

Supporting Information

Fast and efficient Chromium(VI) extraction by colloidal Mg/Al Layer Double Hydroxide nanoparticles

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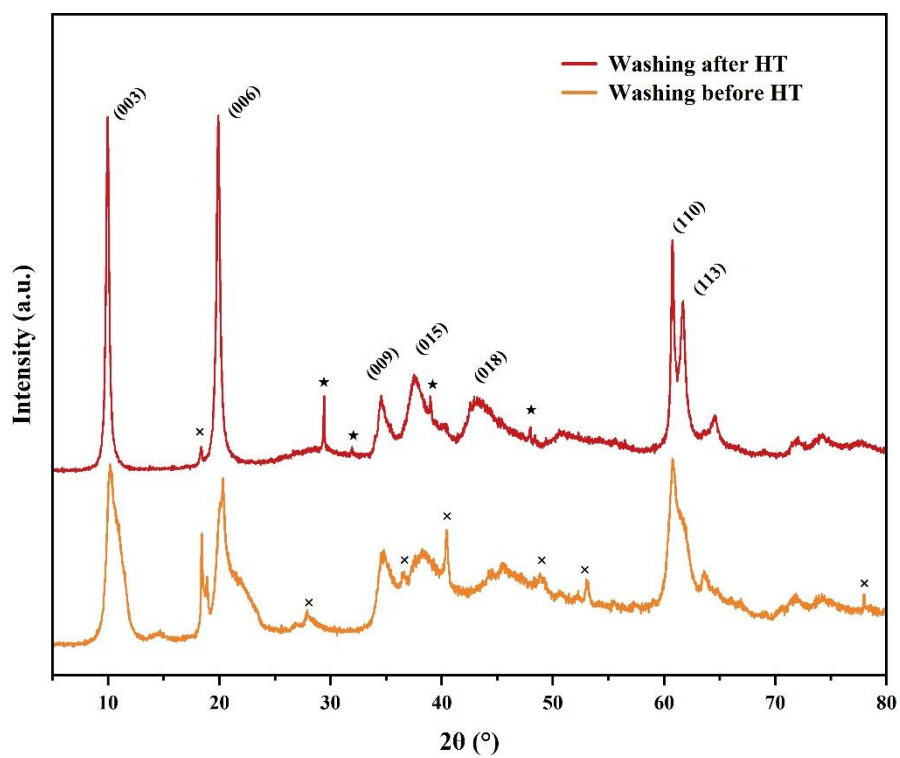


Figure S1: PXRD pattern of $\text{Mg}_2\text{Al-NO}_3$ NPs LDH washed before and after the HT. (X : Al(OH)_3 , ★: NaNO_3).

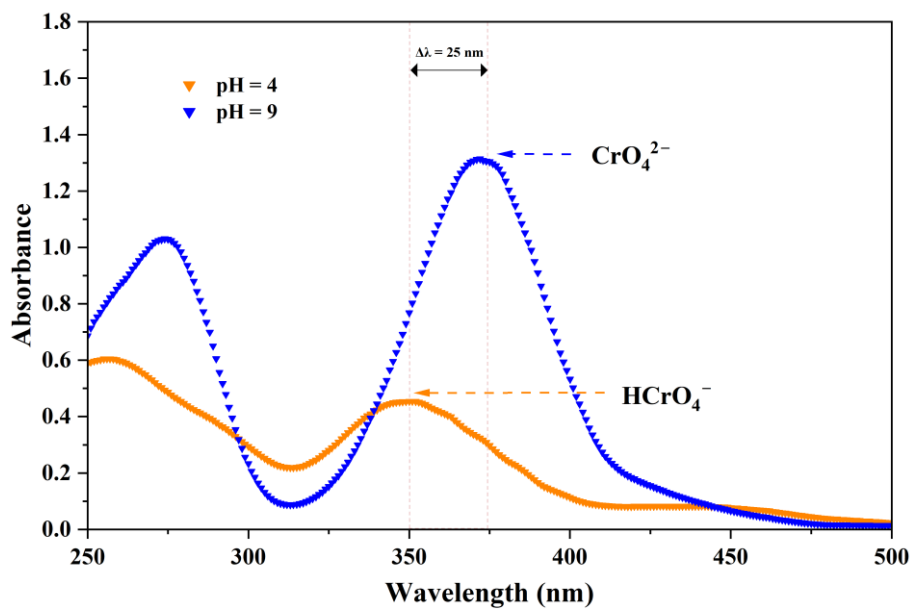


Figure S2: UV-Vis spectra of Cr(VI) at 15 mg L⁻¹ at both tested pH conditions.

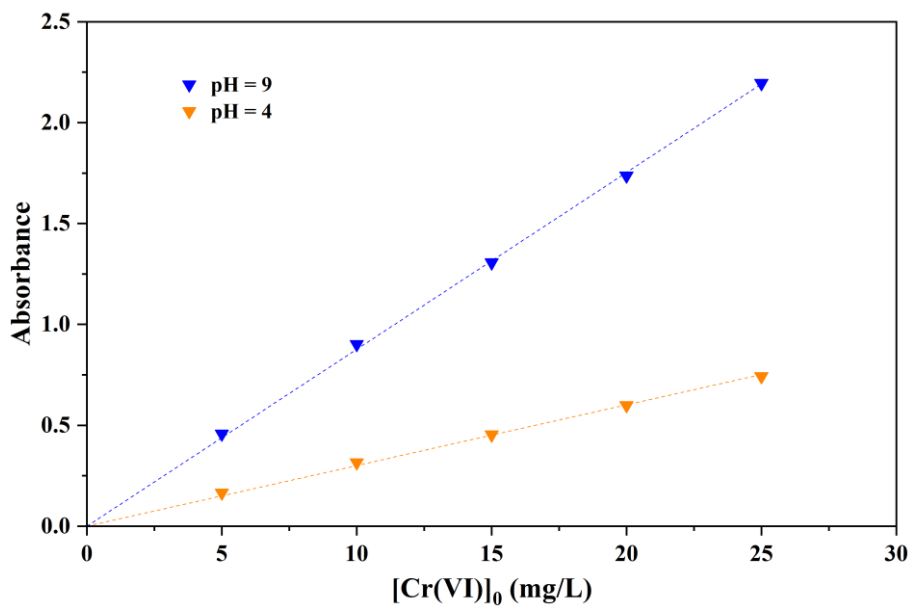


Figure S3: Absorbance plotted against Cr(VI) concentration at $\lambda = 375$ nm for pH = 9 and $\lambda = 350$ nm for pH = 4.

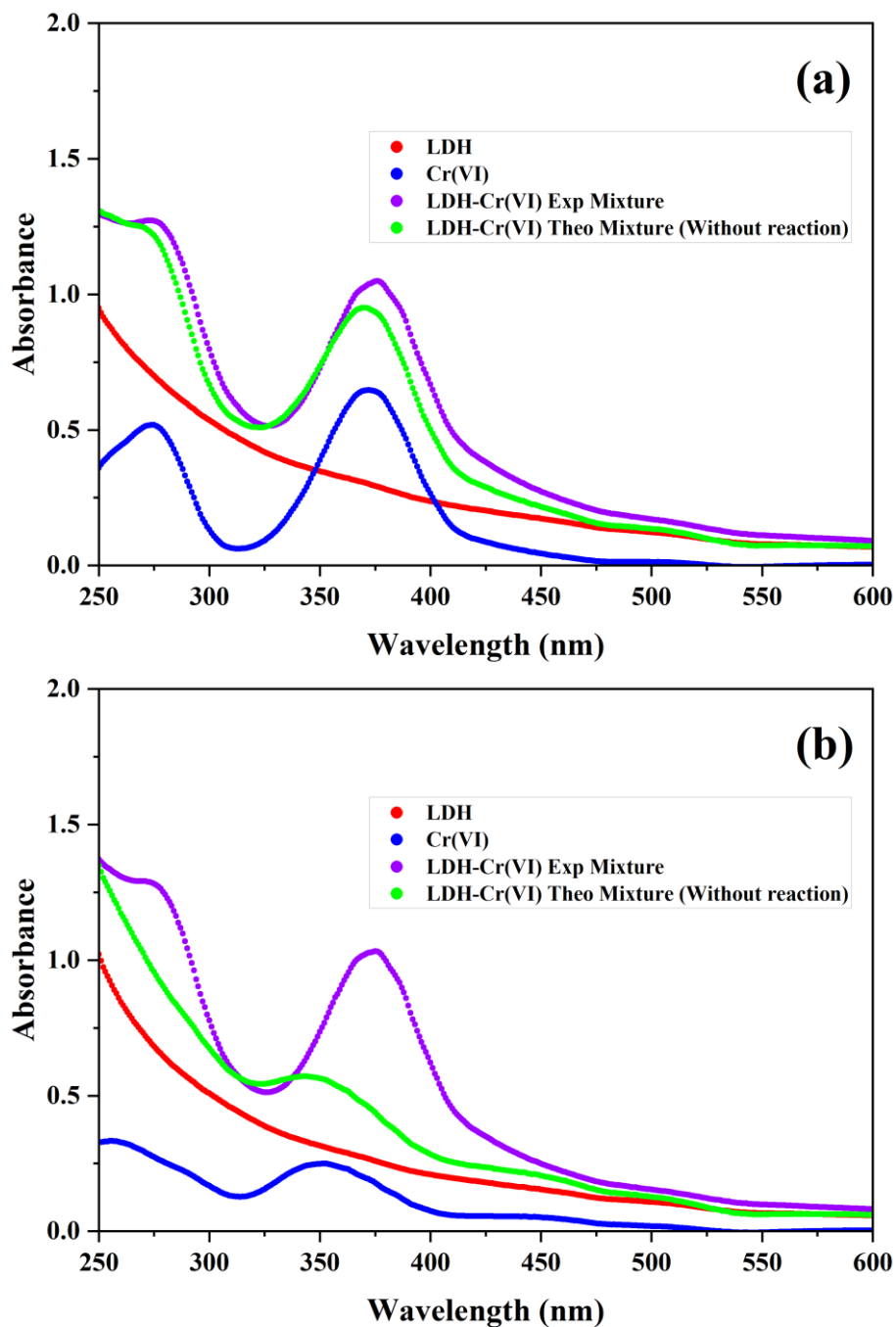


Figure S4: UV-vis absorbance spectra. In (a), a suspension of LDH NPs (0.25 g.L^{-1}) at pH = 9 (●), Cr(VI) solution (7.5 mg.L^{-1}) at pH = 9 (●), and the resulting mixture (●). The theoretical resultant curve (●), calculated as the average of the LDH and Cr(VI) absorbances. Similarly, in (b), the same components are shown but at pH = 4.

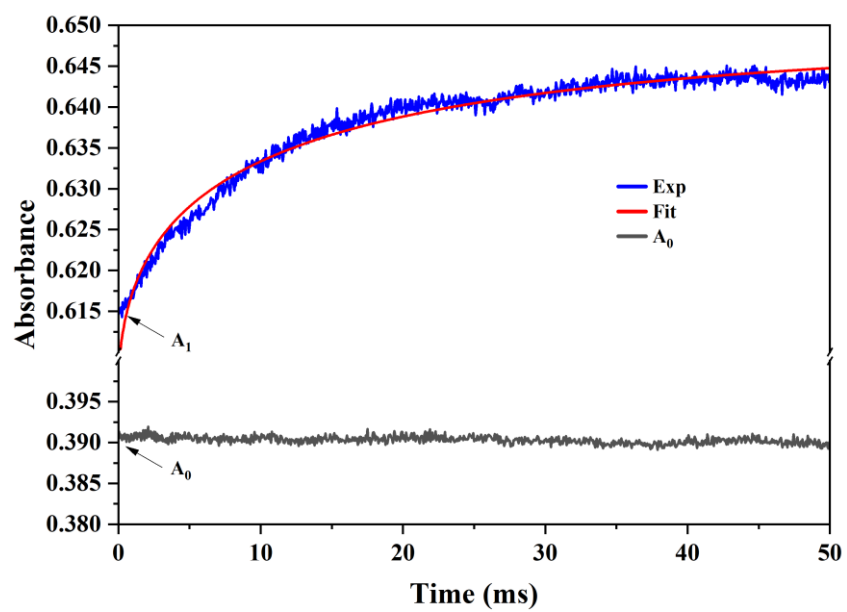


Figure S5: The stopped-flow experimental curve at Cr(VI) concentration of $7.5 \text{ mg}\cdot\text{L}^{-1}$ and LDH $0.25 \text{ g}\cdot\text{L}^{-1}$.

Tested kinetics models:

Three models underwent rigorous testing to determine their fitting capability with the experimental data points obtained from the stopped-flow analysis.

The pseudo-first-order (PFO) model, assuming the interaction, is represented by Eq. 1. In this equation, A_1 , $Abs(t)$, and A_e represent the absorbances at time 0 of the stopped-flow experiment, at time t , and at equilibrium, respectively.

The rate constant of the PFO model is denoted as k_1 (s^{-1}). On the other hand, the pseudo-second-order model, which is rooted in chemical sorption, is characterized by A_1 , $Abs(t)$, and A_e , with the same definitions as the PFO. The rate constant for the PSO model is denoted as k_2 (s^{-1}).

Table S1: The applied kinetic model equation.

Kinetic model	Nonlinear form	Ref
PFO	$Abs(t) = (A_e + A_1)(1 - \exp(-k_1 t)) + A_1$	(Lagergren, 1898)
PSO	$Abs(t) = \frac{A_e^2 k_2 t}{1 + A_e k_2 t} + A_1$	(Ho and McKay, 1999)
Vermeulen	$Abs(t) = (A_e - A_1) \exp\left(-\frac{D\pi^2 t}{R^2}\right) + A_1$	(Vermeulen, 1953)
Shrinking core model	$Abs(t) = (A_1 - A_e) \exp(-k_{obs} t^{0.5}) + A_e$	(Hébrant, 2007)

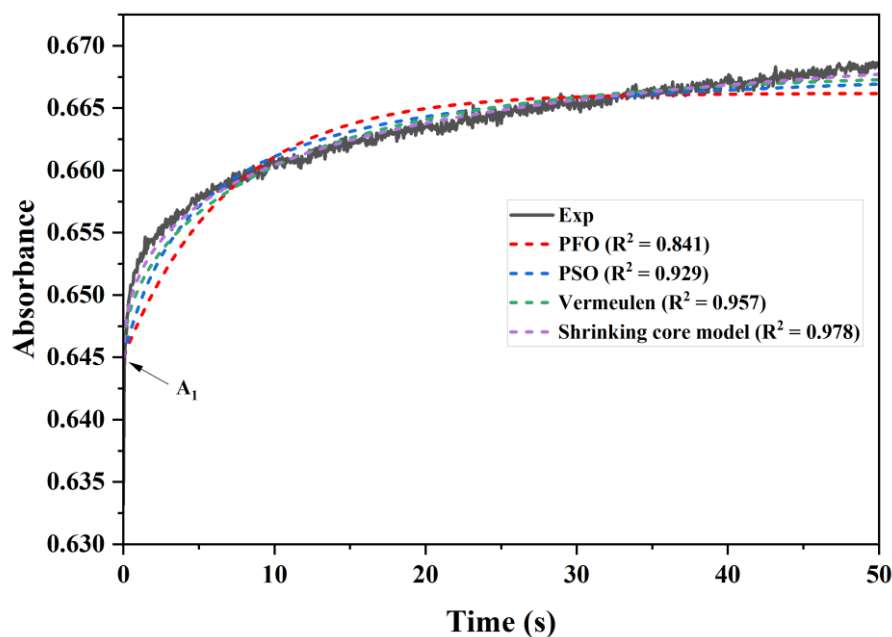


Figure S6: Stopped-flow experimental curve with a Cr(VI) concentration of $7.5 \text{ mg}\cdot\text{L}^{-1}$ and LDH concentration of 0.25 g^{-1} at pH = 4, fitted using nonlinear kinetic models.

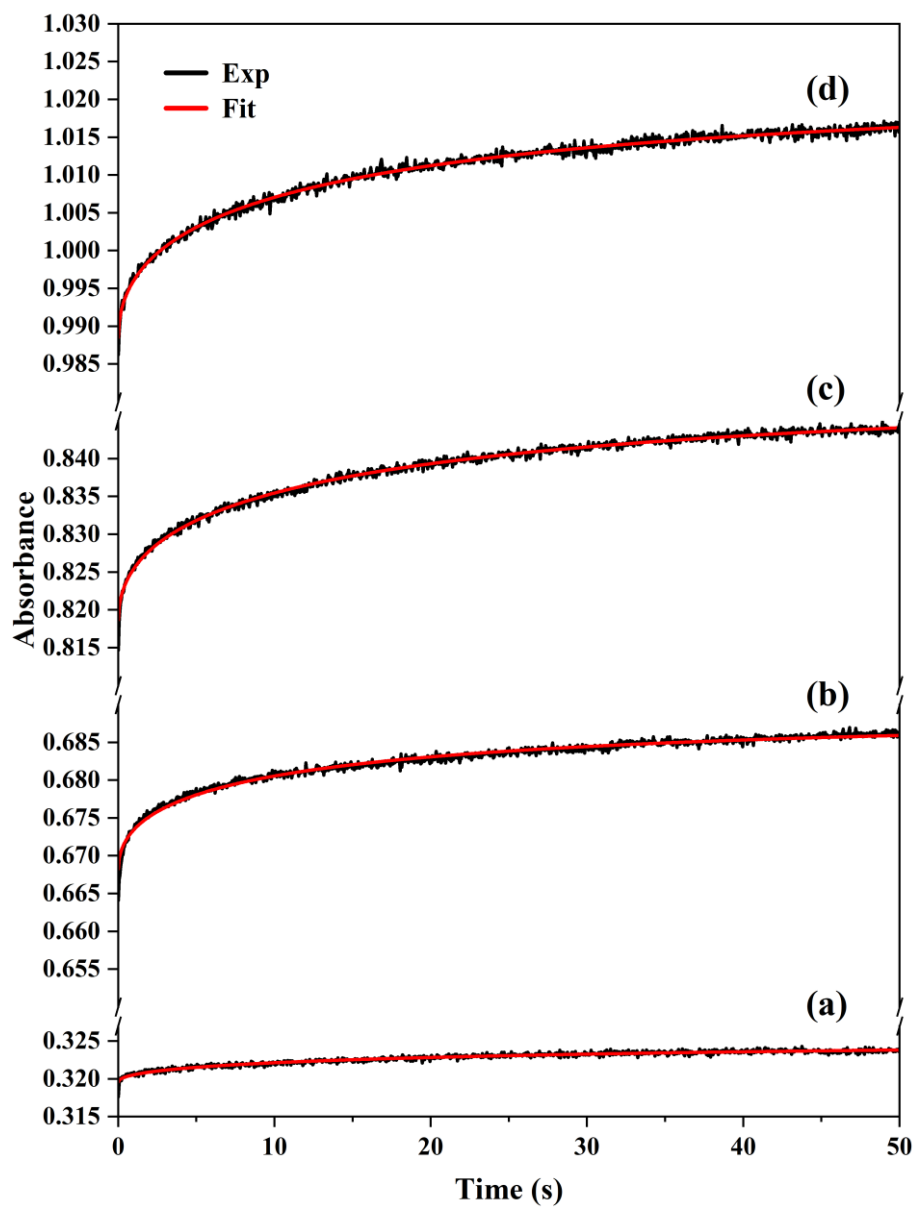


Figure S7: The stopped-flow plots at pH = 4 at different Cr(VI) concentrations (a): 2.5 mg.L⁻¹, (b): 5.0 mg.L⁻¹, (c): 7.5 mg.L⁻¹, (d): 10.0 mg.L⁻¹, (e): 12.5 mg.L⁻¹. [LDH]₀ = 0.25 g.L⁻¹.

Fitted parameters :Table 2a: Fitting parameters for the experimental data in the stopped-flow analysis of the interaction between Cr(VI) and Mg₂Al-NO₃ LDH NPs at pH = 4.

[Cr(VI)] ₀	A ₁ - A _e	k _{obs} (s ^{-0.5})	A _e	R-square	Adj R-square
2.5	0.0118 ± 0.0003	0.189 ± 0.003	0.3091 ± 0.0003	0.9876	0.9875
5.0	0.0163 ± 0.0003	0.218 ± 0.018	0.5013 ± 0.0006	0.9723	0.9723
7.5	0.0263 ± 0.0003	0.243 ± 0.015	0.6726 ± 0.0006	0.9792	0.9791
10.0	0.0317 ± 0.0006	0.251 ± 0.018	0.8509 ± 0.0009	0.9717	0.9714
12.5	0.0460 ± 0.0006	0.247 ± 0.015	1.0177 ± 0.00012	0.9762	0.9761

Table 2b: Fitting parameters for the experimental data in the stopped-flow analysis of the interaction between Cr(VI) and Mg₂Al-NO₃ LDH NPs at pH = 9.

[Cr(VI)] ₀	A ₁ - A _e	k _{obs} (s ^{-0.5})	A _e	R-square	Adj R-square
2.5	0.0059 ± 0.0003	0.179 ± 0.027	0.3255 ± 0.0003	0.9336	0.9335
7.5	0.0201 ± 0.0003	0.301 ± 0.015	0.6883 ± 0.0003	0.9824	0.9823
10.0	0.0306 ± 0.0003	0.253 ± 0.006	0.8492 ± 0.0003	0.9926	0.9925
12.5	0.0330 ± 0.0003	0.261 ± 0.009	1.0215 ± 0.0003	0.9910	0.9910

Ultrafiltration :

In this context, $[LDH]_0$ and $[Cr]_0$ represent the initial concentrations of the LDH suspension and Cr(VI) species, respectively. Both $[\text{NO}_3^-]_0$ and $[\text{H}^+]_0$ was approximated to be 10^{-4} mol. L⁻¹ due to the pH adjustment of both the LDH suspension and Cr(VI) solution to a fixed value of 4 using HNO₃ solution:

$$[\text{NO}_3^-]_{\text{LDH}} = [\text{LDH}]_0 - \frac{2Y}{100} [\text{Cr}]_0$$

$$[\text{CrO}_4^{2-}]_{\text{W}} = [\text{Cr}]_0 - \frac{Y}{100} [\text{Cr}]_0$$

$$[\text{NO}_3^-]_{\text{W}} = [\text{NO}_3^-]_0 + \frac{2Y}{100} [\text{Cr}]_0$$

$$[\text{CrO}_4^{2-}]_{\text{LDH}} = \frac{Y}{100} [\text{Cr}]_0$$

Expressing the terms in Eq. 4 to parameters as: $a = [\text{Cr}]_0$, $b = [\text{NO}_3^-]_0$, $c = [\text{H}^+]_0$ and the independent variable $d = [\text{LDH}]_0$, the K_4 can be expressed in a more simplified form :

$$K_4 = \frac{(b + 2aY)^2(acY)}{(d - 2aY)^2(a(100 - Y))}$$

Give the third degree equation:

$$\left(\frac{4a^2}{10^4}(K_4 + c)\right)Y^3 + \left(\frac{4a}{10^2}(-dK_4 - a.K_4 + bc)\right)Y^2 + (d^2K_4 + 4adK_4 + b^2c)Y - 100d^2K_4 = 0$$

At pH = 4, the parameter c is set to 10^{-4} , while at pH = 9, c is set to 10^{-9} .

If the initial chromium concentration is varied, the parameter 'a' becomes the independent variable while 'd' remains constant. Conversely, when the LDH concentration is varied, then the reverse will be applied.

In an Excel® procedure, the physically meaningful root Y_{calc} is obtained using the Cardan method for a given K value. Subsequently, a solver routine is employed to optimize this K value, aiming to minimize the sum of squares of the differences $\Sigma(Y_{\text{exp}} - Y_{\text{calc}})^2$ between the experimental (Y_{exp}) and calculated (Y_{calc}) values.

References

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