Supplementary Information

A Facile Synthesis of Monodispersed Hierarchical Layered Double Hydroxide on Silica Spheres for Efficient Removal of Pharmaceuticals from Water

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1. Experimental Section

1.1 Materials

Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99%, Merck), Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99%, ACROS Organics), Ammonia (28-30 wt%, Merck), Tetraethyl orthosilicate ($Si(OC_2H_5)_4$, ≥ 99%, Sigma-Aldrich), Ethanol (C_2H_5OH, >99%, Sigma-Aldrich), Cobalt(II) nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 98%, GCE), Oxone ($2KHSO_5 \cdot KHSO_4.K_2SO_4$, Alfa Aesar, 4.7% active oxygen) Ibuprofen sodium salt ($C_{13}H_{17}O_2Na$, ≥98%, Sigma-Aldrich), Folic acid ($C_{19}H_{19}N_7O_6$, 96-102%, ACROS Organics) and Diclofenac sodium salt ($C_{14}H_{10}C_{l2}NNaO_2$, Sigma-Aldrich)were used without further purification.

1.2 Preparation of monodispersed SiO_2 spheres

The monodispersed SiO_2 spheres were synthesized using a modified stöber method. Generally, 9.15 mL of Tetraethyl orthosilicate (TEOS) was added quickly into the mixture solution of ethanol, water and ammonia (50 mL, 30 mL, and 10 mL, respectively). The white suspension was stirred vigorously for 17 h. The final solid were washed thoroughly with ethanol and water followed by drying in oven at 60 ^oC for overnight.

1.3 Synthesis of well-dispersed SiO_2@LDH-HSs

The well-dispersed SiO_2@LDH-HSs were synthesized by a slow coprecipitation followed by ultrasound treatment. Briefly, 100 mg of silica spheres were first dispersed in 20 mL of water followed by adding 0.8 mL of aqueous ammonia solution (12.3 mmol) to form Solution **A**. Then 19.2 mL of an aqueous solution containing 0.96 mmol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.48 mmol of $Al(NO_3)_3 \cdot 9H_2O$ was dropped at a constant rate of 60 mL/h into Solution A under vigorous stirring followed by ultrasonication (ultrasonic cleaner, DC200H) for 1 h. The obtained solid was collected and re-dispersed in 40 mL of deionized water under ultrasonication for 1 h. The collection and ultrasonication processes were repeated once. The final solid was re-dispersed in deionized water to form a uniform suspension with a concentration of the solid at around 5 mg/mL. Part of the suspension was dried under vacuum for materials characterization. The as-formed hierarchical

spheres of LDH on SiO_2 were named as SiO_2@LDH-HSs. During this formation process, the free electrolytes introduced by the counter ions were removed. To study the effect of electrolytes, a control sample was prepared without removing the electrolytes (i.e. without washing) under the same experimental conditions. This sample was named as SiO_2@LDH Control-I. Another control sample was synthesized without ultrasound treatment by simple stirring and was named as SiO_2@LDH Control-II. In order to investigate the effect of coprecipitation rate, the experimental parameters including the amount of ammonia, the amount of metal source and the dropping rate of the metal solutions were varied as shown in Table S2. LDH sample without SiO_2 support was prepared using the conventional co-precipitation method as a control sample, in order to study the effect of LDH dispersibility on its efficiency in PhAcs adsorption. Briefly, 75 mL of the mixed aqueous solution dissolved with 75 mmol of $Mg(NO_3)_2 \cdot 6H_2O$ and 25 mmol of $Al(NO_3)_3 \cdot 9H_2O$was added dropwise into 100 mL of aqueous solution of 1.6 M NaOH. The resultant mixture was aged at 80 ^oC for 24 h under continuous stirring. The final solid was collected by centrifugation and washed with deionized water followed by drying in vacuum overnight. This sample was named as LDH-C.

1.4 Adsorption of PhAcs

To obtain the adsorption kinetic of SiO_2@LDH-HSs, the suspension sample containing 5.5 mg of LDH were added into 50 mL of the aqueous solution Diclofenac at 10 ppm or 400 ppm (1 ppm = 1 mg/L). Any mixing/stirring during adsorption process was performed at room temperature. The concentration of Diclofenac in the solution was monitored by High-performance Liquid Chromatography (HPLC) at various time intervals after filtrating the solution using a PTFE syringe filter with an average pore size of 200 nm. The same procedure was repeated for LDH-C dry powder. The adsorption capacities to Diclofenac, Ibuprofen and Folic acid were carried out at room temperature. The suspension sample containing1.1 mg of LDH were added into 10 mL of the aqueous solution containing each PhAcs with their initial concentrations in the range of 10 -1000 ppm. The mixtures were shaken at 150 rpm for 48 h and the concentration of PhAcs in the final

solution was measured with HPLC after filtration with the PTFE syringe filter. The adsorption capacity of LDH-C to Diclofenac was obtained under the same conditions except using a higher amount of LDH (5.5 mg).

In the recycle procedure, the as-prepared suspension sample SiO_2@LDH-HSs containing 50 mg of LDH was added into 15 mL of the aqueous solution of Diclofenac at 50 mg/L under stirring at 300 rpm. After 1 min, the solids were collected by centrifugation and re-dispersed into 9 mL of $Co(NO_3)_2 \cdot 6H_2O$aqueous solution (9.74 mM) as the catalyst. The adsorbed Diclofenac was degraded within 1 min after adding 37.5 mg of oxone [oxone: 0.25 mmol; drug: 2.5 μmol; ratio: 1:100]. Afterward, the regenerated sample was collected and washed with deionized water for the next run by the same procedure. During the whole recycle runs, the same $Co(NO_3)_2 \cdot 6H_2O$ solution bath was reused in order not to generate secondary wastewater.

1.5 Characterization

The particle size and morphology of the samples were observed using transmission electron microscopy (TEM, JEOL 3010) and field emission scanning electron microscopy (FESEM, JEOL JSM 6700 F).Zeta potential of the suspensions prepared with deionized water was measured at room temperature on Zeta PALS Zeta Potential Analyzer Brookhaven Instruments Corporation. Particle size distribution in various suspensions was obtained using dynamic light scattering (DLS) technique on 90 Plus Particle Size Analyzer Brookhaven Instruments Corporation. The powder X-ray diffraction (XRD) patterns of as-prepared samples were recorded on a Bruker AXS D8 X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 20 mA. Fourier transform infrared (FTIR) spectra were obtained on a Digilab FTS 3100 FTIR with a 4 cm^{-1} resolution and in the range of 400-4000 cm^{-1} using a standard KBr disk technique. The thermogravimetric analysis (TGA) were carried outin TA Instrument SDT Q600 using a constant heating rate of 10 ^oC/min from 50 ^oC to 800 ^oC with the air flow rate of 100 mL/min. The metal contents in the samples were obtained by inductively coupled plasma emission spectroscopy (ICP, Perkin-Elmer ICP Optima 2000 DV). The weight percentages of C, H and N elements were determined by an Elementarvario

elemental analyzer. The surface area was obtained from the adsorption isotherms of nitrogen at −196 ^{o}C in a Quantachrome Autosorb-6B apparatus by using the Brunauer–Emmett–Teller (BET) method. The concentration of PhAcs was measured by Agilent 1260 HPLC with a Eclipse Plus C18 column and a VWD detector.The detailed operation condition was summarized in Table S4.

2. Supported Tables and Figures

2.1 Supporting Tables

Table S1 Control samples and the samples synthesized with different experimental parameters.

Sample	Ammonia (mL)	Metal (Mg+Al, mM)	Drop Rate (mL/h)	Removal of electrolytes (Y/N)	Ultrasound treatment (Y/N)
SiO_2@LDH-HSs	0.8	36	60	Y	Y
SiO_2@LDH-Control I	0.8	36	60	N	Y
SiO_2@LDH-Control II	0.8	36	60	Y	N
Ca1	0.4	36	60	Y	Y
Ca2	1.2	36	60	Y	Y
Cm1	0.8	18	60	Y	Y
Cm2	0.8	48	60	Y	Y
Cd1	0.8	36	20	Y	Y
Cd2	0.8	36	100	Y	Y
Cd3	0.8	36	Instant mixing	Y	Y

Table S2 Chemical composition of SiO_2@LDH-HSs and the estimated formula of LDH.

Sample	Mg wt%[a]	Al wt%[a]	N wt%[b]	C wt%[b]	H wt%[b]	H_2O wt%[c]	LDH wt%	Chemical Formula
SiO_2@LDH-HSs	6.42	4.78	0.67	0.09	2.52	6.70	44.4	$Mg_{1.49}Al(OH)_{5.67}(NO_3)_{0.27}(CO_3)_{0.04}\cdot 2.1H_2O$

a, the weight percentages of Mg and Al were measured by ICP method; *b*, the weight percentages of N, C and H were measured by CHN elemental analysis; *c*, the weight percentage of H_2O was determined by the weight loss percentage during 25 ^oC to 200 ^oC from TGA analysis.

Table S3 The performance of various adsorbent materials for pharmaceuticals removal.

Materials	Drugs	Initial Concentration of Drugs	Removal	Contact time for equilibrium (h)	Maximum Capacity (mg g^{-1})	Ref.
SiO_2@LDH-HSs	Diclofenac Ibuprofen Folic acid	10 ppm	96%	<5 min	758 400 332	This work
Molecularly imprinted polymer	Diclofenac	300-1000 ppm	-	2	324.8	[1]
Activated carbon	Ibuprofen	20-60 ppm	-	4	~300	[2]
Carbon nanotube	Ibuprofen	0.05-2 ppm	-	144	101	[3]
SBA-15	Diclofenac	10-300 ppb	60-70%	<15 min	0.34	[4]
Sand columns	Diclofenac	10 ppb	<10 %	4080	-	[5]
Membrane bioreactors	Diclofenac	2.8 ppb	23%	24	-	[6]
Activated sludge	Diclofenac	1 ppb	40%	12	-	[7]

Table S4 Analytical conditions of HPLC for concentration determination of various pharmaceutical compounds in water.

Drugs	**Diclofenac**	**Folic acid**	**Ibuprofen**
Injection volume	20 μL	20 μL	40 μL
Mobile phase	30 v% acetonitrile in phosphate buffered solution pH 7		
Flow rate	1 mL/min	0.5 mL/min	1 mL/min
Temperature	40 °C	40 °C	40 °C
Detector VWD	275 nm	283 nm	222 nm
Analysis time	7 min	5 min	4 min

2.2 Supporting Figures

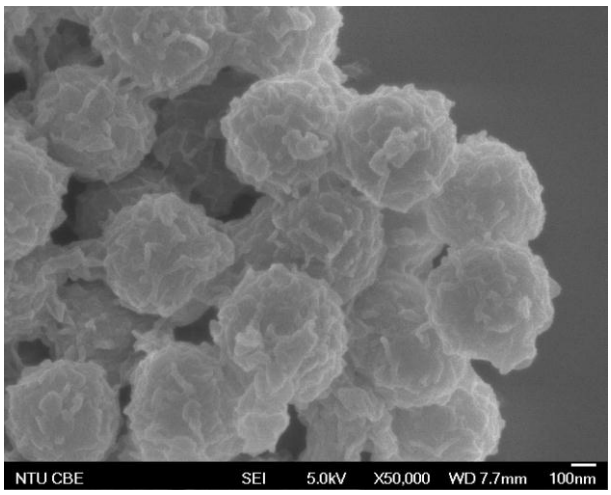

Fig. S1 FESEM image of LDH precursors deposited on SiO_2 after precipitation before ultrasound treatment.

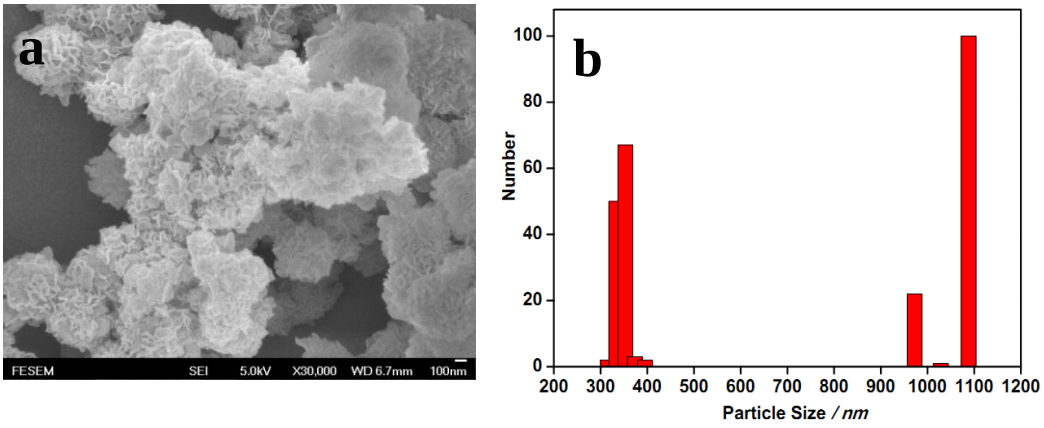

Fig. S2 (a) FESEM image and (b) particle size distribution of SiO_2@LDH Control-I sample without removal of electrolytes.

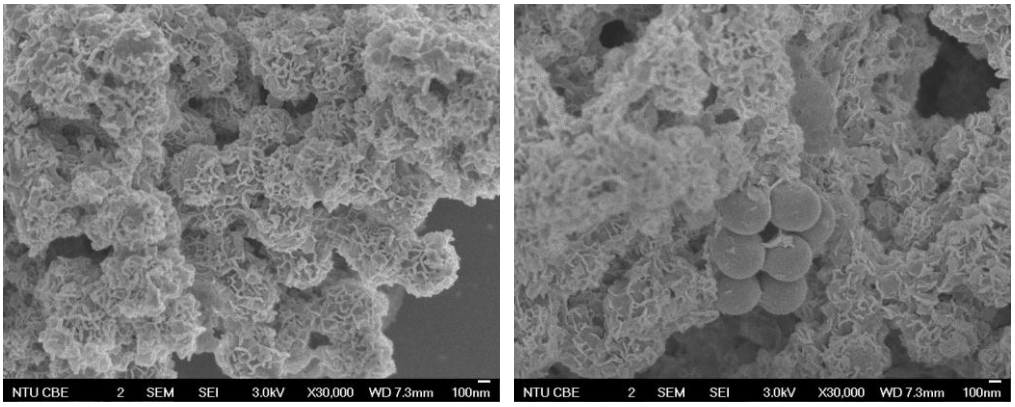

Fig. S3 FESEM images of SiO_2@LDH Control-II sample without ultrasound treatment.

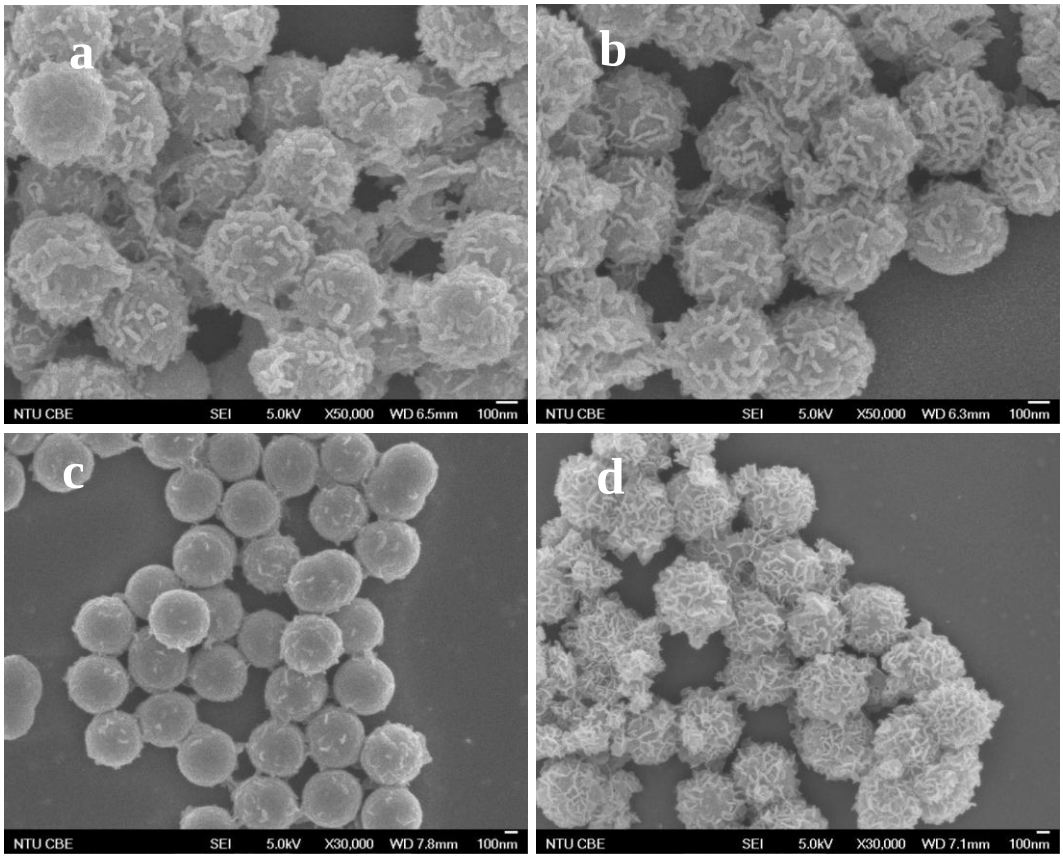

Fig. S4 FESEM images of SiO_2@LDH using different amount of ammonia, (a) Ca1 (b) Ca2, and different concentration of metal precursors, (c) Cm1 and (d) Cm2 (see Table S1).

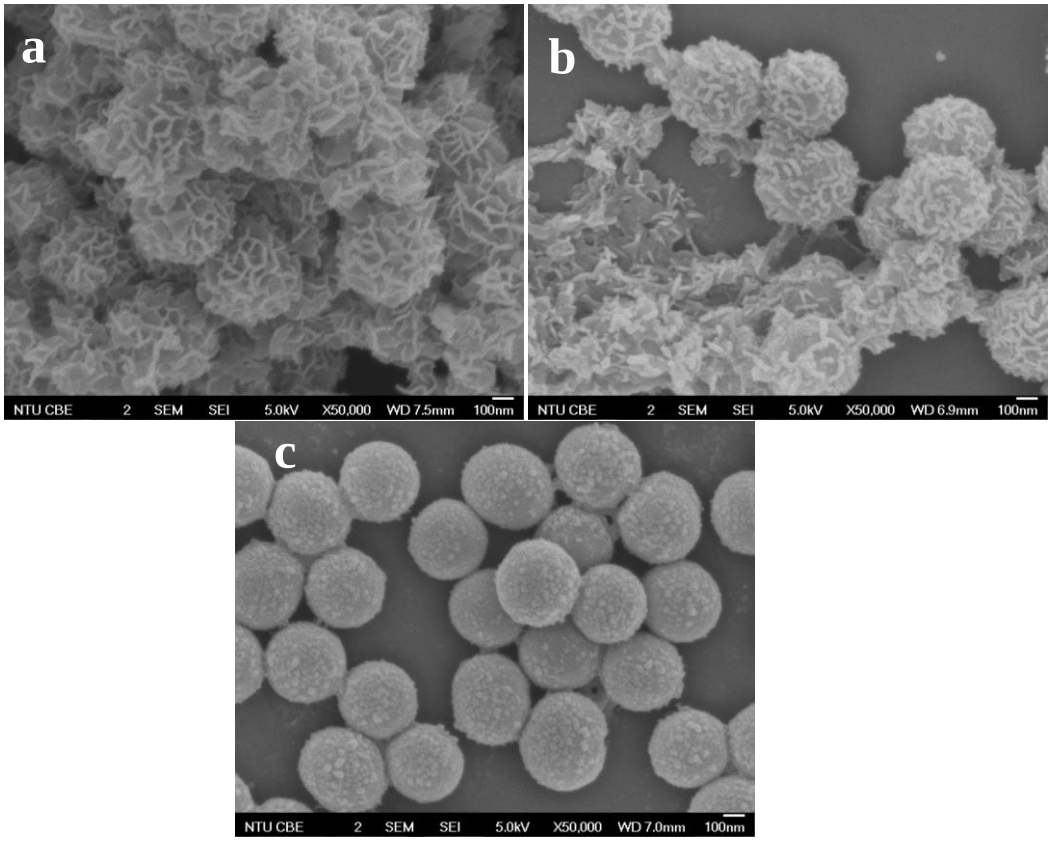

Fig. S5 FESEM images of SiO_2@LDH samples using different addition rate of metal precursor solutions, (a) Cd1, (b) Cd2 and (c) Cd3 (see Table S1).

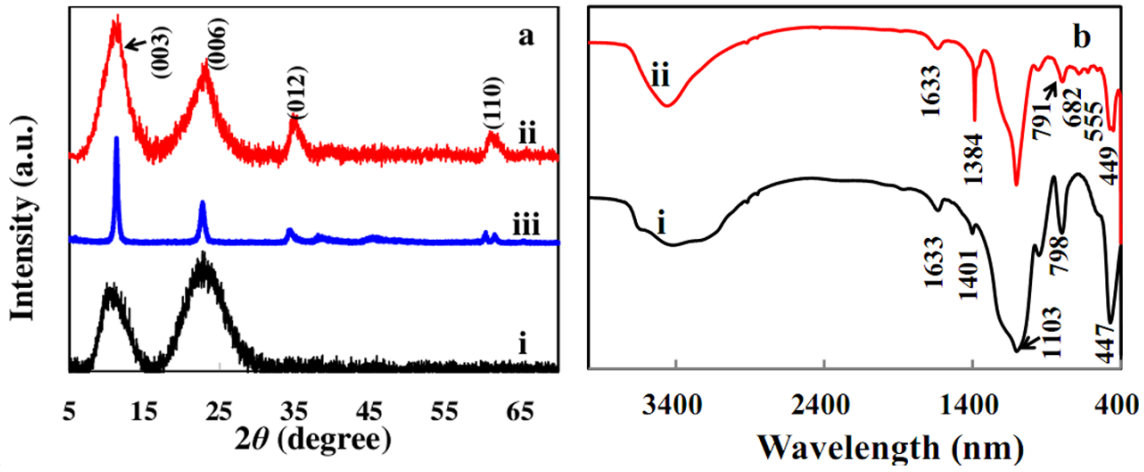

Fig. S6 (a) XRD patterns of (i) SiO_2 spheres, (ii) SiO_2@LDH-HSs and (iii) LDH-C, and (b) FTIR spectra of (i) SiO_2 spheres, (ii) SiO_2@LDH-HSs.

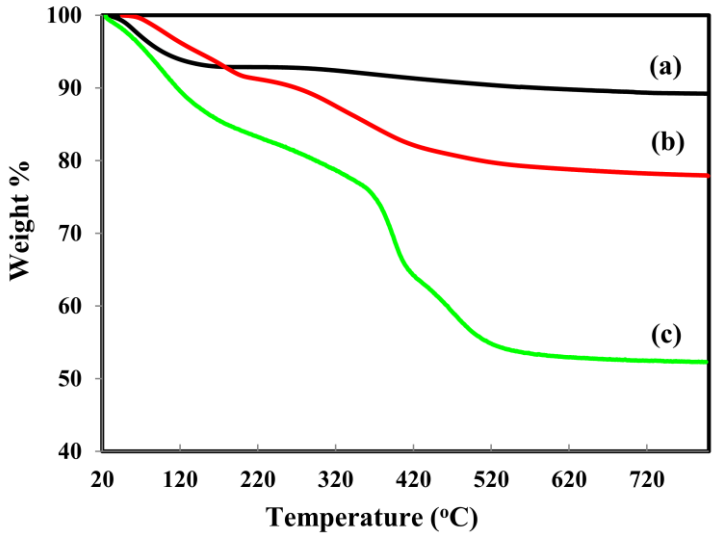

Fig. S7 TGA curves of (a) SiO_2, (b) SiO_2@ LDH-HSs, (d) LDH-C.

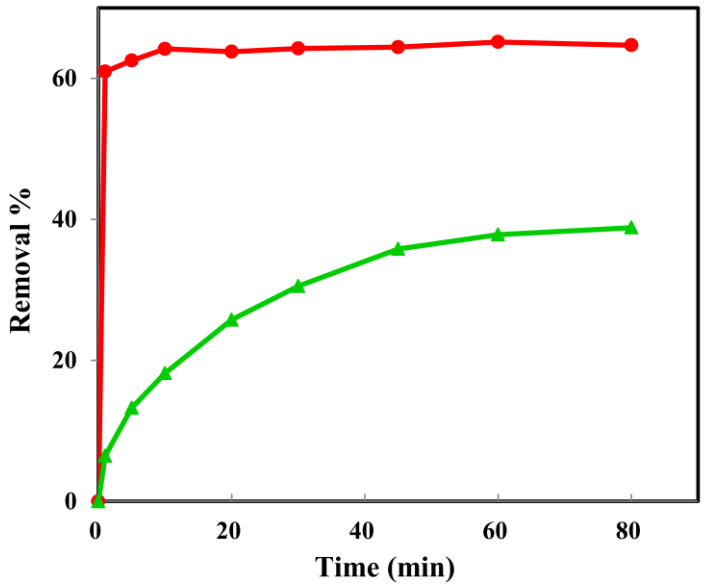

Fig. S8 Kinetic study of Diclofenac on (i) SiO_2@LDH-HSs and (ii) LDH-C. Dosage of LDH: 0.11 g/L, initial concentration of Diclofenac: 400 ppm.

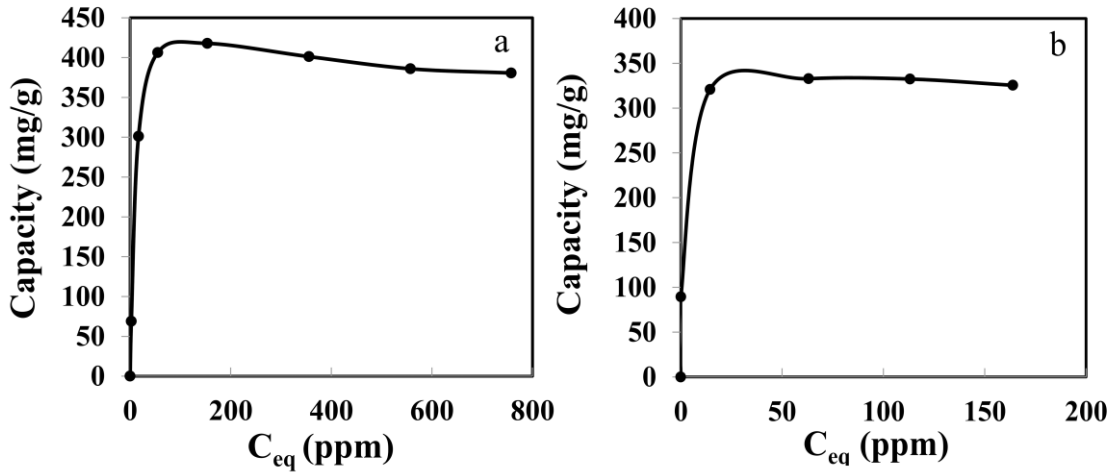

Fig. S9 Adsorption isotherm of (a) Ibuprofen and (b) Folic acid on SiO_2@ LDH-HSs (Dosage, 0.25 mg/mL, 10 mL; Contact time, 48 h).

References:

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