

Synthesis of a Novel Adsorbent Based on Chitosan Magnetite Nanoparticles for the High Sorption of Cr (VI) ions: A Study of Photocatalysis and Recovery on Tannery Effluents

Maram H. Zahra ¹, Mohammed F. Hamza ^{2,3,*}, Gehan El-Habibi ⁴, Adel A.-H. Abdel-Rahman ^{4,*}, Hamed I. Mira ³, Yuezhou Wei ^{2,5,*}, Saad H. Alotaibi ⁶, Hamada H. Amer ⁶, Adel E.-S. Goda ⁷ and Nora A. Hamad ⁴

¹ Research Core for Interdisciplinary Sciences, Graduate School of Natural Science and Technology, Okayama University, Tsushima naka, Kita, Okayama 700-8530, Japan; maram@okayama-u.ac.jp

² School of Nuclear Science and Technology, University of South China, Hengyang 421001, China

³ Nuclear Materials Authority, POB 530, El-Maadi, Cairo 11728, Egypt; hamedmira@yahoo.com

⁴ Chemistry Department, Faculty of Science, Menofia University, Shebin El-Kom 32511, Egypt; gehanelhabibi2255@yahoo.com (G.E.-H.); nhamad059@gmail.com (N.A.H.)

⁵ School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

⁶ Department of Chemistry, Turabah University College, Taif University, Taif 21944, Saudi Arabia; s.alosaimi@tu.edu.sa (S.H.A.); h.amer@tu.edu.sa (H.H.A.)

⁷ Tanta Higher Institute of Engineering and Technology, Tanta 31739, Egypt; adelgoda1969@gmail.com

* Correspondence: m_fouda21@hotmail.com (M.F.H.); adelnassar63@yahoo.com (A.A.-H.A.-R.); yzwei@sjtu.edu.cn (Y.W.); Tel.: +20-111-668-1228 (M.F.H.); +2-01221678094 (A.A.-H.A.-R.); +86-771-322-4990 (Y.W.)

Table S1. Elemental analysis of MCH and MC-TDPD sorbents.

Sorbent	C	N	H	O	S
	[%]	[%]	[%]	[%]	[%]
<u>MCH</u>	34.65	3.98	4.97	27.14	
<u>MC-TDPD</u>	37.09	5.63	5.15	32.96	1.11

Table S2. 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; C₀ (mmol L⁻¹): initial concentration of the solution).

Table S3. 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:

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

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.

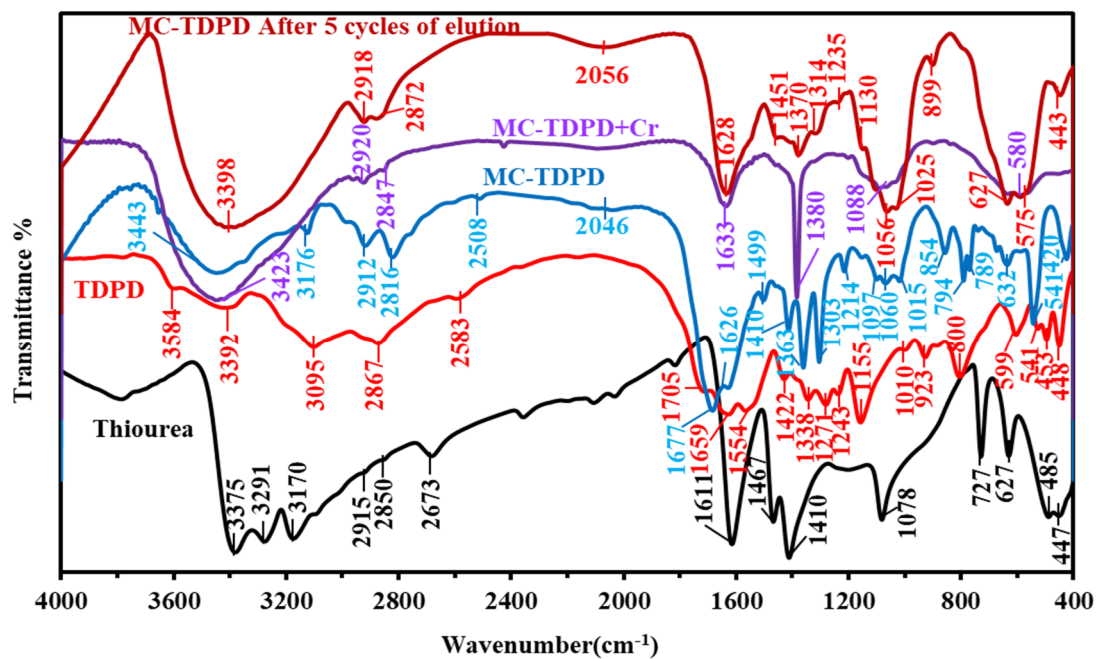


Figure S1. FTIR spectra of thiourea, TDPD, MC-TDPD, after sorption and after five cycles of sorption desorption.

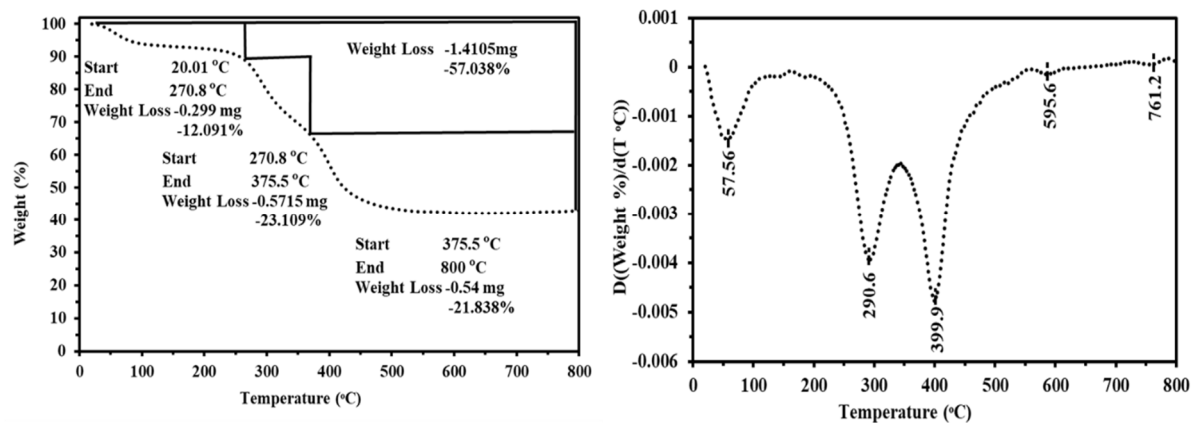


Figure S2. TGA and DrTG analyses of MC-TDPD sorbent T: 23-800 °C.

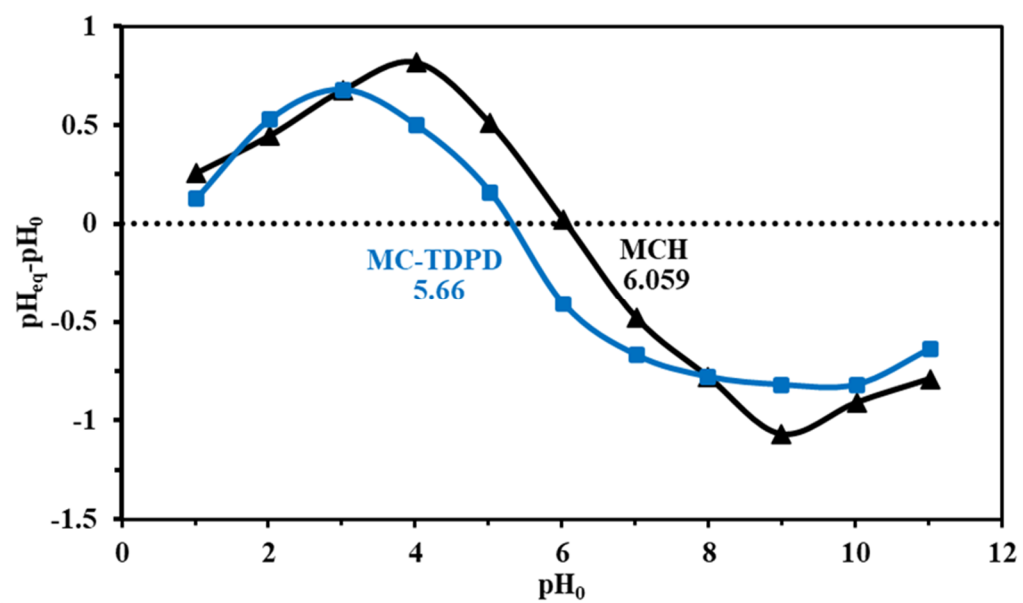


Figure S3. pHpzc of the MCH and MC-TDPD sorbents in range of pH 1-14.

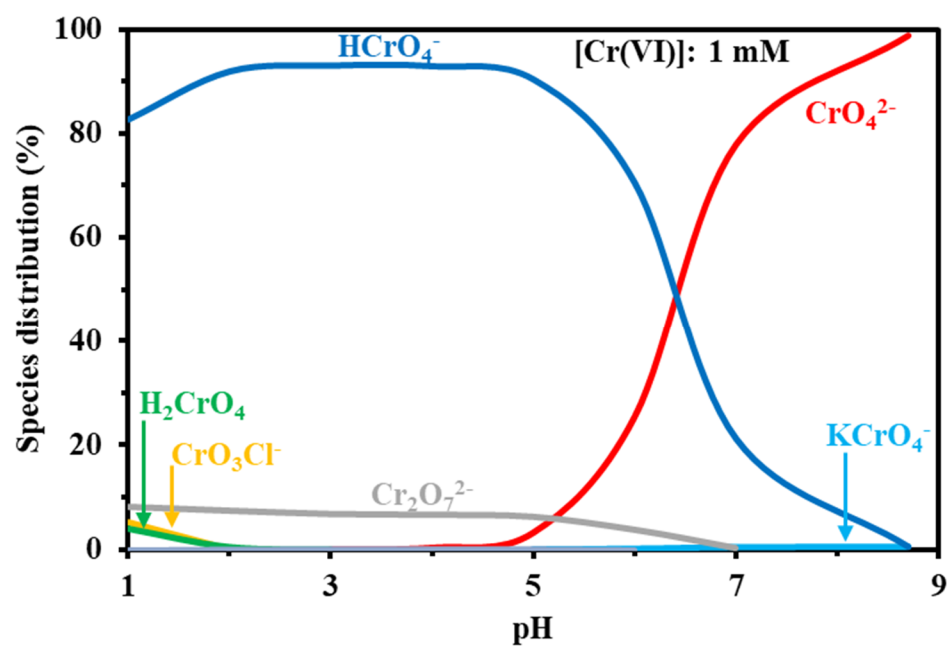


Figure S4. Cr(VI) species at pH 1-9.

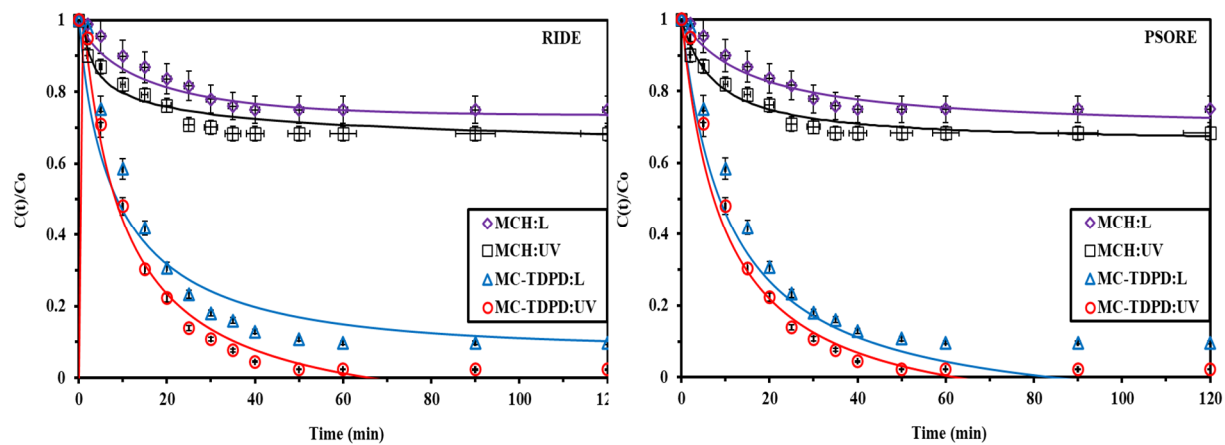


Figure S5. Cr(VI) uptake kinetics using MCH, MC-TDPD in light and UV condition- Modeling with the PSORE and RIDE.

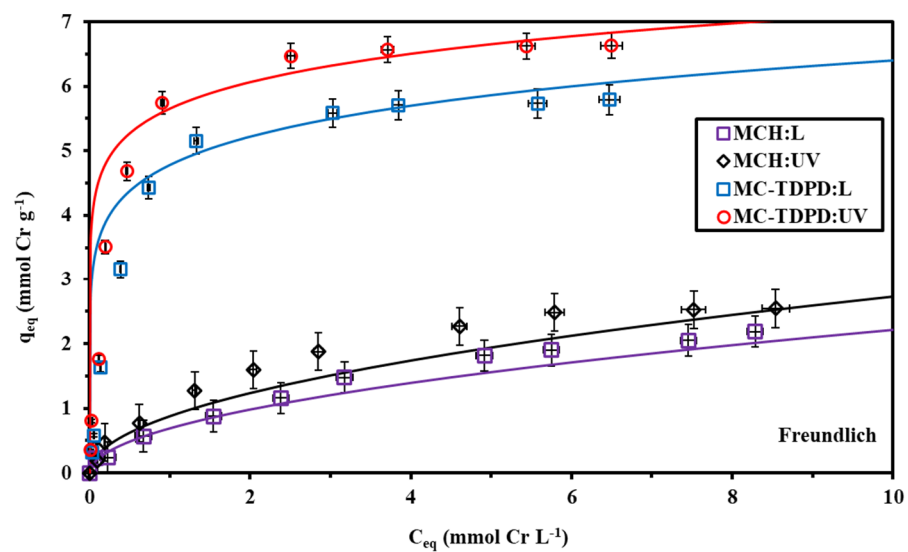


Figure S6. Cr(VI) sorption isotherms using MCH, MC-TDPD in light and UV condition- with the Freundlich equations. .

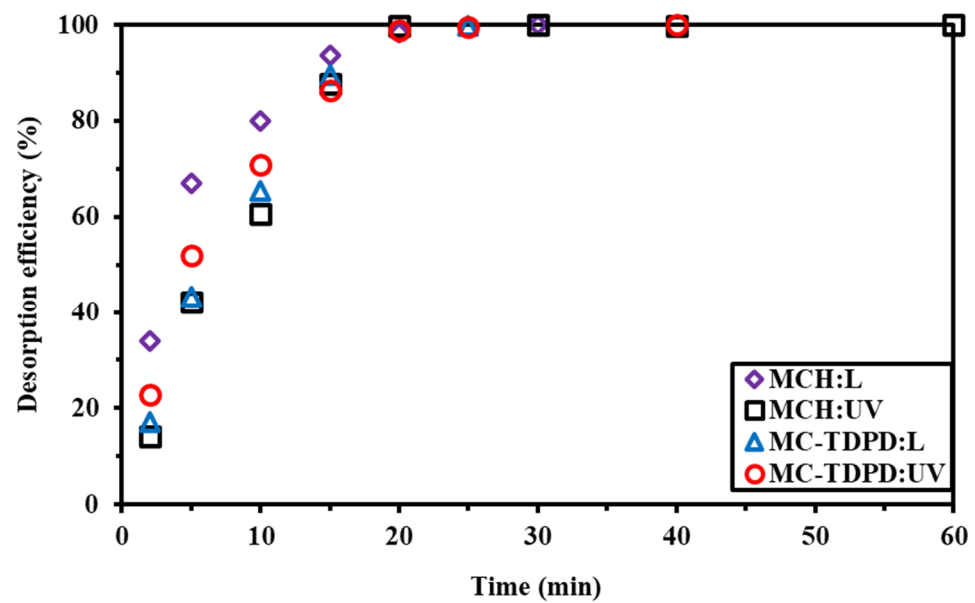


Figure S7. Desorption kinetics of MCH:L, MCH:UV, MC-TDPD:L and MC-TDPD:UV sorbents.

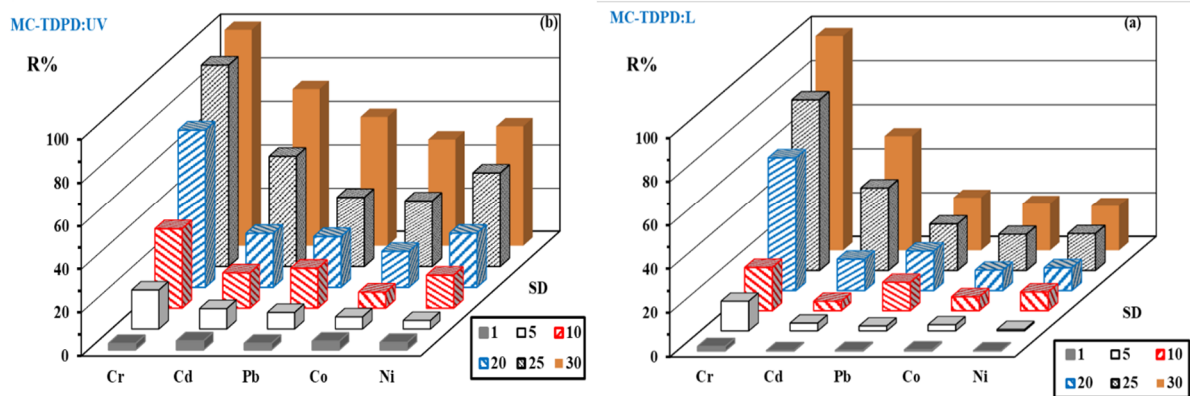


Figure S8. Recovery efficient of MC-TDPD at visible light (a) and Ultraviolet (b).

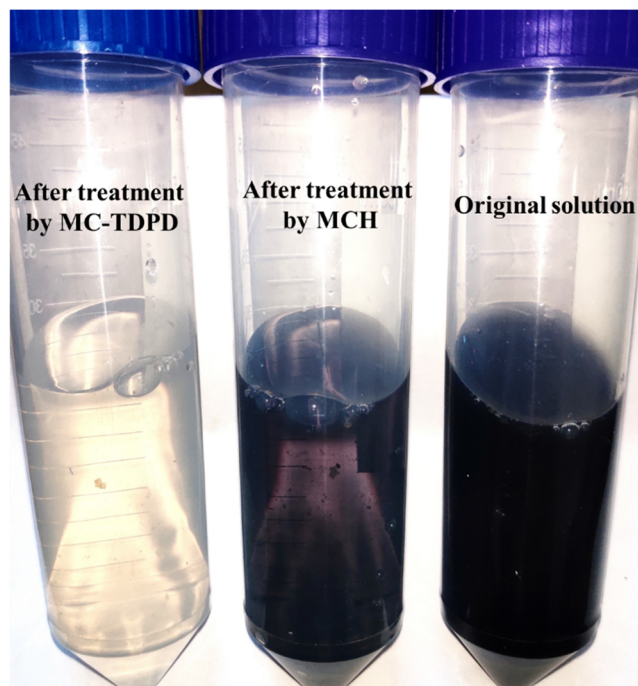


Figure S9. Removal efficient of Cr(VI) using MCH and MC-TDPD

References

1. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: Oxford, UK, 1975; p. 414.
2. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5).
3. Zhang, R.; Leiviska, T. Surface modification of pine bark with quaternary ammonium groups and its use for vanadium removal. *Chem. Eng. J.* **2020**, *385*, 123967. <https://doi.org/10.1016/j.cej.2019.123967>.
4. Freundlich, H.M.F. Über die adsorption in lasungen. *Z. Phys. Chem.* **1906**, *57*, 385–470.
5. Tien, C. *Adsorption Calculations and Modeling*; Butterworth-Heinemann: Newton, MA, USA, 1994; p. 243.