Electronic Supplementary Information

Highly stable magnetic multiwalled carbon nanotube composites for solid-phase extraction of linear alkylbenzene sulfonates in environmental water samples prior to high-performance liquid chromatography analysis

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Table S1 Recoveries of LAS homologues sorbed onto the MMWCNTs surface in the presence of foreign inorganic species (LAS homologues concentration: 50 μg L^{-1}).

Co-existing ions	At concentration	Recovery (%)[a]			
		C10-LAS	C11-LAS	C12-LAS	C13-LAS
K^+	100 mg L^{-1}	94.06±6.93	94.37±1.06	101.27±2.65	99.18±3.78
Ca^{2+}	100 mg L^{-1}	49.33±1.73	50.98±0.71	23.34±1.01	39.15±2.16
Ca^{2+}	30 mg L^{-1}	66.47±3.10	63.18±0.67	72.33±1.96	56.33±4.04
Ca^{2+}–NaF*	30 mg L^{-1}	97.83±1.63	91.23±3.46	92.41±5.05	95.04±4.58
Mg^{2+}	50 mg L^{-1}	98.35±1.73	97.46±1.42	95.30±5.31	97.65±1.62
NH_4^+	2 mg L^{-1}	106.01±3.03	98.13±0.95	105.19±1.93	103.39±5.41
SO_4^{2-}	200 mg L^{-1}	101.11±3.03	99.05±4.14	103.31±3.14	102.62±1.08
NO_3^-	50 mg L^{-1}	101.41±3.47	94.87±0.83	94.78±4.10	102.24±3.78
PO_4^{3-}	30 mg L^{-1}	103.25±1.73	96.21±0.35	95.81±1.21	99.56±4.33
CO_3^{2-}	30 mg L^{-1}	99.27±3.03	99.30±1.42	101.95±3.14	94.21±3.24
Al^{3+}	100 μg L^{-1}	98.69±1.81	95.47±2.45	92.94±3.99	94.54±3.06
Pb^{2+}	100 μg L^{-1}	103.05±1.45	102.47±1.67	97.60±2.95	94.18±1.53
Mn^{2+}	20 μg L^{-1}	93.56±4.72	99.40±4.67	103.49±1.91	102.11±5.61
Zn^{2+}	100 μg L^{-1}	98.95±2.90	96.96±4.79	101.77±1.91	96.34±1.53
Fe^{3+}	50 μg L^{-1}	21.45±0.43	21.89±0.24	26.54±1.69	25.77±1.62
Fe^{3+}	30 μg L^{-1}	69.21±2.32	60.48±1.35	56.72±2.78	54.90±3.03
Fe^{3+}–NaF*	30 μg L^{-1}	98.62±1.17	92.11±2.37	95.66±1.30	95.04±2.01

[a] Mean value±standard deviation (n = 3). * NaF concentration: 200 μmol L^{-1}.

Table S2 Recoveries of LAS homologues sorbed onto the MMWCNTs surface in the presence of foreign organic species (LAS homologues concentration: 50 μg L^{-1}).

Co-existing organic substances	Reported concentration	Ref.	Selected concentration	Recovery (%)[a]			
				C10-LAS	C11-LAS	C12-LAS	C13-LAS
Acetic acid	13.01 mg L^{-1}	[1]	10 mg L^{-1}	94.34±1.28	95.24±4.31	91.90±2.85	93.37±2.42
Propionic acid	1.72 mg L^{-1}	[1]	5 mg L^{-1}	92.99±1.92	98.79±1.67	94.67±2.50	97.66±3.64
n-butyric acid	2.71 mg L^{-1}	[1]	2 mg L^{-1}	92.08±5.76	106.57±1.67	106.53±1.43	99.38±6.07
Isobutyric acid	1.25 mg L^{-1}	[1]	2 mg L^{-1}	98.41±7.04	106.91±1.20	101.48±2.85	98.52±3.28
Pentanoic acid	n.d	[1]	2 mg L^{-1}	98.41±7.04	106.91±1.20	101.48±2.85	98.52±7.28
Isopentanoic acid	0.40 mg L^{-1}	[1]	0.5 mg L^{-1}	102.94±5.76	105.39±1.91	103.75±3.21	101.95±4.85
Hexoic acid	n.d	[1]	0.2 mg L^{-1}	99.77±1.28	106.40±1.91	100.73±2.50	101.95±4.85
Phenol	8.43 μg L^{-1}	[1]	10 μg L^{-1}	94.03±3.84	96.93±3.23	91.32±1.60	95.00±1.82
4-methylphenol	1.44 μg L^{-1}	[1]	2 μg L^{-1}	103.34±1.85	103.60±2.07	104.90±3.26	109.28±4.23
Pentachlorophenol	0.56 μg L^{-1}	[2, 3]	0.5 μg L^{-1}	102.48±3.84	105.55±1.67	95.94±2.14	98.52±2.43
Bisphenol A	0.032-0.139 μgL^{-1}	[4,5]	50 ng L^{-1}	103.51±3.71	109.14±3.69	102.14±5.08	96.13±5.64
2,4-dinitrophenol	0.2-6 μg L^{-1}	[6]	2 μg L^{-1}	99.32±3.20	109.78±1.91	109.55±1.43	100.24±7.28
2,4,6-trinitrophenol	0.2-6 μg L^{-1}	[6]	2 μg L^{-1}	102.03±0.64	106.23±1.67	104.51±0.71	99.38±3.64
p-Nitroaniline	5.89×10^{-8}M	[7]	5×10^{-8}M	98.09±0.62	101.16±2.30	108.49±1.81	104.90±5.64
2,4-dinitroaniline	5.18×10^{-8}M	[7]	5×10^{-8}M	103.77±4.95	105.39±3.23	109.78±3.63	108.89±.64
Ciprofloxacin	33-87 ng L^{-1}	[8]	50 ng L^{-1}	94.16±2.47	106.37±1.84	103.37±3.26	103.90±4.23
Fleroxacin	26-61 ng L^{-1}	[8]	50 ng L^{-1}	96.78±3.71	108.98±0.46	105.42±0.36	105.89±4.23
Norfloxacin	＜45 ng L^{-1}	[9]	50 ng L^{-1}	97.65±1.24	104.25±0.23	100.80±3.26	94.93±2.82
Levofloxacin	n.d	[9]	50 ng L^{-1}	95.03±1.24	108.33±0.92	96.96±2.18	101.91±4.23
Toluene	0.75 μg L^{-1}	[1]	0.5 μg L^{-1}	96.78±1.24	103.44±3.23	103.37±4.71	102.90±2.82
Naphthalene	0.16 μg L^{-1}	[1]	50 ng L^{-1}	97.22±3.09	105.07±2.76	108.75±2.18	109.88±1.41
Pyrene	n.d	[10]	50 ng L^{-1}	97.65±2.47	107.51±2.07	110.54±0.36	111.88±1.41
Anthracene	0.011 μg L^{-1}	[10]	50 ng L^{-1}	100.28±1.24	107.67±1.84	104.39±1.81	109.88±4.23

References

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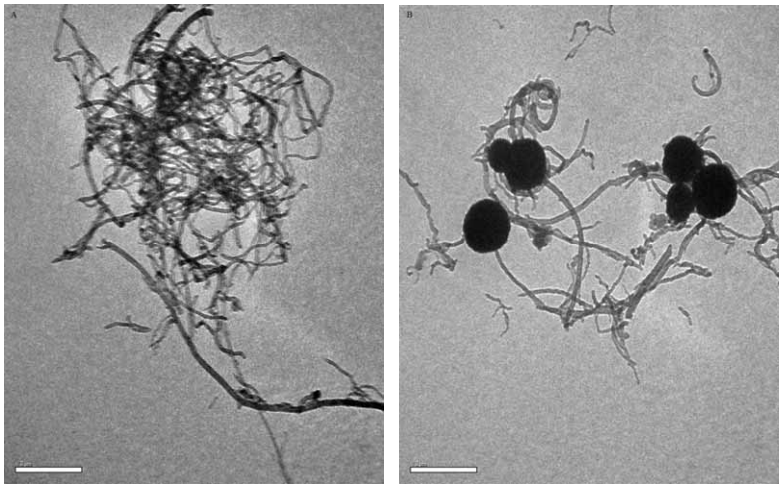
Table S3. Reproducibility of the MMWCNTs as SPE adsorbent for extraction of LAS from water samples.

Compounds	Concentration level ($\mu g\ L^{-1}$)	RSD (%) (for single batch)[a]			RSD (%) (among batches)[a]
		Batch 1	Batch 2	Batch 3	
C10-LAS	9.60	1.9	1.5	1.8	1.5
C11-LAS	15.10	0.7	0.5	0.9	0.6
C12-LAS	14.10	1.2	1.0	1.0	3.2
C13-LAS	11.00	3.8	2.7	2.8	4.8

[a] Averages of three determinations.



A B

Figure S1. TEM images of pristine MWCNTs (A) and magnetic MWCNTs (B).

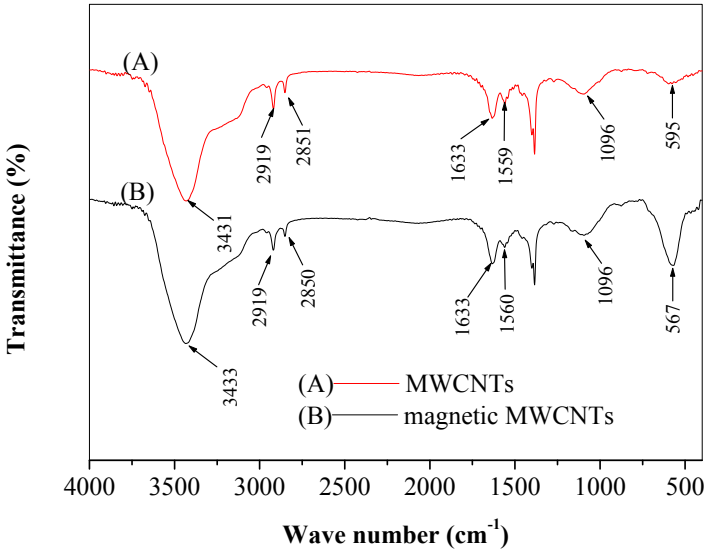


Figure S2. FT-IR spectra of pristine MWCNTs (A) and magnetic MWCNTs (B).

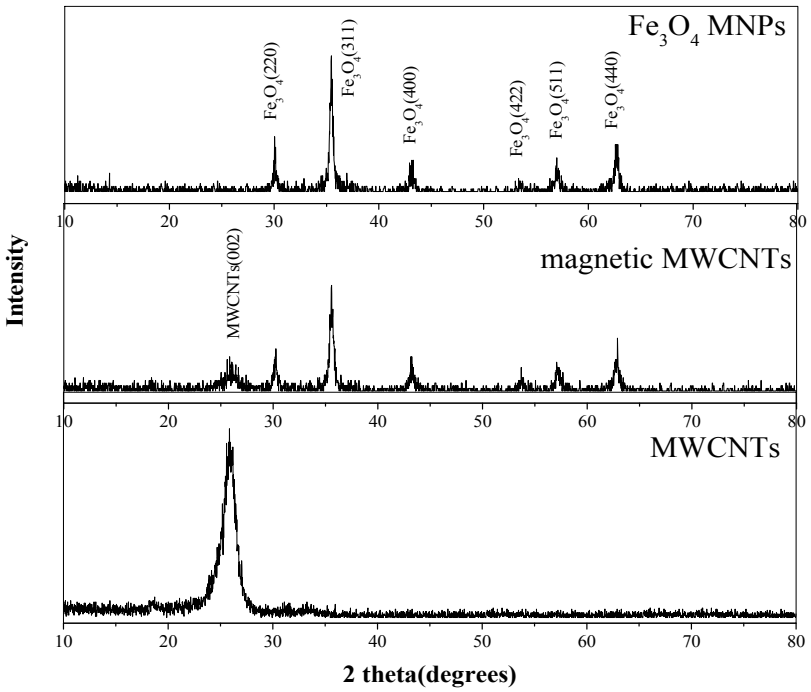


Figure S3. XRD patterns of Fe_3O_4 MNPs, magnetic MWCNTs composites and the pristine MWCNTs.

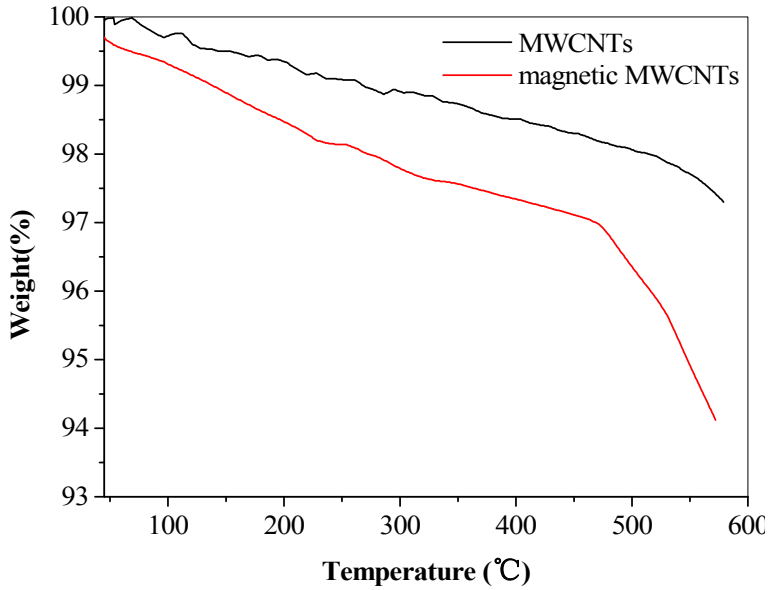


Figure S4. TGA curves of MWCNTs (dark line) and magnetic MWCNTs (red line).

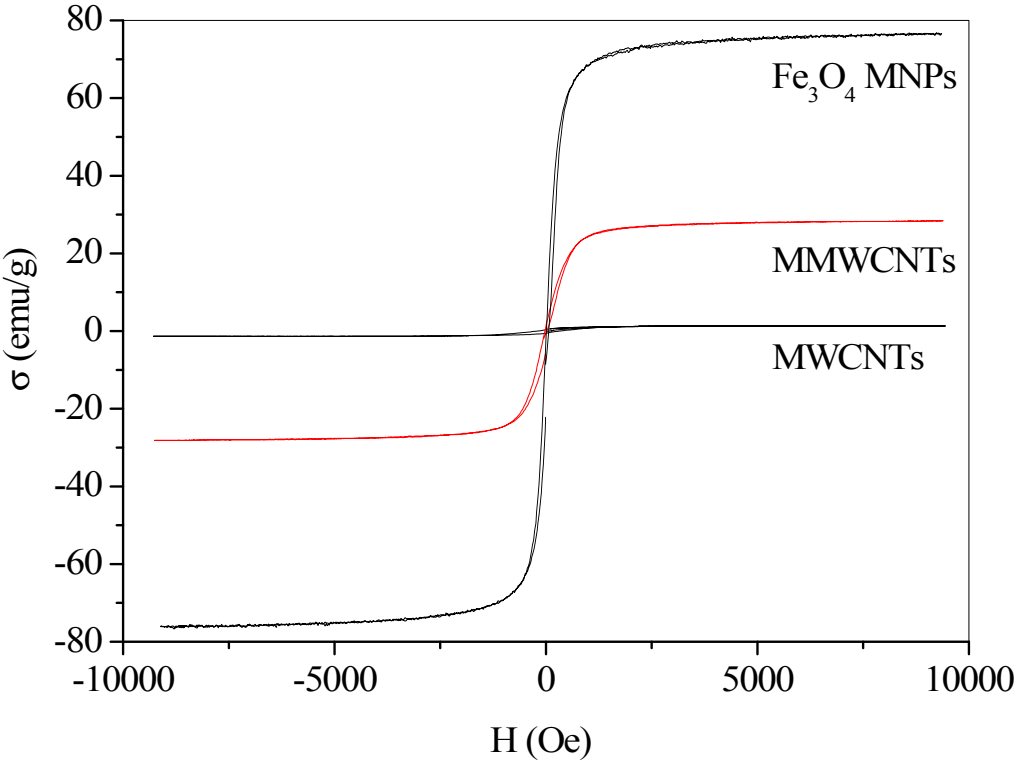


Figure S5. VSM magnetization curves of MWCNTs, Fe_3O_4, and the synthesized MMWCNTs.

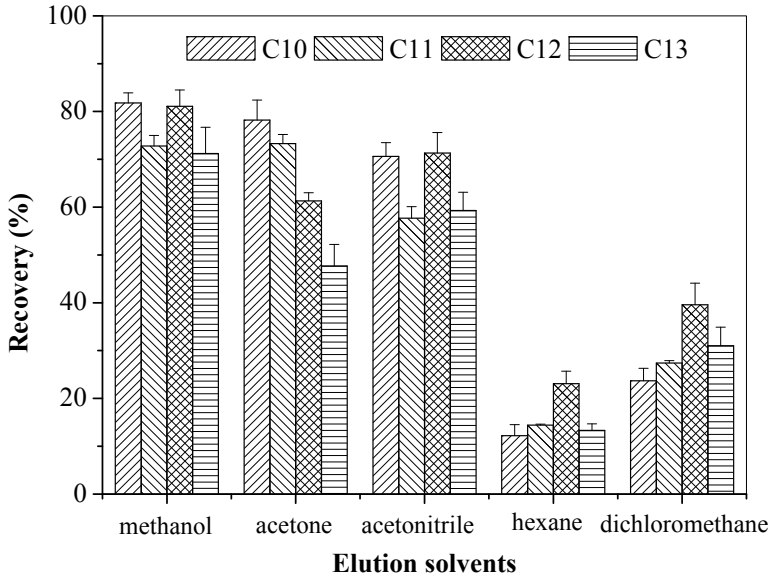


Figure S6. Effect of eluent solvent on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH 5.0); adsorption time: 40 min; adsoption temperature: 40 °C; ultrasonic desorption time: 30 s. Error bars represent one standard deviation for three measurements.

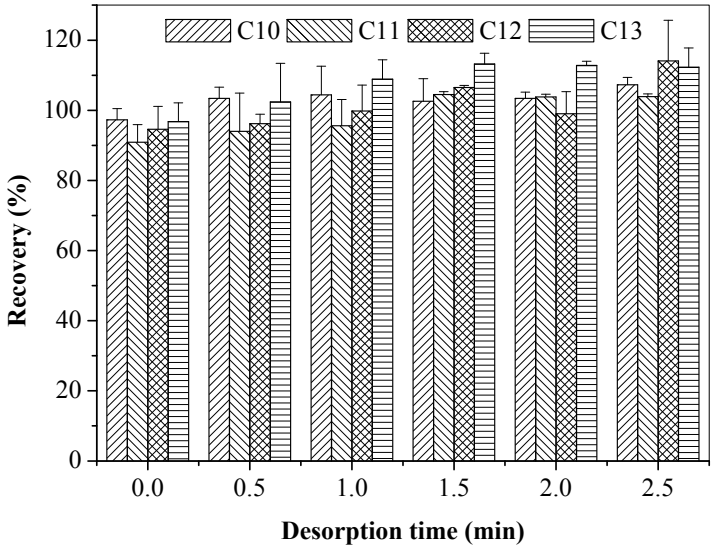


Figure S7. Effect of ultrasonic desorption time on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH 7.0); adsoption temperature: 40 °C; adsoption time: 40 min; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

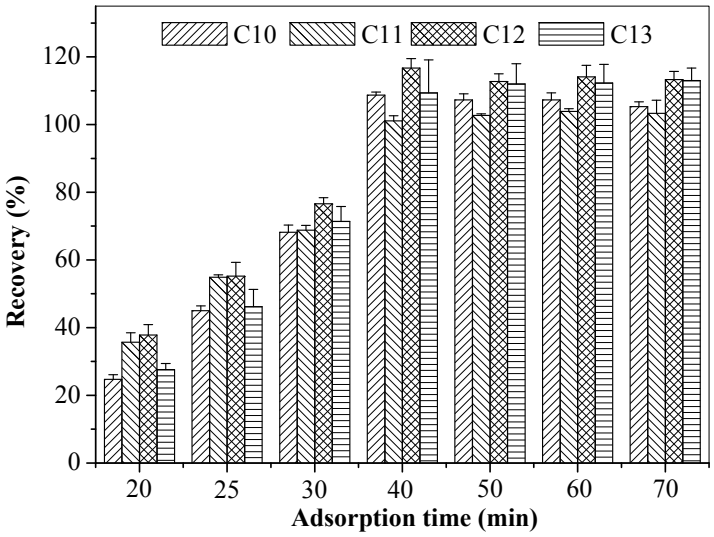


Figure S8. Effect of contact time on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH 7.0); adsoption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

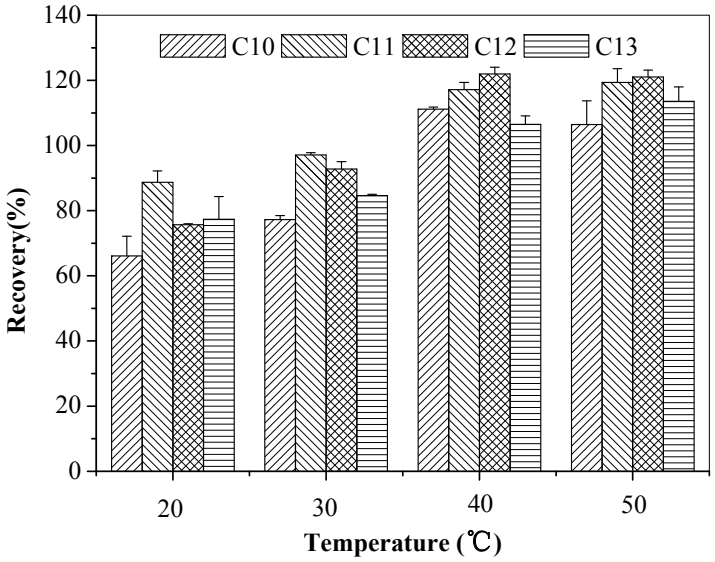


Figure S9. Effect of adsorption temperature on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH 7.0); adsoption time: 40 min; ultrasonic desoption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

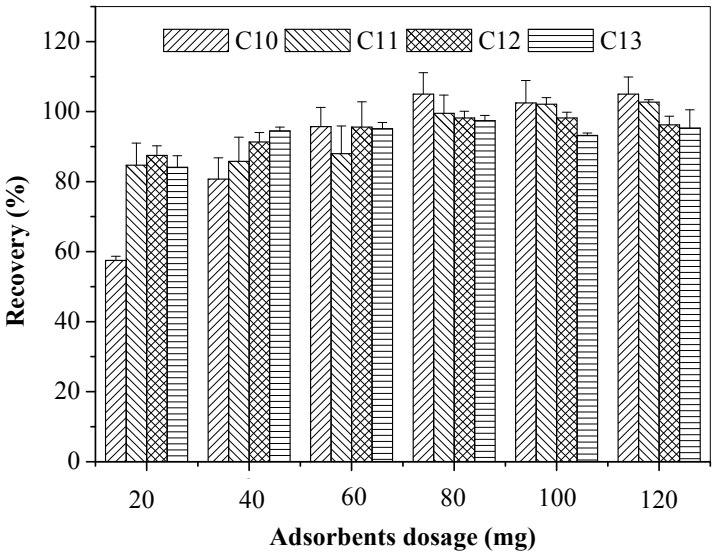


Figure S10. Fig. 2 Effect of amounts of the adsorbents on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH=7.0); adsorption time: 40 min; adsorption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

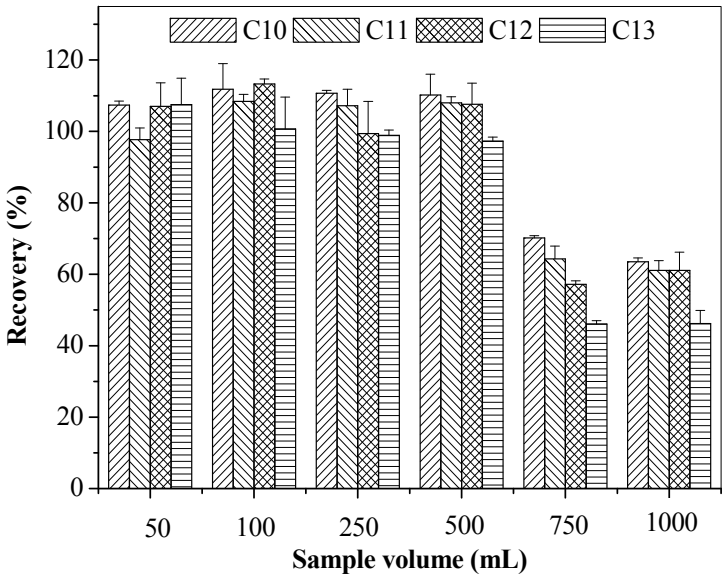


Figure S11. Effect of sample solution volume on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution pH: 7.0; sample solution volume: 100 mL; adsorption time: 40 min; adsoption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

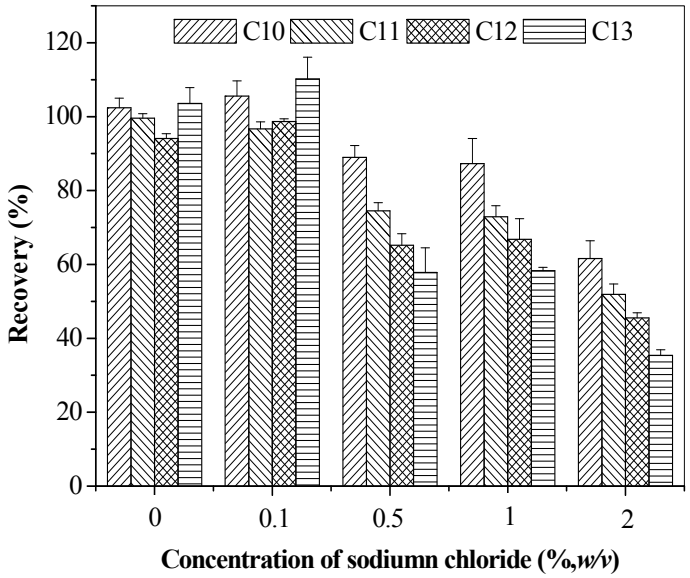


Figure S12. Effect of sodium chloride concentration on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH=7.0); adsorption time: 40 min; adsorption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements. Error bars represent one standard deviation for three measurements.

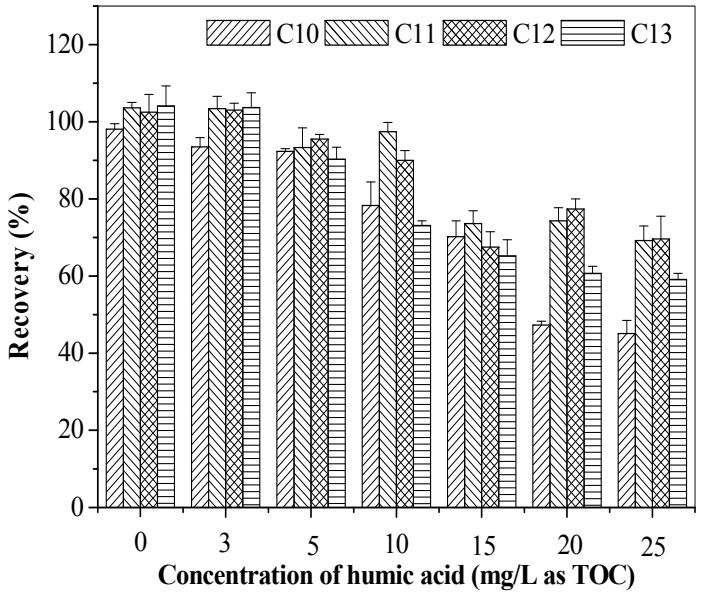


Figure S13. Effect of humic acid concentration on extraction efficiency of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 100 mL (pH=7.0); adsorption time: 40 min; adsorption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol. Error bars represent one standard deviation for three measurements.

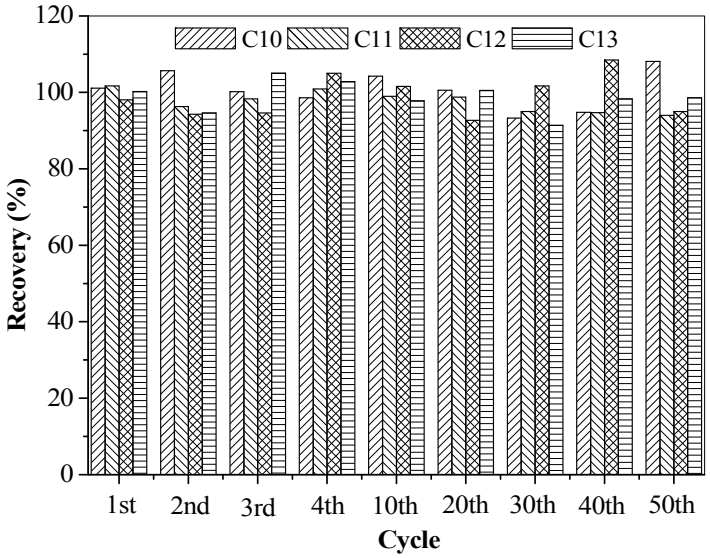


Figure S14. Reusability of the MMWCNTs as SPE adsorbent for extraction of LAS. MMWCNTs: 0.1 g; LAS concentration: 50 μg L^{-1}; sample solution volume: 500 mL (pH=7.0); adsorption time: 40 min; adsorption temperature: 40 °C; ultrasonic desorption time: 30 s; elution: 6 mL methanol.