). P=petroleum, D=diesel, S=soy bean

CB[6] content (%)	Sponge volume (cm^3)	Sponge mass (g)	Sponge + oil mass (g)	Adsorbed Oil (g)	Recovered (%)	Oil
54	0.4	0.1368	0.4632	0.3264	**85.8**	P
54	0.4	0.1403	0.4409	0.3061	**80.5**	P
54	0.4	0.1361	0.4348	0.2987	**78.6**	P
0	0.3	0.2858	0.3842	0.0984	25.9	P
0	0.7	0.5442	0.6708	0.1266	33.3	P
0	0.5	0.583	0.663	0.08	21	P
54	0.5	0.1554	0.6207	0.4653	**93.4**	D
54	0.5	0.1555	0.6488	0.4933	**98.9**	D
54	0.4	0.1322	0.5872	0.455	**91.3**	D
0	0.4	0.171	0.382	0.211	38.2	S
0	0.4	0.194	0.3995	0.2055	37.1	S
0	0.4	0.1876	0.4032	0.2156	38.9	S
54	0.4	0.173	0.637	0.464	**84**	S
54	0.4	0.1526	0.612	0.4594	**83.1**	S
54	0.4	0.189	0.6768	0.4878	**88.2**	S

24 G. Demets, F. Sousa e Silva and S. de Lima, *Patent application, BR 10 2014 003621-0*, 2014.

25 W. A. Freeman, W. L. Mock and N. Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367–7368.

26 S. Karcher, A. Kornmüller and M. Jekel, *Acta Hydrochim. Hydrobiol.*, 1999, **27**, 38–42.