Capture of Perfluorooctanoic Acid using Oil-Filled Graphene Oxide–Silica Hybrid Capsules

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This document contains:

11 pages (including this cover page)
8 Figures
7 Tables

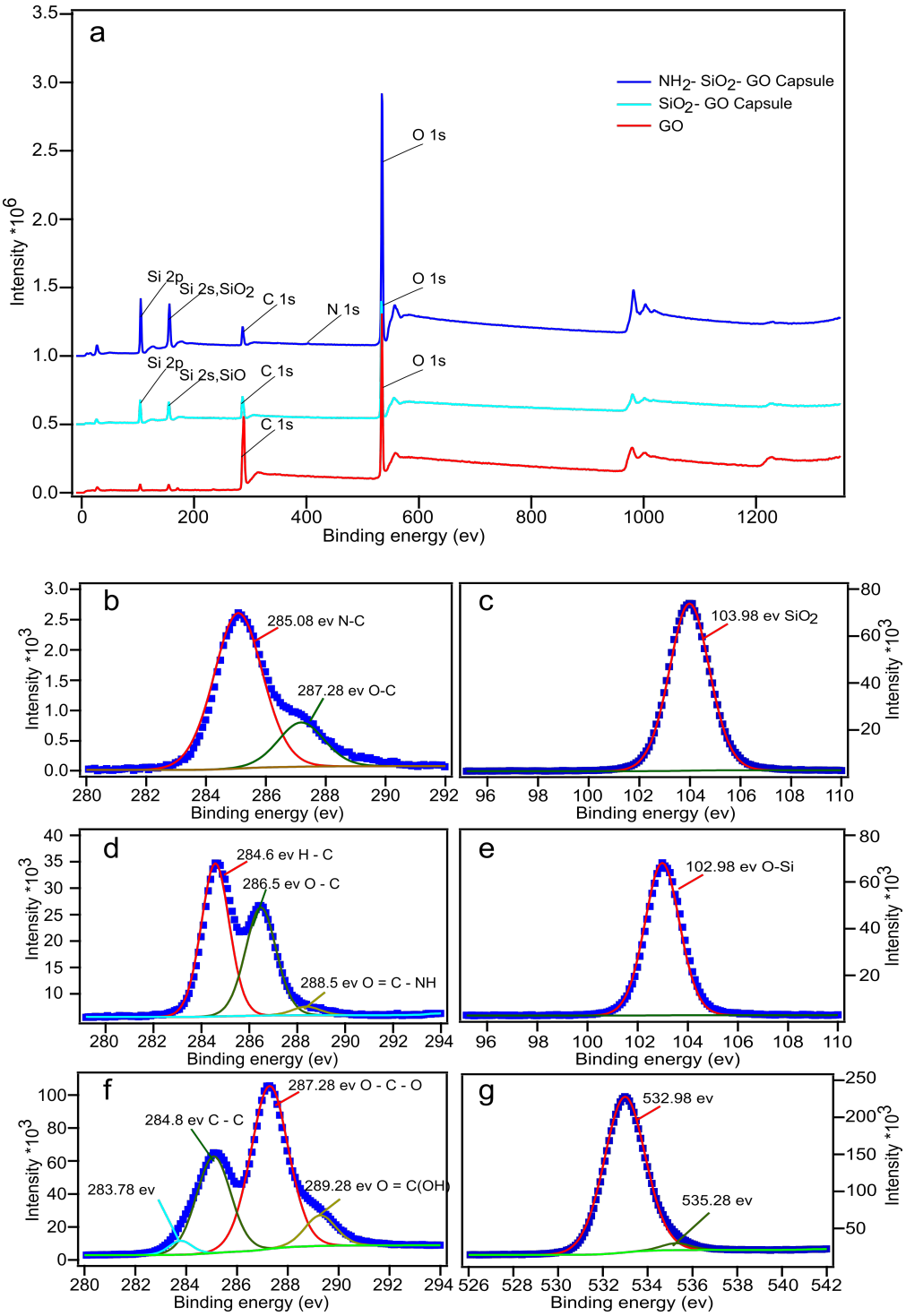

Figure S1. (a) XPS survey spectrum of pure GO, SiO_2-GO microcapsules, and NH_2-SiO_2-GO microcapsules, (b & c) C 1s and Si 2p peaks respectively of NH_2-SiO_2-GO microcapsules, (d & e) C 1s and Si 2p peaks respectively of SiO_2-GO microcapsules, (f & g) C 1s and O 1S peaks respectively of GO sheets. Symbols indicate experimental XPS data, and the solid lines are model fits for individual components.

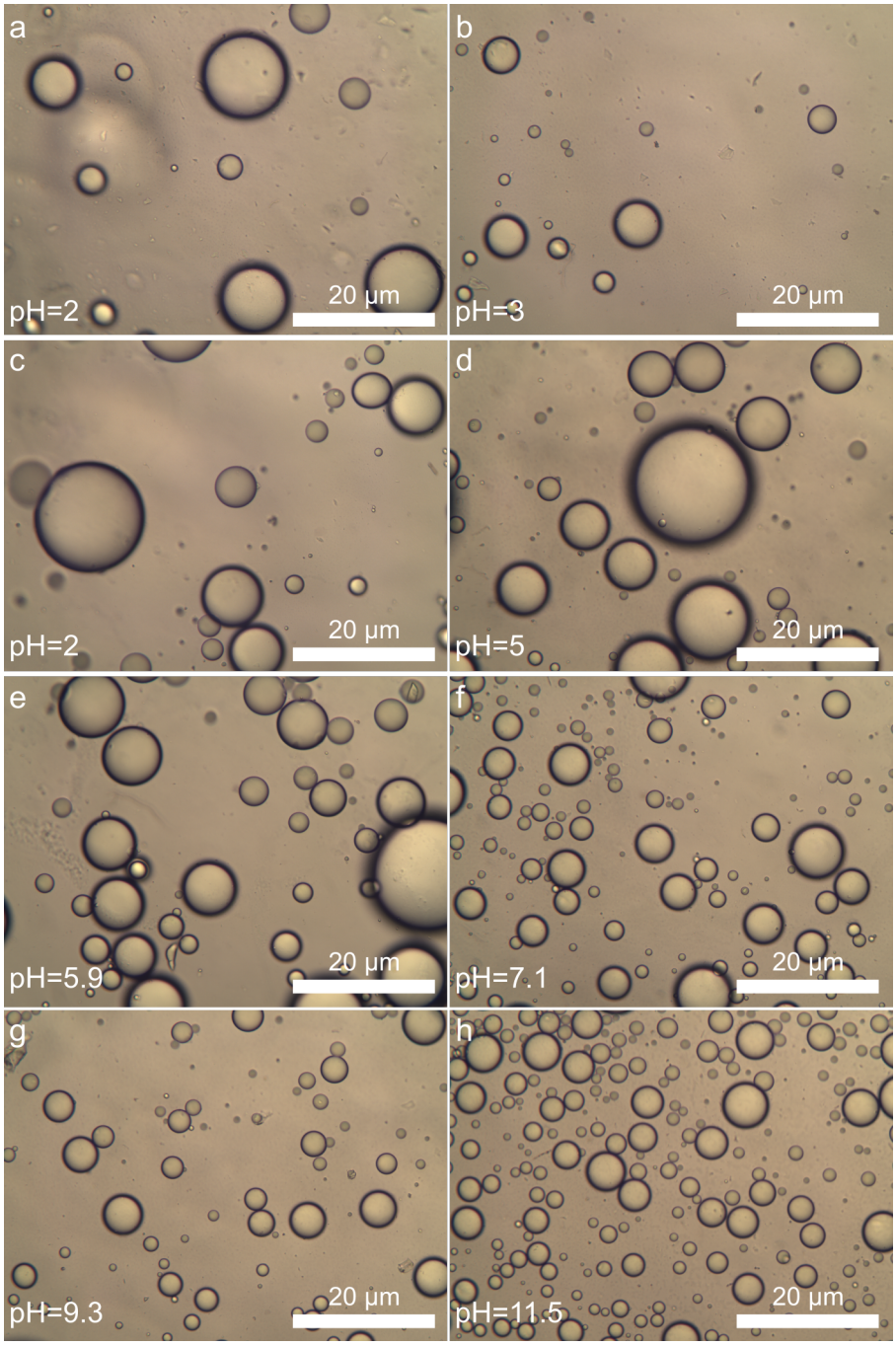

Figure S2. Photographs and optical microscopy images of SiO_2–GO microcapsules prepared from GO-stabilized Pickering emulsions made using 20% TEOS in toluene and 2 mg/mL GO in water at different pHs, with a 1:1 volume ratio of oil:water.

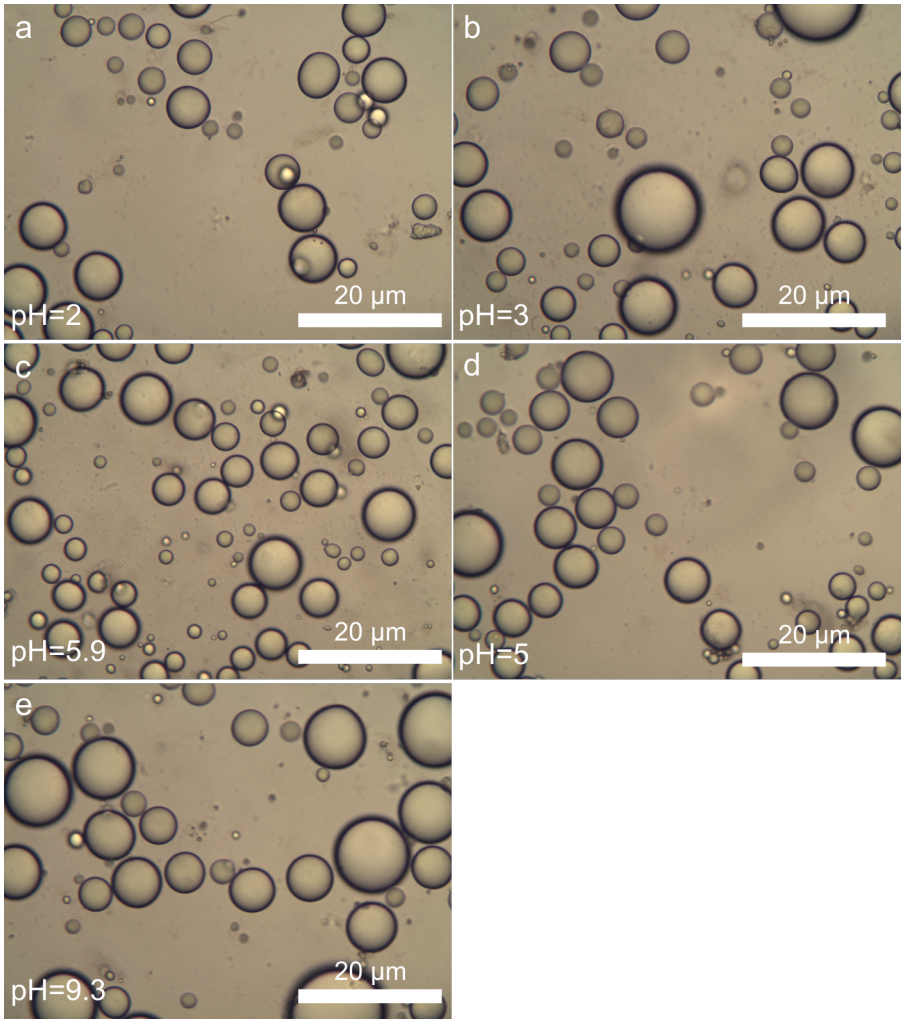

Figure S3. Photographs and optical microscopy images of NH_2-SiO_2-GO microcapsules obtained from GO-stabilized Pickering emulsions as Figure 2 above but with 0.027 wt.% added APTES.

Calibration curve of PFOA: A calibration curve was made using a wide range of PFOA concentrations from 20 mg/L to 600 mg/L, and is shown in Fig S4, covering the desired concentration range under study, linking area under LC peak with the corresponding concentration. This could thereby be applied to determine unknown concentrations of PFOA. The trend shows a linear response with high R^2 = 0.998.

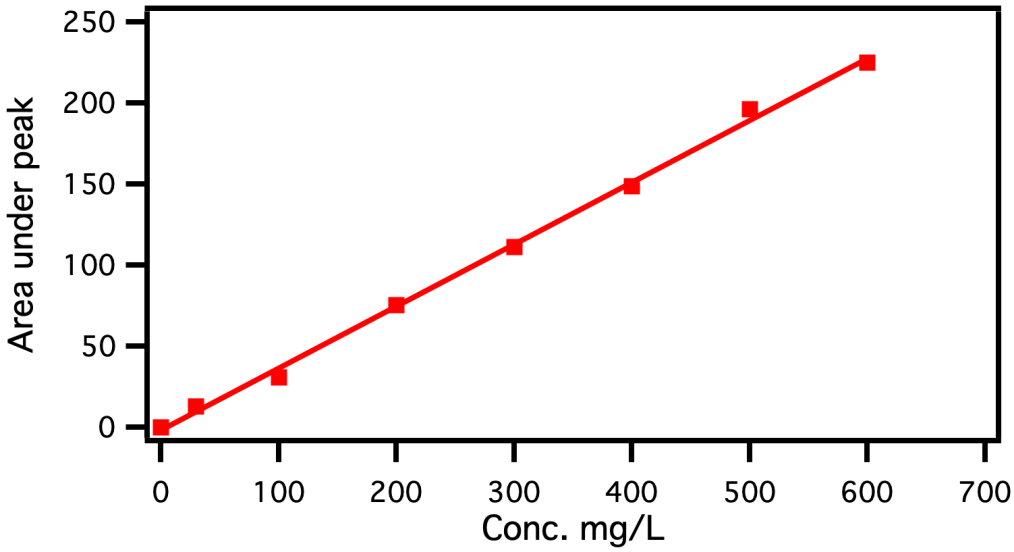

Fig. S4. Calibration curve for PFOA using a wide concentration range (20 mg/L to 200 mg/L); injection amount 5 μL and detection wavelength 205 nm.

Table S1. Tabulated data of corresponding area under peak for different concentrations of PFOA solution.

PFOA concentration mg/L	0	30	100	200	300	400	500	600
Area under peak	0.0	13.0	75.5	75.5	111.1	148.6	196.4	225.0

Effect of initial PFOA concentration on adsorption efficiency of microcapsules: To investigate the optimum efficiency of the PFOA adsorption procedure using microcapsules, adsorbed amount as a function of initial PFOA concentration ranging from 50 mg/L to 600 mg/L was monitored using HPLC (Fig. S2).

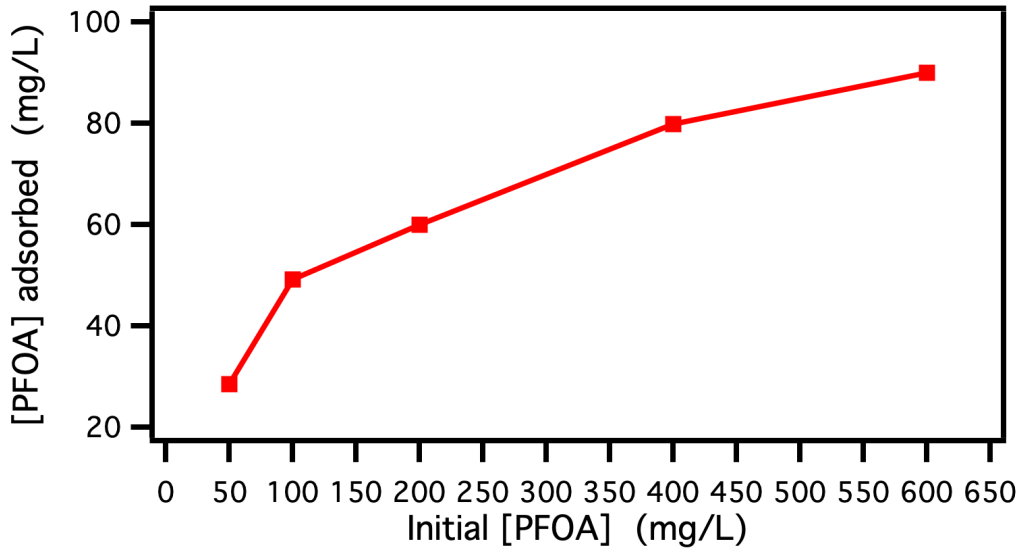

Figure S5. The adsorbed amount of PFOA by NH_2–SiO_2–GO microcapsules for different initial concentrations of PFOA.

Table S2. Tabulated data showing PFOA adsorbed for different initial concentrations of PFOA.

PFOA initial concentration mg/L	50	100	200	400	600
PFOA adsorbed mg/L	28.6	49.2	60.0	79.9	90.0

Effect of injection amount on detection procedure for PFOA: further experiments were conducted to investigate the sensitivity of the polymer column for PFOA. It was found that the adsorption of PFOA corresponding to the area under peak increased with decreasing injection amount, recording 33.8% and 31.0% at 5 μL and 10 μL injection amount respectively. This value decreased significantly to reach 12.7% at 50 μL injection amount (Fig. S3 and table S3). In accordance with these data, the polymer column was used due to its high sensitivity for PFOA detection.

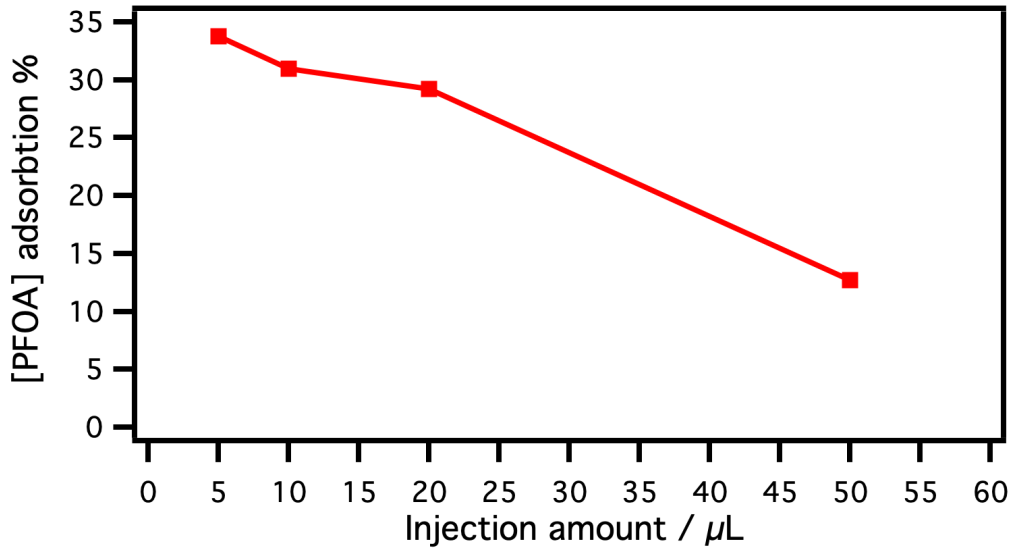

Figure S6. Effect of different injection amounts of 200 mg/L PFOA solution in water on area under peak value.

Table S3. Tabulated data indicating the relationship between injection amount of 200 mg/L PFOA solution of and adsorption %.

Injection amount / μL	5	10	20	50
Area under peak before adsorption	75.5	168.0	346.0	913.0
Area under peak after the adsorption	50.0	116.0	245.0	797.0
Adsorption %	33.75	30.95	29.20	12.70

Table S4. Partitioning quantification for 200 mg/L PFOA between olive oil and water at 1:1 mole ratio at different pH values as determined using HPLC, where AUP= Area under peak and CC=corresponding concentration.

Area under peak / Time/h	pH1		pH2		pH5		pH7		pH10	
	AUP	CC	AUP	CC	AUP	CC	AUP	CC	AUP	CC
0	75.5	200.0	75.5	200.0	75.5	200.0	75.5	200.0	75.5	200.0
2	14.0	37.1	42.0	111.3	57.0	151.0	60.4	160.0	24.0	63.6
5	0.0	0.0	0.0	0.0	54.0	143.0	54.7	145.0	32.0	84.8
9	0.0	0.0	0.0	0.0	42.0	111.3	45.3	120.0	59.0	156.3
17	0.0	0.0	0.0	0.0	31.0	82.1	34.0	90.0	93.0	246.4
24	0.0	0.0	0.0	0.0	23.0	60.9	28.3	75.0	98.0	259.6

Table S5. Effect of pH on PFOA adsorption by NH_2-SiO_2-GO capsules at 1:1 olive oil: water mole ratio, where AUP= Area under peak and CC= corresponding concentration.

Area under peak / Time	pH 2			pH 5		
	AUP	CC (mg/L) of remaining PFOA	CC (mg/L) of Adsorbed PFOA	AUP	CC (mg/L) of remaining PFOA	CC (mg/L) of Adsorbed PFOA
0	75.5	200.0	0.0	75.5	200.0	0.0
30m	44.0	116.6	83.4	56.0	148.3	51.7
1.0h	40.0	106.0	94.0	50.0	132.5	67.5
1:30h	37.0	98.01	102.0	50.0	132.5	67.5
2h	35.0	92.7	107.3	46.0	121.9	78.1
4h	32.8	84.8	115.2	44.0	116.6	83.4
6h	29.0	76.8	123.2	39.0	103.3	96.7
8h	25.0	66.2	133.8	36	95.4	104.6
17h	9.0	23.8	176.2	23.0	60.9	139.1
24h	7.0	18.5	181.5	20.0	53.0	147.0
2 days	0.0	0.0	200.0	13.0	34.4	165.6
3 days	0.0	0.0	200.0	11.0	29.1	170.9
Breaking capsule	73.8	195.5	4.5	78.5	208.0	0.0

Table S6. Effect of pH on the PFOA adsorption by SiO_2-GO capsules at 1:1 olive oil: water mole ratio, where AUP= Area under peak and CC= corresponding concentration.

Area under peak / Time	pH 5			pH 2		
	AUP	CC (mg/L) of remaining PFOA	CC(mg/L) of Adsorbed PFOA	AUP	CC (mg/L) of remaining PFOA	CC (mg/L) of Adsorbed PFOA
0	75.5	200	0	75.5	200	0
1h	67.1	177.7	22.3	69.9	185.1	14.9
2h	72.3	191.5	8.5	70.3	186.2	13.8
3h 30min	75.3	199.5	0.5	69.9	185.1	14.9
4h 15min	72.8	192.8	7.2	67.4	178.5	21.5
6h	73.1	193.6	6.4	61	161.6	38.4
8h	73.5	194.7	5.3	62.1	164.5	35.5
21h	66.1	175.0	25	61.8	163.7	36.3
24h	62.9	166.6	33.4	60.6	160.5	39.5
2 days	73.6	194.9	5.1	47	124.5	75.5
3 days	72	190.7	9.3	45.3	120	80
Breaking Capsule	77.4	205	0	74.6	197.5	2.5

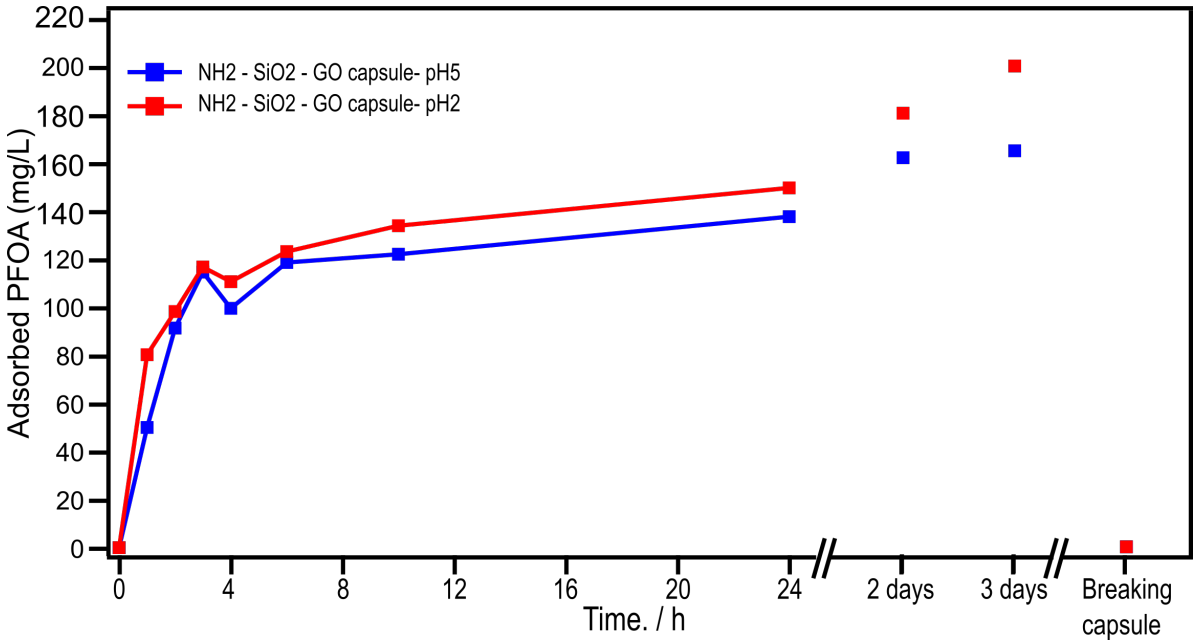

Figure S7. Effects of pH on PFOA adsorption by NH_2-SiO_2-GO microcapsules prepared using 2:1 volume ratio of olive oil: water.

Table S7. Effect of pH on PFOA adsorption by NH_2-SiO_2-GO capsules synthesised using a 2:1 olive oil: water volume ratio, where AUP= Area under peak and CC= corresponding concentration.

Area under peak / Time	pH 5			pH 2		
	AUP	CC (mg/L) of remaining PFOA	CC(mg/L) of Adsorbed PFOA	AUP	CC (mg/L) of remaining PFOA	CC (mg/L) of Adsorbed PFOA
0	75.5	200	0	75.5	200	0
1h	56.6	150.0	50	45.2	119.7	80.3
2h	41.0	108.6	91.4	38.4	101.7	98.3
3h	32.2	85.3	114.7	31.4	83.2	116.8
4h	37.9	100.4	99.6	33.7	89.3	110.7
6h	30.7	81.3	118.7	29.0	76.8	123.2
10h	29.4	77.9	122.1	24.9	66.0	134
24h	23.5	62.3	137.7	19.0	50.3	149.7
2days	14.4	38.1	161.9	7.4	19.6	180.4
4 days	13.3	35.2	164.8	0	0	200
Breaking Capsule		201	0		206	0

LC-MS analysis for PFOA adsorption: LC-MS was exploited to measure the decrease of PFOA concentration, after adsorption by microcapsules. Fig. S8 shows the MS signals of PFOA residuals in solution, and the results demonstrate the strong and sharp main signal (red line) 412 (m/z) corresponding to PFOA, with some weak signals at around 350 and 370 (m/z), likely to indicate either PFOA isomerism or contamination.

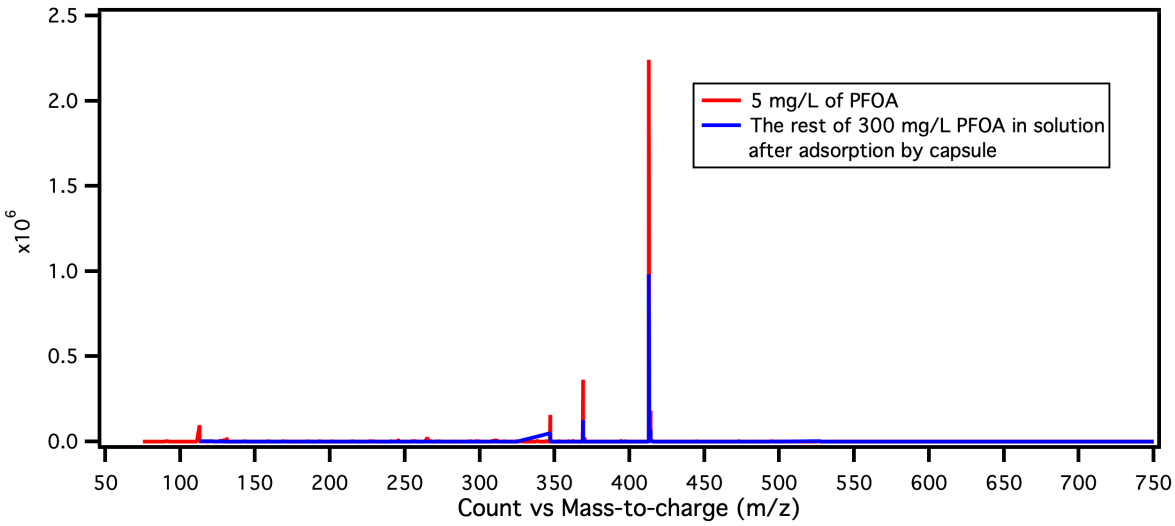

Fig. S8. Mass spectra (MS) of 5 mg/L PFOA solution (red trace) and the remaining PFOA after adsorption by NH_2–SiO_2–GO microcapsules from an initial PFOA concentration of 300 mg/L (blue trace).