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Synthesis and Characterization of Functionalized Chitosan Nanoparticles with Pyrimidine Derivative for Enhancing Ion Sorption and Application for Removal of Contaminants

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Table S1a. Modeling of uptake kinetics [1-3].

Model	Equation	Parameters	Ref.
PFORE	$q(t) = q_{eq,1}(1 - e^{-k_1 t})$	$q_{eq,2}$ (mmol g^{-1}): sorption capacity at equilibrium k_1 (min^{-1}): apparent rate constant of PFORE	[2]
PSORE	$q(t) = \frac{q_{eq,2}^2 k_2 t}{1 + k_2 q_{eq,2} t}$	$q_{eq,2}$ (mmol g^{-1}): sorption capacity at equilibrium k_2 (g mmol^{-1} min^{-1}): apparent rate constant of PSORE	[2]
RIDE	$\frac{q(t)}{q_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp\left(\frac{-D_e q_n^2}{r^2} t\right)}{9 + 9\alpha + q_n^2 \alpha^2}$ With q_n being the non-zero roots of $\tan q_n = \frac{3\, q_n}{3 + \alpha q_n^2}$ and $\frac{m\, q}{V\, C_0} = \frac{1}{1+\alpha}$	D_e(m^2 min^{-1}) : Effective diffusivity coefficient	[1]

(m (g): mass of sorbent; V (L): volume of solution; C_0 (mmol L^{-1}): initial concentration of the solution).

Table S1b. Modeling of sorption isotherms [4,5].

Model	Equation	Parameters	Ref.
Langmuir	$q_{eq} = \frac{q_{m,L} C_{eq}}{1 + b_L C_{eq}}$	$q_{m,L}$ (mmol g^{-1}): Sorption capacity at saturation of monolayer b_L (L mmol^{-1}): Affinity coefficient	[5]
Freundlich	$q_{eq} = k_F C_{eq}^{1/n_F}$	k_F and n_F: empirical parameters of Freundlich equation	[4]
Sips	$q_{eq} = \frac{q_{m,S} b_S C_{eq}^{1/n_S}}{1 + b_S C_{eq}^{1/n_S}}$	$q_{m,L}$, b_S and n_S: empirical parameters of Sips equation (based on Langmuir and Freundlich equations)	[5]

Akaike Information Criterion, AIC:

$$AIC = N \ln\left(\frac{\sum_{i=0}^{N}\left(y_{i,exp.} - y_{i,model}\right)^2}{N}\right) + 2N_p + \frac{2N_p\left(N_p+1\right)}{N - N_p - 1}$$

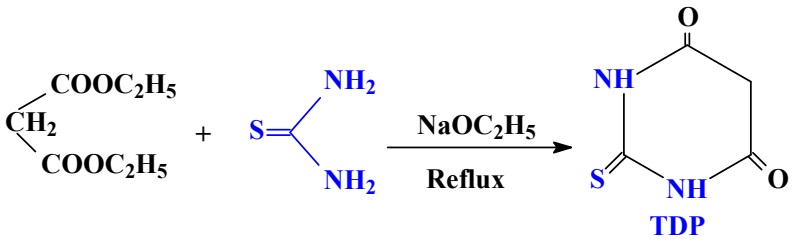
Where N is the number of experimental points, N_p the number of model parameters, $y_{i,exp.}$ and $y_{i,model}$ the experimental and calculated values of the tested variable.

Table S2. Cost evaluations of 10 g MC-TDP sorbent for treatment of Cr(VI) ions.

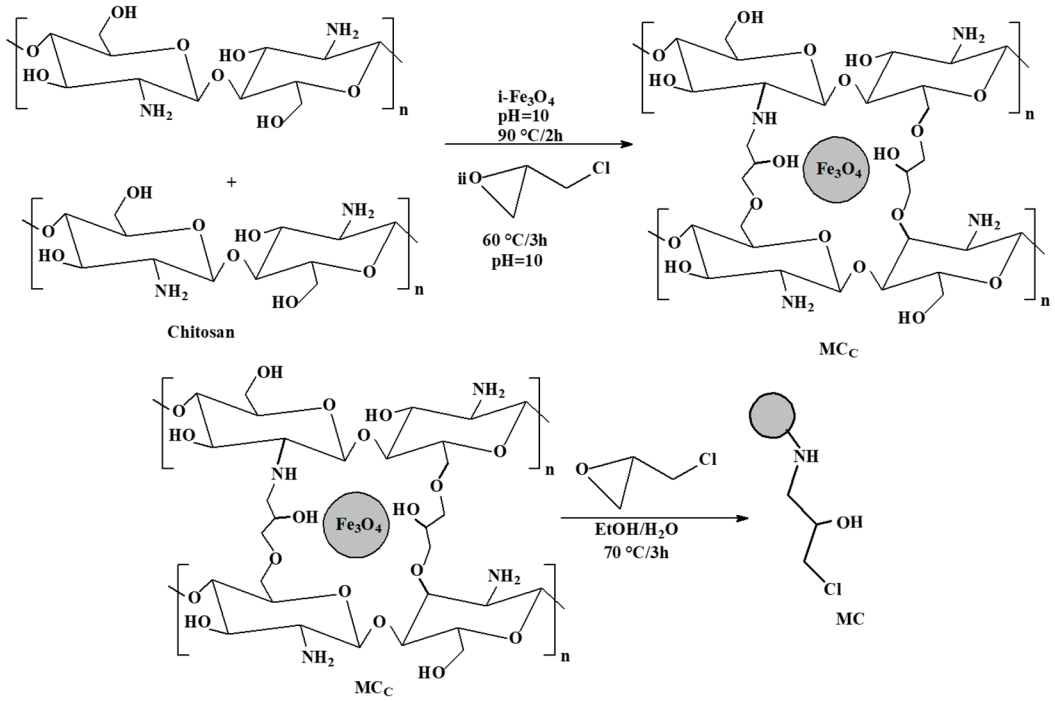
Chemicals used	**Available units and prices**		**Units/prices for 10 g sorbent**	
	Unit	**Price (Euro)**	**Unit**	**Price (Euro)**
Synthesis of TDP				
Diethyl malonate	500 g	49	3.75 g	0.367
Thiourea	1000 g	121	1.5 g	0.1815
Sodium ethoxide	500 g	74	50 g	7.4
Synthesis of magnetite				
Ferrous sulfate	250 g	30	4.166 g	0.4999
ammonium ferric (III) sulfate dodecahydrate	500 g	61	6.125 g	0.747
acetic acid	1000 mL	27	9 mL	0.243
Synthesis of modified sorbent				
Chitosan	50 g	72	3 g	4.32
EPI	1000 mL	60	17 mL	1.02
Ethanol	2500 mL	61	50 mL	1.22
DMF	2500 mL	51	140 mL	2.856
Acetone	1000 mL	21	30 mL	0.63
Overall prices for 10 g sorbent				19.4844 euro

Table S3. FTIR characterization of thiourea, TDP, MC-TDP, after sorption and after five cycles of sorption desorption.

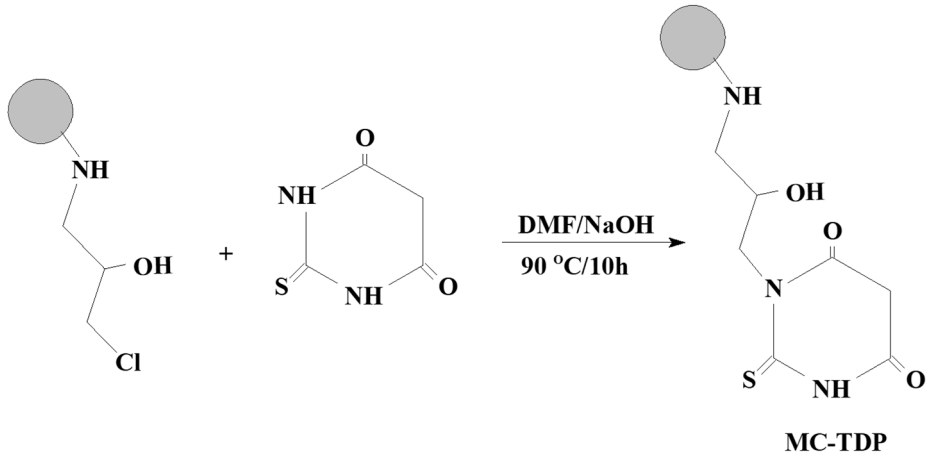
Assignment	Thiourea	TDP	MC-TDP	MC-TDP+Cr	Sorbent after 5th cycles	Ref.
N-H and OH str.	3375, 3291, 3170	3584, 3392	3443	3423	3398	[6,7]
C-H (aromatic str.)		3095				[8]
C-H (aliphatic str.)	2915, 2850	2867	2912, 2816	2920, 2847	2918, 2872	[9,10]
S-H str. of thiol group	2673	2583	2583		overlapped	[11]
Multiple of bonded C-O			2046		2056	[11]
C=C aromatic str.		1705				[11]
C=O, C=N str. and N-H bend.	1611	1659, 1554	1626, 1499	1633	1628	[12-14]
C-N str., C-H bend, and C-C str.	1467, 1410	1422	1410		1451	[12,13,15-17]
Arom. (secondary amine)/ quaternary ammonium		1338	1363	1380	1370	[11]
Tert. amine		1271	1303		1314	[11]
OH bend (in-plane) and C-O str.,		1243	1214		1235	[7,18,19]
N-C str. and NH_2 (rock.)	1078	1155	1097, 1060	1088	1130	[12,18,20]
C-O str bridge oxygen and C-O-C. str. (asymm)					1056	[21]
NH_2 rock.			1015		1025	[12]
Aromatic C-H bend (in-plane)		923	854		899	[17,21]
NH_2+CO wag. (out-of-phase)	727	800				[11,12]
N-C-N in-plane (bend), and Fe-O	627	599	632	580	627	[15,16,22,23]
O-H out-of-plane (bend.)		541	541		575	[24,25]
C-S str.	485	453				[26,27]
Polysulfide str.	447	448	420		443	[11]



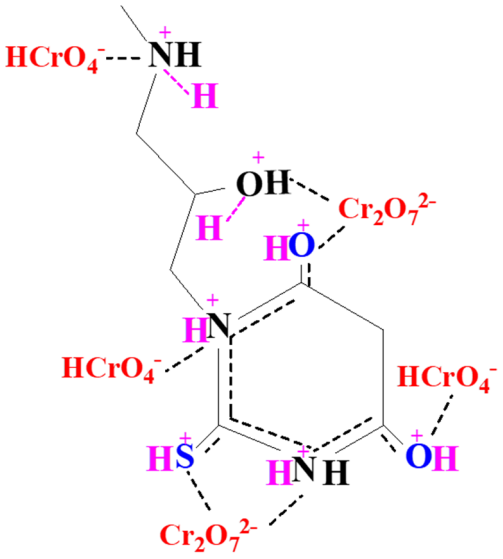
Scheme S1. Synthesis of 2-thioxodihydropyrimidine-4,6(1H,5H)-dione: TDP.



Scheme S2. synthesis of chitosan nanoparticles and activated chitosan (spacer arm).



Scheme S3. Synthesis of grafted TDP chitosan nanoparticles.



Scheme S4. Expected binding mechanism of chromate ions with MC-TDP sorbent at acidic pH medium.

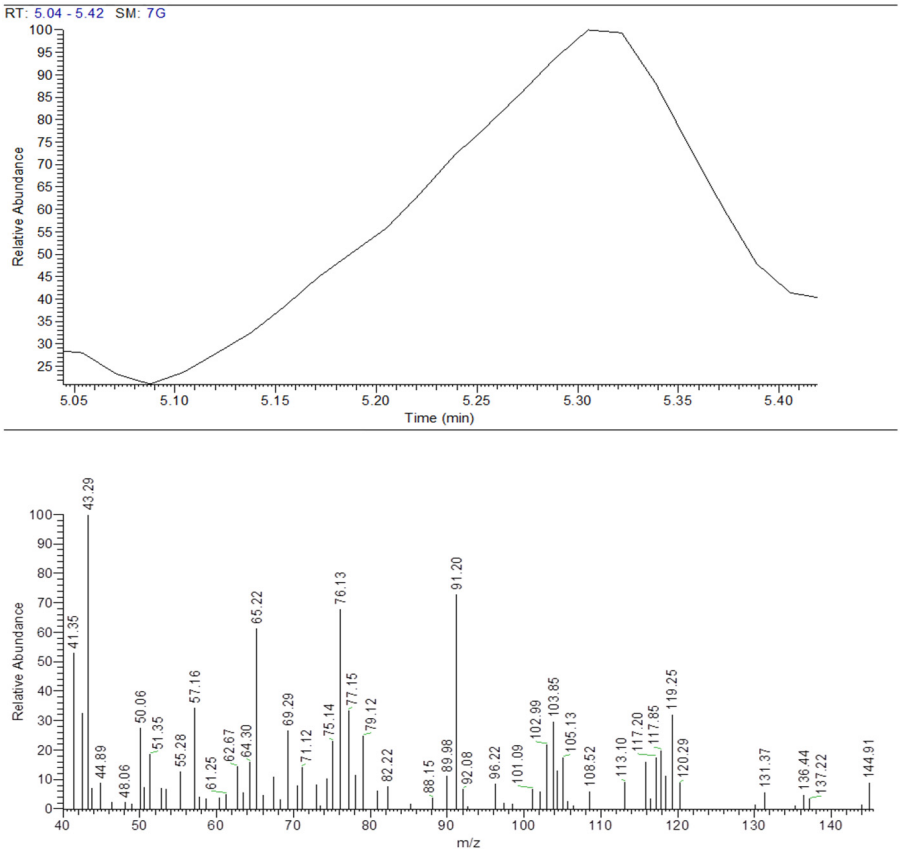


Figure S1. Completed data of the mass spectroscopy for the TDP moiety.

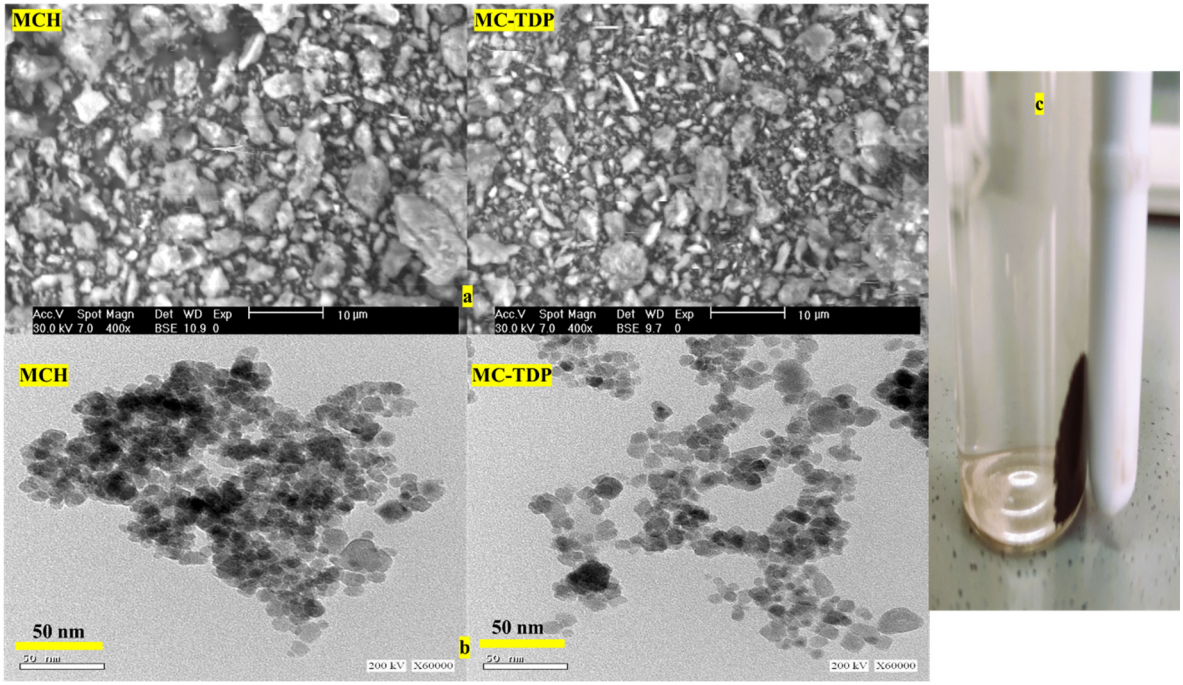


Figure S2. SEM (**a**) and TEM (**b**) graphs of MCH and MC-TDP sorbents and the effect of external magnet on the modified sorbent (**c**).

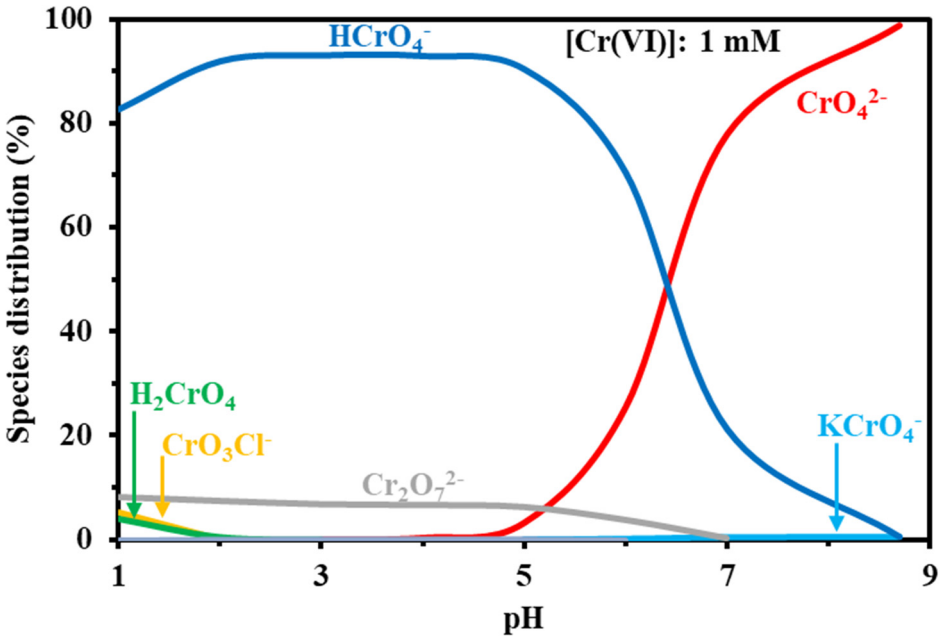


Figure S3. Cr(VI) species at pH 1-9.

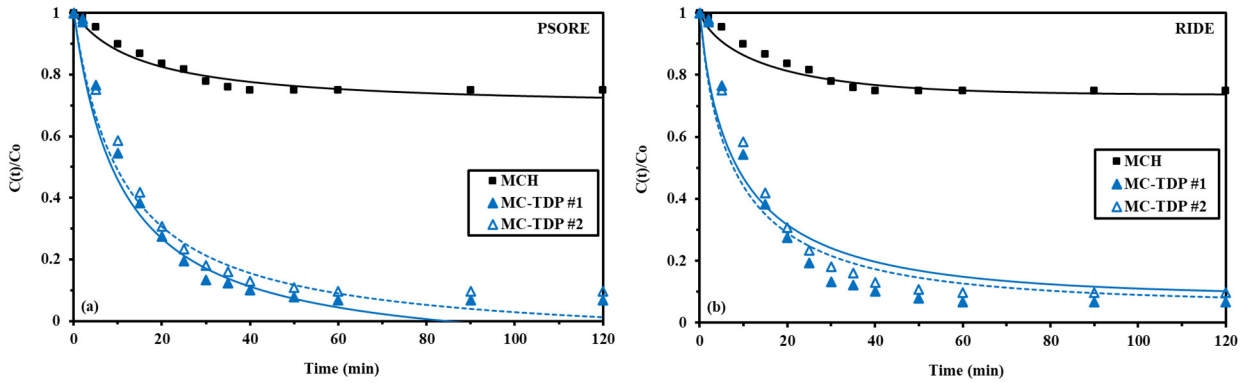


Figure S4. Unfitted uptake Cr(VI) kinetics on MCH, and MC-TDP Modeling with the PSORE (**a**) and RIDE (**b**).

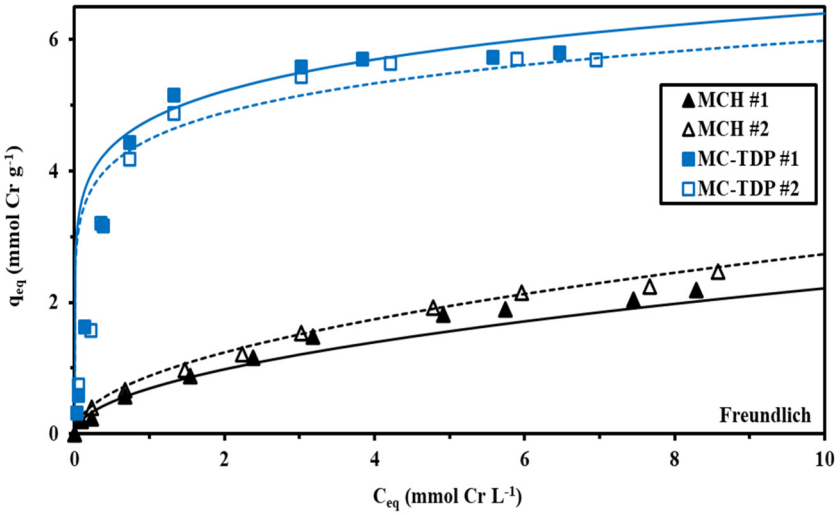


Figure S5. Freundlich modeling equations of sorption isotherms for Cr(VI) using MCH, MC-TDP.

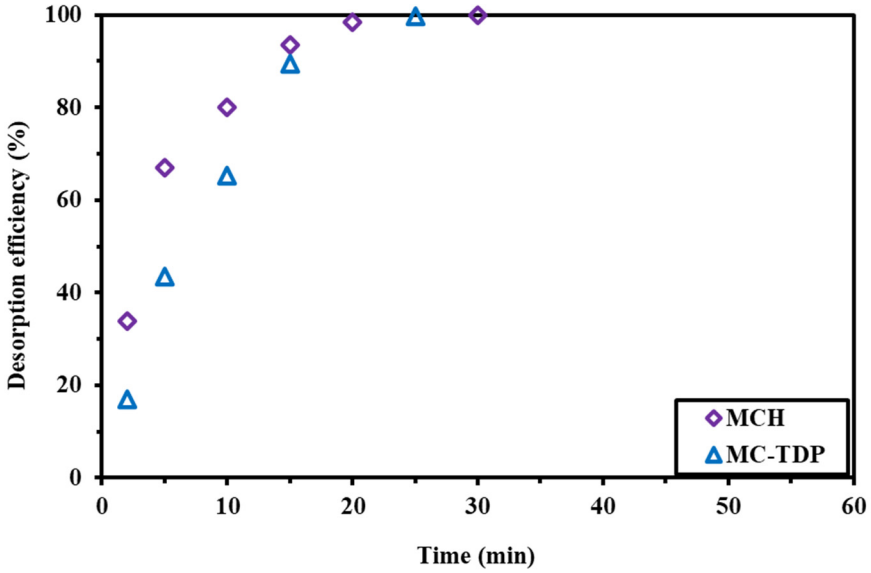


Figure S6. Desorption kinetics of MCH and MC-TDP sorbents.

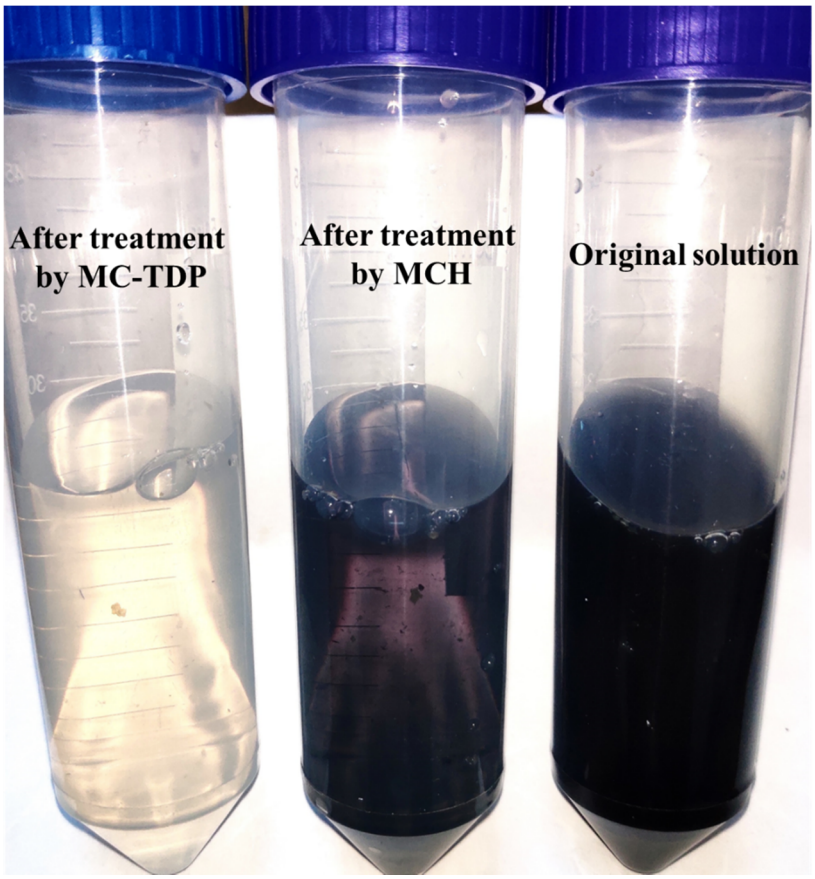


Figure S7. Removal efficient of Cr(VI) using MCH and MC-TDP.

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