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Phosphorylation Triggered Growth of Metal Phosphate on Halloysite and Sepiolite Nanoparticles: Preparation, Entrapment in Chitosan Hydrogels and Application as Recyclable Scavengers

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S1: Experimental section

S1a: Characterization of materials.

General Commercially available reagents and solvents were purchased from Across and Sigma-Aldrich and used without further purification. Chitosan of high molecular weight (viscosity: 800–2000 cP, 1 wt. % in 1% acetic acid and a deacetylation degree of >75%) was purchased from Sigma-Aldrich and used as received. Sepiolite, referred to as here SP, was purchased from TOLSA. Its degree of purity is superior to 85% and is built from slightly aggregated fibers with length of few micrometers. Halloysite nanotubes, referred herein as HNT, with the following parameters was made available by Dragonites company (Length: 0.2–2 μm , Outside Diameter 50–70 nm, Inside Diameter 15–45 nm). Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum 100FT-IR spectrometer on neat samples (ATR FT-IR) (resolution of 4 cm^{-1} with 32 scan, Perkin-Elmer, Shelton, CT, USA). ^{31}P , ^{27}Al , and ^{29}Si MAS NMR spectra were acquired on a Bruker Avance 400 WB spectrometer (Bruker Biospin, Rheinstetten, Germany) operating at 162 MHz, 104 MHz and 80 MHz respectively, with a magic angle spinning (MAS) speed of at least 4.0 kHz. Nitrogen sorption isotherms at 77 K were obtained with a Micromeritics ASAP 2010 apparatus (Micromeritics, Norcross, GA, USA). Prior to measurement, the samples were degassed for 8 h at 120 °C to remove any physisorbed species. The surface area of the samples was evaluated as $S_g = N_m A / r$, where N_m are the N_2 molecules adsorbed in a statistical monolayer on a gram of sample, A is the Avogadro number and r is the molecular area of adsorbed N_2 (r commonly used being 0.162 nm^2). The values are taking in the range of $0.03 < p/p_0 < 0.3$. Thermogravimetric analyses (TGA) were performed on a Q500 (TA instrument, New Castle, DE, USA) using a heating rate of 10 °C/min from room temperature to 900 °C under air. Prior to measurement, the solid sample was heated in oven at 100°C for 2 hours. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system (Bruker D8 Advance; Bruker Corp, Billerica, MA, EUA) using $\text{CuK}\alpha$ radiation with a step size of 0.02° in the 2θ range from 0.45 to 87° . UV spectra were measured in the 200–800 nm range using spectralon as the reference on a Perkin-Elmer Lambda 1050 spectrometer (PerkinElmer, Labsphere, North Sutton, NH, USA). Scanning electronic microscopy (SEM) images were obtained using a JEOL JSM 6700F (SEMTEch Solution, North Billerica, MA, USA). The samples were dispersed in ethanol and placed onto a carbon coated copper microgrid and left to dry before observation.

S1b: Experimental section.

Synthesis of phosphorylated clay. In a typical procedure, 1mL (1.06 mmol) of POCl_3 was dropped into the suspension of 200 mg of clay (HNT or SEP) in 5 mL of solvent (ethanol, THF or toluene) and the resulting solution was stirred at room temperature for 24 hours. Then 1 mL deionized water were added to mixture and kept under stirring for 2 hours. Finally, the product was collected through centrifugation, was washed several times by ethanol and was dried at 60 °C for 24 h.

Synthesis of phosphorylated cellulose P-CNC. 1mL (1.06 mmol) of POCl_3 was dropped into the suspension of 200 mg of CNC in 5 mL of THF and the resulting solution was stirred at room temperature for 24 hours. Then 10 mL deionized water were added to mixture and kept under stirring for 1 hours. Finally, the product was collected through centrifugation and was dried at 60 °C for 24 h.

Synthesis of phosphorylated Graphene oxide P-GO

80 mg of graphene oxide is dispersed in 250 mL of THF. The mixture is sonicated until the formation of a homogeneous suspension. Then 42.9 mmol of K_2CO_3 is added to the suspension and the mixture is kept under stirring for 3h. Subsequently, 42.9 mmol of POCl_3 is dropped into the suspension and the mixture is kept under stirring for 4 days. The phosphorylated product is

dispersed in deionized water and kept under stirring for 18h. Finally the product is collected through filtration and is thoroughly washed/rinsed with DI water and ethanol.

Synthesis of phosphorylated Silica P-SBA. 0.5 mL of POCl₃ was dropped into the suspension of 100 mg of SBA-15 in 5 mL of THF and the resulting solution was stirred at room temperature for 24 hours. Then 1 mL deionized water were added to mixture and kept under stirring for 1 hours. Finally, the product was collected through centrifugation and was dried at 60°C for 24h.

General procedure for the preparation of chitosan-clay microspheres. Chitosan solution was prepared by dissolving 222 g of chitosan in 10 mL of 1% (v/v) acetic acid solution and stirred for 3 h to obtain homogenous mixture. The various clay particulates (HNT, SEP, P-HNT or P-SEP) were swelled in distilled water and sonicated for 30 min (29 kHz, 150W). The clay suspension was then added to the chitosan solution with clay contents of (10 wt%, 20 wt%, 35 wt% and 50 wt%), followed by stirring at ambient temperature for 2 h. The homogenous chitosan-clay suspension was added dropwise through a 0.8 mm syringe needle into a NaOH solution (0.1 M). The resulting chitosan microspheres were stored in the alkaline solution for 2h and, filtered, and washed until a neutral pH solution. For comparison, pure chitosan microspheres were also prepared in the same way, but without addition of clay.

Synthesis of CS@P-HNT xerogel. The chitosan microspheres CS@P-HNT were dried at ambient temperature for 72.

Synthesis of CS@P-HNT powder. Chitosan solution was prepared by dissolving 177.6 mg of chitosan in 10 mL of 1% (v/v) acetic acid solution and stirred for 3 h to obtain homogenous mixture. 44.4 mg of P-HNT were then added. The new mixture was stirred 2 hours at ambient temperature. Finally, 30 mL of NaOH aqueous solution (4N) were added to trigger chitosan precipitation and the product was collected through filtration and was dried at 60 °C for 24 h.

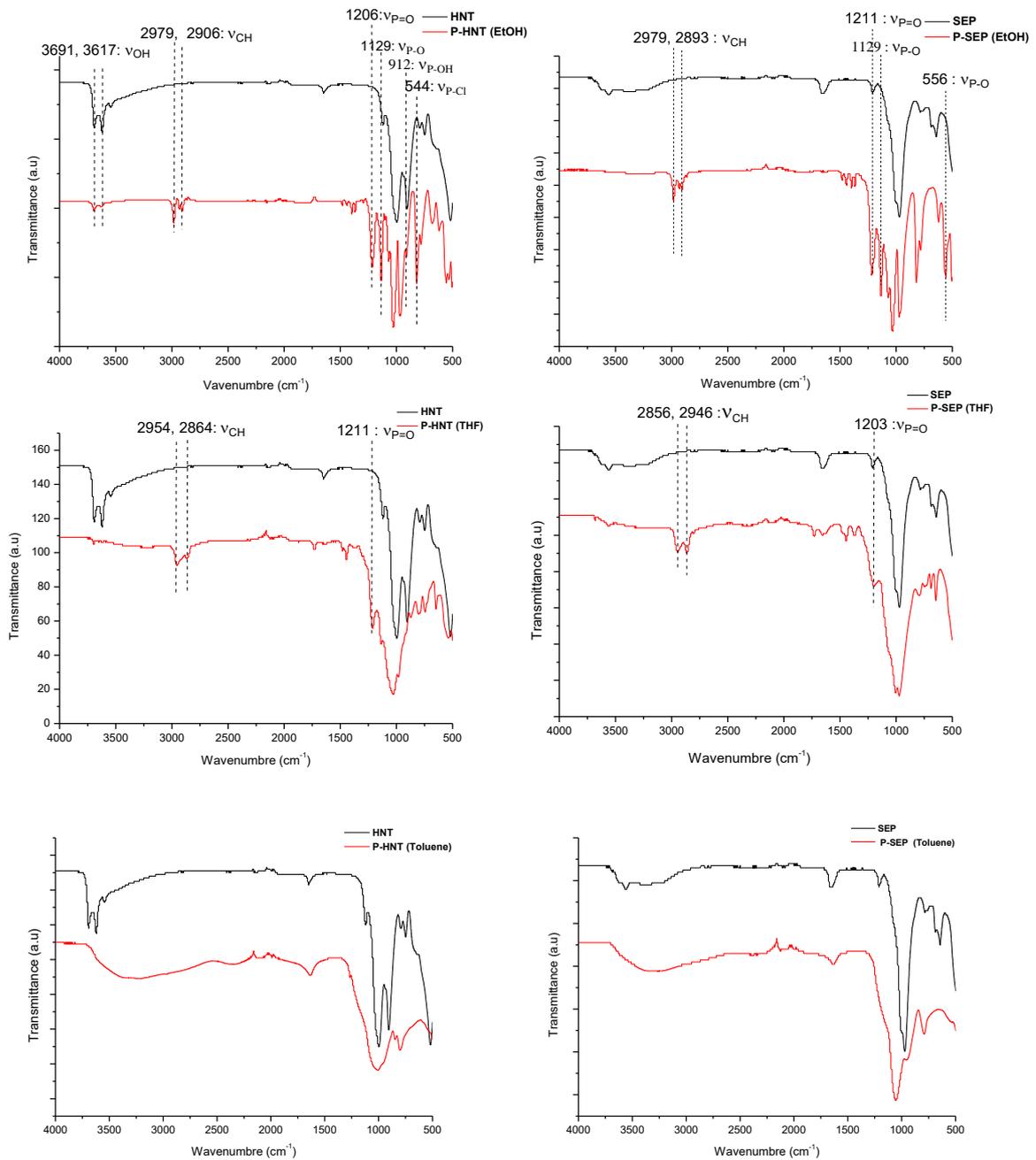
Adsorption study. The adsorption of Congo red (CR) or Malachite green (MG) onto the different materials were examined by the batch adsorption experiments. The Material (8 mg) in dye solution (10 ml) was stirred (450 rpm) at 25 °C. A portion of the solution was withdrawn at specific times to analyze the residual dye concentration using a UV spectrophotometer at (CR: 498 nm, MG: 618 nm). The amount of adsorbed dye was calculated based on the following equation:

$$Q_{ads} = \frac{(C_0 - C_e) * V}{m}$$

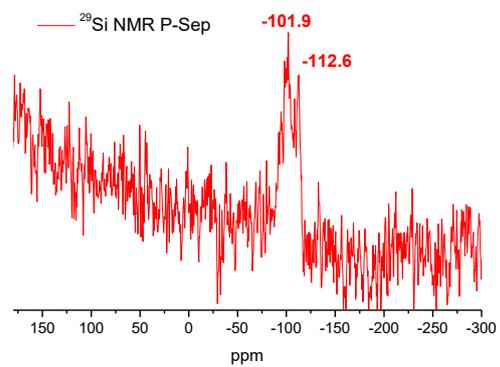
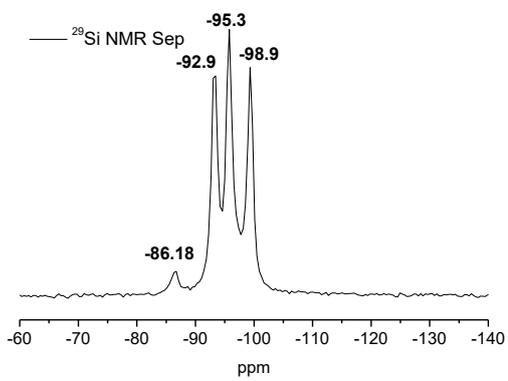
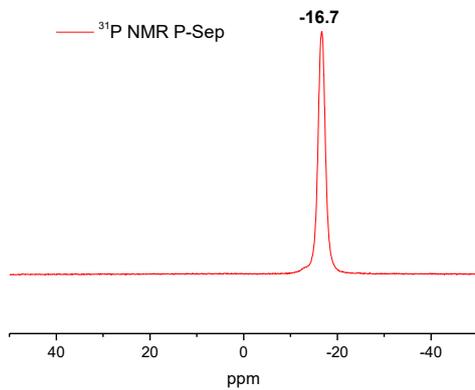
Where C₀ is the initial dye concentration (mg/L), C_e is the dye concentration at time t, V is the solution volume (L), and m is the dry weight of the sample (g).

Reusability study. To determine the reusability of clay materials, successive adsorption-desorption cycles were performed. For desorption, the CR loaded clay powder was treated with 0.05 M NaOH solution (10 mL) for 20 min. After desorption of CR, the powder was collected through centrifugation, was thoroughly washed/rinsed with DI water and ethanol and was dried at 60 °C for 24 h. The CR loaded chitosan-clay microspheres was treated with NaOH solution (2N) (10 mL) for 20 min and washed until a neutral pH solution.

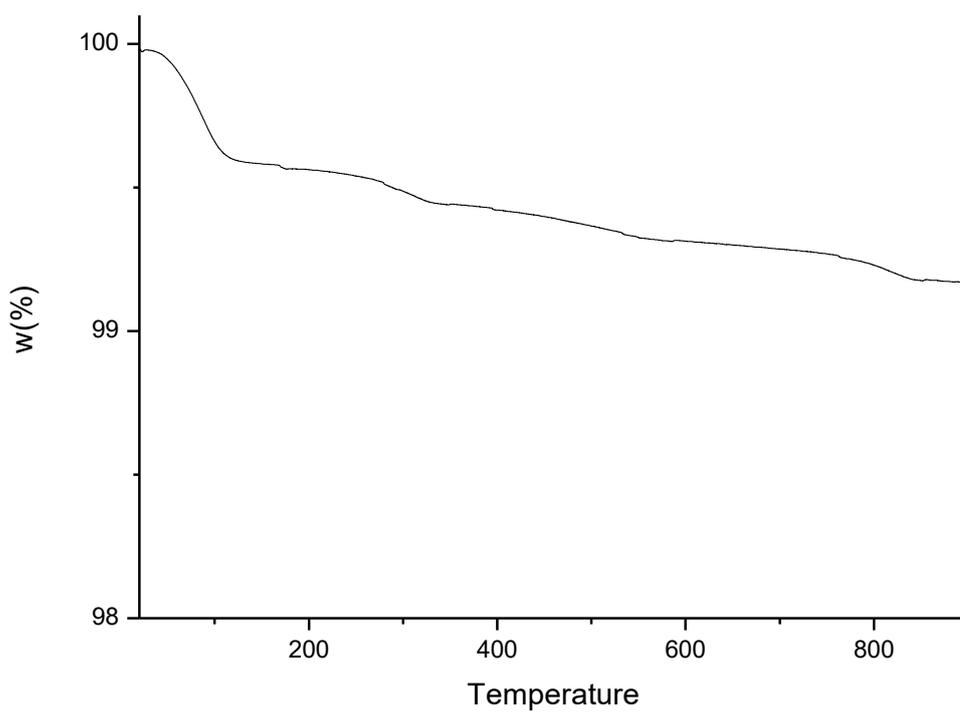
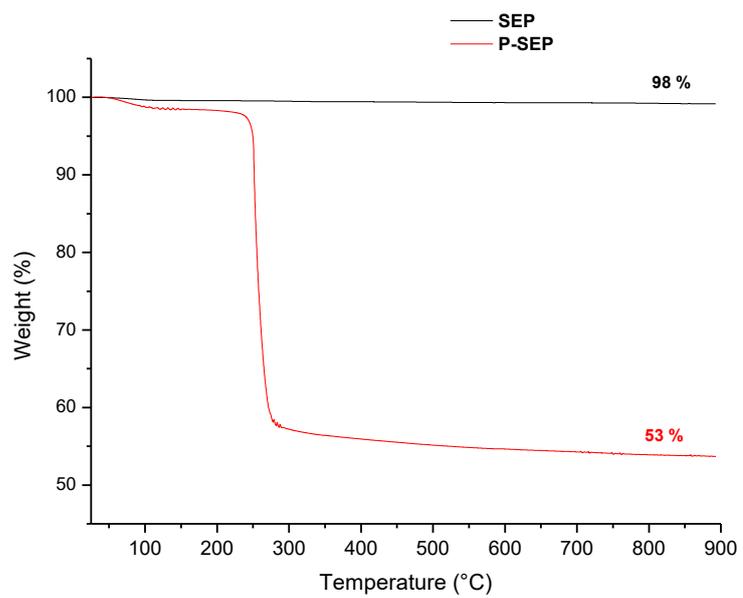
S2. FTIR spectra of phosphorylated Clay



S3. ^{31}P and ^{29}Si CP MAS NMR of SEP and P-SEP

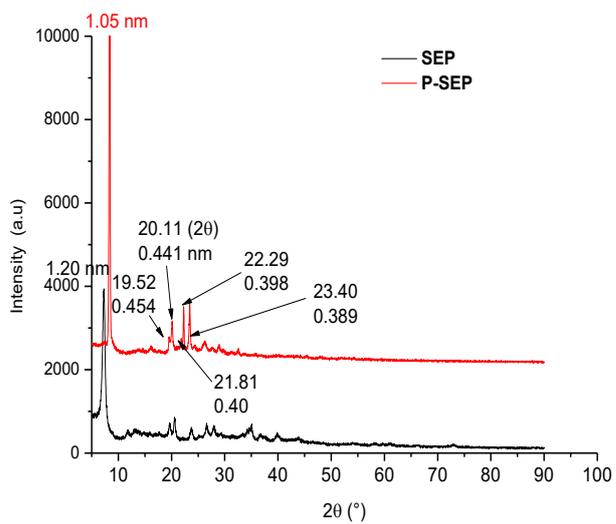
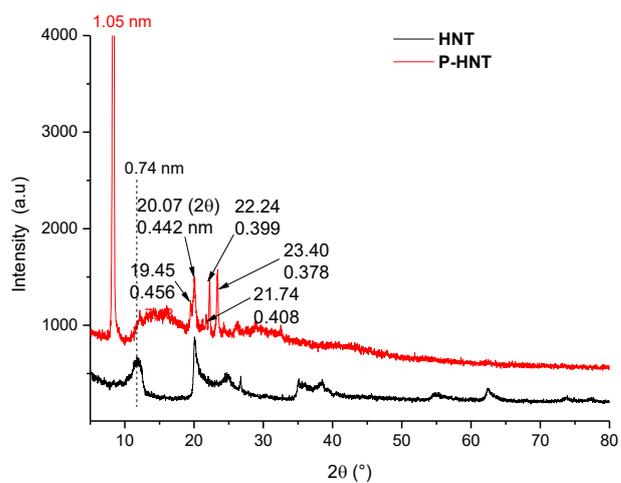


S4. TGA analysis of SEP and P-SEP

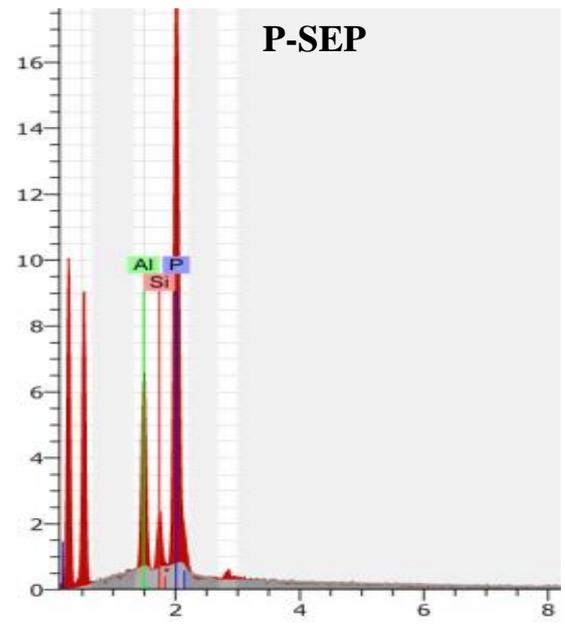
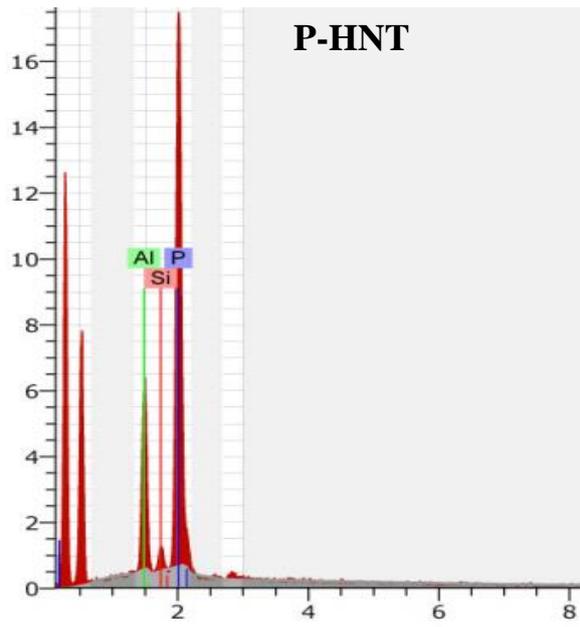


TGA of native SEP.

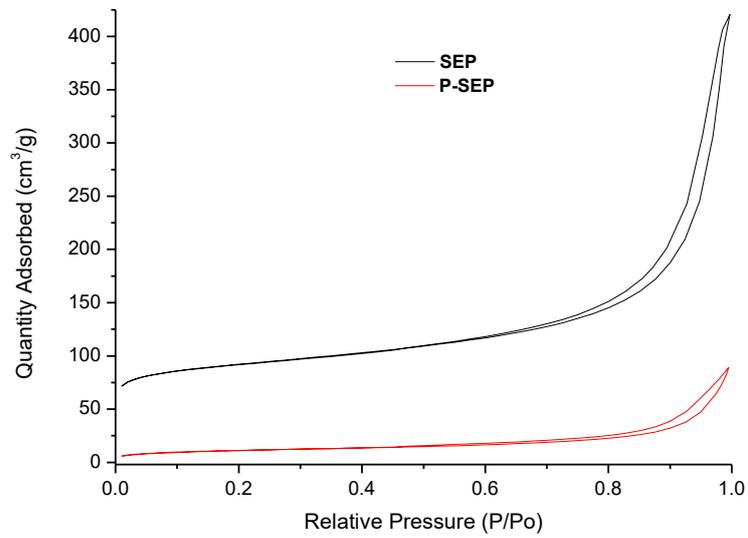
S5. XRD analyses of HNT, P-HNT, SEP and P-SEP



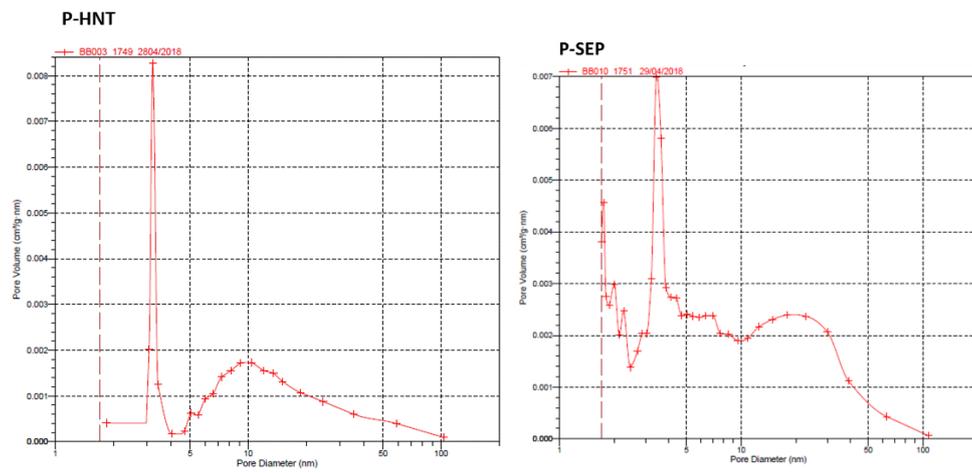
S6. EDX analyses of P-HNT and P-SEP



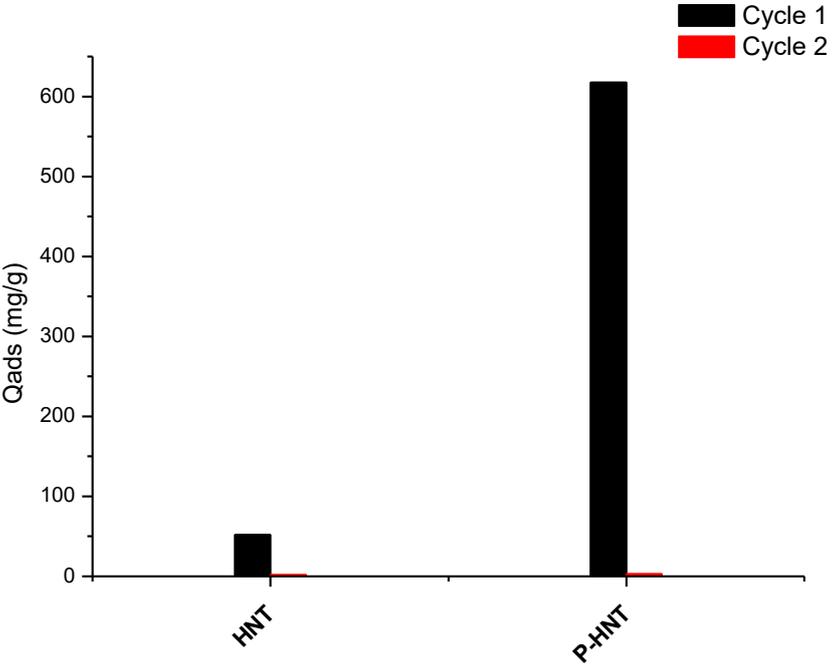
S7. Nitrogen adsorption-desorption of SEP and P-SEP



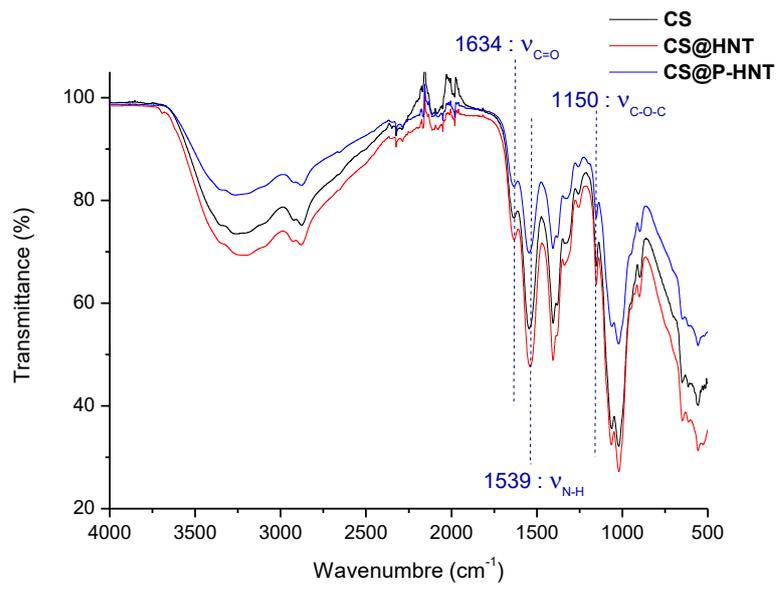
Pore size distribution



S8. Reusability study of HNT and P-HNT



S9. FTIR analyses of CS, CS@HNT and CS@P-HNT microspheres



S10. Comparison of Congo red adsorption by CS@P-HNT hydrogel, CS@P-HNT xerogel and CS@P-HNT powder

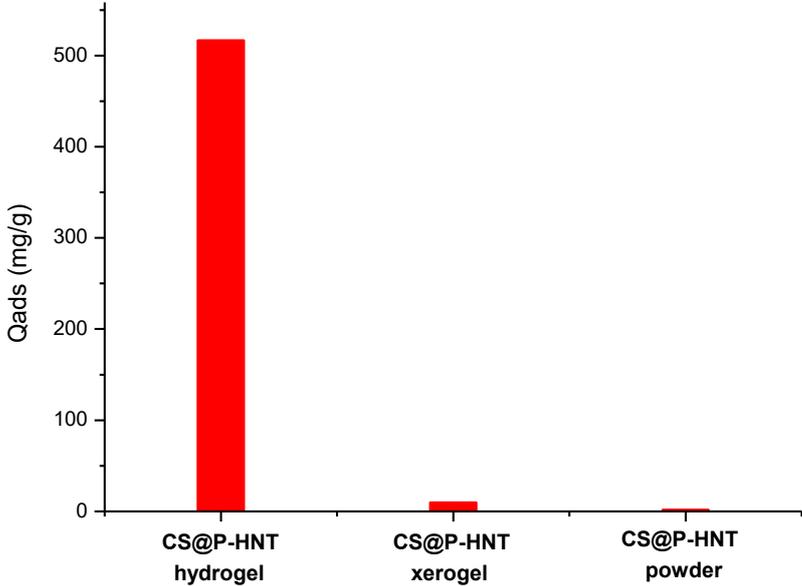


Table S1: Adsorption of congo red dye from aqueous solutions by different materials

Adsorbents	Adsorption capacity (mg/g)	Reference
Na-Bentonite	35.84	[1]
Kaolin	5.44	
Zeolithe	3.77	
CTAB modified chitosan beads	433.12	[2]
ZnO–clay–alginate hydrogel beads	546.89	[3]
NH ₂ -ASEP	539.71	[4]
Fe(OH) ₃ @Cellulose PHFs	689.65	[5]
Amine modified activated carbon (AmMAC1.35)	319.49	[6]
Hierarchical porous zinc oxide (ZnO) microspheres	334	[7]
organo-vermiculite (BDEE-Vt)	298	[8]
organo-montmorillonite (BDEE-Mt)	154	
organo-silica nanosheets (BDEE-SiNSs)	64	
Organo-vermiculites (12-P-12-VT)	197.59	[9]
improved gluten material (IGM)	211.1	[10]
DTA-QS-1.2	684.01	[11]
ZnAl-CO ₃ -LDH	462.96	[12]
ZnAl-NO ₃ -LDH	571.43	
MG-Al-CO ₃ -LDH	934.43	[13]
P-HNT	1238	This work
P-SEP	1238	This work
CS@HNT	704	This work
CS@SEP	733	This work
CS@P-HNT	857	This work
CS@P-SEP	717	This work

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Table S2:

Langmuir, Freundlich, Temkin and the D-R isotherm model constants and correlation coefficients for adsorption of Congo Red on HNT, P-HNT, SEP, P-SEP.

<i>isotherm</i>	<i>clays</i>			
	HNT	P-HNT	SEP	P-SEP
Langmuir				
<i>qm (mg/g)</i>	47.17	1949	227	1887
<i>KL (l/mg)</i>	0.38	0.0873	0.074	0.057
<i>RL (pour C0=100mg/l)</i>	0.025	0.102	0.119	0.149
<i>RL (pour C0=1000mg/l)</i>	0.0026	0.0113	0.013	0.017
<i>R2</i>	0.999	0.991	0.998	0.989
Freundlich				
<i>Kf</i>	42.3	255.7	97.21	198.3
<i>n</i>	62.5	2.18	7.47	2.18
<i>R2</i>	0.766	0.536	0.921	0.618
Temkin				
<i>A (L/g)</i>	1.015	1.733	45.38	0.98
<i>B</i>	0.732	355.63	22.139	353.32
<i>b (j/mol)</i>	3383.274	6.966	111.909	7.0122
<i>R2</i>	0.765	0.66	0.942	0.814
D-R				
<i>β (*10-6)</i>	0.2	3	4	4
<i>qm (mol/g)</i>	46.87	1480	215.78	1318.6
<i>E (kj/mol)</i>	0.129	0.408	0.354	0.354
<i>R2</i>	0.9213	0.921	0.972	0.856