Supporting Information (SI)

Langmuir adsorption kinetics in liquid media: interface reaction model

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Appendix A: Conversion of standard equations for saturation type curves into PFO and PSO kinetic equations

Standard Equation I for saturation type curves:

Linearizing Eq.(7) from the main text, we have

$$-\ln\left(1-\frac{q}{q_e}\right)=at \tag{S1}$$

With a = k_{E1}, the Eq. (S1) is identical with the linearized pseudo-first-order (PFO) kinetic equation (Eq. (4)) in EA.

Differentiating the Eq. (7) with respect to t, we have

$$\frac{dq}{dt}=q_e(ae^{-at}) \tag{S2}$$

Combining Eqs. (7) & (S2), we have

$$\frac{dq}{dt}=a(q_e-q) \tag{S3}$$

Again, with a = k_{E1}, the Eq. (S3) is identical with the pseudo-first-order (PFO) kinetic equation in differential form (Eq. (3) in EA.

Standard Equation II for saturation type curves:

Linearizing Eq.(8) we have

$$\frac{t}{q}=\frac{1}{bq_e}+\frac{1}{q_e}t \tag{S4}$$

For b = $k_{E2}q_e$, the Eq. (S4) is identical with the linearized pseudo-second-order (PSO) kinetic equation (Eq. (6)) in EA.

Differentiating the Eq. (8) with respect to t, we have

$$\frac{dq}{dt} = q_e b \frac{1}{(1 + bt)^2} \tag{S5}$$

Combining Eq. (8) & (S5), we have

$$\frac{dq}{dt} = \frac{b}{q_e}(q_e - q)^2 \tag{S6}$$

Again, for $b = k_{E2}q_e$, the Eq. (S6) is identical with the pseudo-second-order (PSO) kinetic equation in differential form (Eq. (5)) in EA.

Appendix B: Derivation of kinetic equation (Eq. (22)) in Hybrid Order Approach (HOA)

Rearranging Eq. (15) from the main text, we have

$$W\frac{dq}{dt} = k_a w_a q^2 - (k_a q_\infty w_a + k_a C_{A,0} + k_d)q + k_a C_{A,0} q_\infty \tag{S7}$$

Rewriting the Eq. (S7) for equilibrium:

$$0 = k_a w_a q_e^2 - (k_a q_\infty w_a + k_a C_{A,0} + k_d)q_e + k_a C_{A,0} q_\infty \tag{S8}$$

Subtracting Eq. (S8) from Eq. (S7) and after simple algebraic manipulation, one obtains,

$$W\frac{dq}{dt} = k_a w_a (q_e - q)^2 - k_a w_a.2q_e(q_e - q) \tag{S9}$$

$$+ k_a(q_\infty w_a + C_{A,0} + 1/K)(q_e - q)$$

Rearranging Eq. (19), we have

$$w_a.2q_e = (q_\infty w_a + C_{A,0} + 1/K) - \sqrt{\Delta} \tag{S10}$$

Inserting Eq. (S10) in Eq. (S9), we obtain Eq. (22).

$$\frac{dq}{dt} = k_{H1}(q_e - q) + k_{H2}(q_e - q)^2 \tag{22}$$

Appendix C: Derivation of the expression for the dimensionless number, $N_{OD,0}$ (Eq. (40))

Rearranging the Eq. (21), one obtains

$$\frac{\sqrt{\Delta}}{w_a q_e} = \frac{q_\infty}{q_e} + \frac{C_{A,0}}{w_a q_e} + \frac{1}{K}.\frac{1}{w_a q_e} - 2 \quad \text{(S11)}$$

Combining Eqs. (39) and (S11), we have

$$N_{OD,0} = \frac{q_\infty}{q_e} + \frac{C_{A,0}}{w_a q_e} + \frac{1}{K}.\frac{1}{w_a q_e} - 2 \quad \text{(S12)}$$

Rearranging the Eq. (1), we have

$$\frac{1}{K} = C_{A,e}\left(\frac{q_\infty}{q_e} - 1\right) \quad \text{(S13)}$$

Inserting Eq. (S13) in Eq(S12), we have

$$N_{OD,0} = \frac{q_\infty}{q_e} + \frac{C_{A,0}}{w_a q_e} + \frac{C_{A,e}}{w_a q_e}.\left(\frac{q_\infty}{q_e} - 1\right) - 2 \quad \text{(S14)}$$

From the material balance at equilibrium:

$$VC_{A,e} + Wq_e = VC_{A,0} \quad \text{(S15)}$$

Rearranging Eq. (S15), we can write

$$\frac{C_{A,e}}{w_a q_e} = \frac{C_{A,0}}{w_a q_e} - 1 \quad \text{(S16)}$$

Inserting Eq. (S16) in Eq. (S14), we have

$$N_{OD,0} = \frac{q_\infty}{q_e} + \frac{C_{A,0}}{w_a q_e} + \left(\frac{C_{A,0}}{w_a q_e} - 1\right).\left(\frac{q_\infty}{q_e} - 1\right) - 2 \quad \text{(S17)}$$

In terms of Dimensionless numbers, N_1 and N_2, the Eq. (S17) will take the form of Eq. (40).

$$N_{OD,0} = \frac{\sqrt{\Delta}}{w_a q_e} = \frac{1}{N_1} + \frac{1}{N_2} + \left(\frac{1}{N_1} - 1\right)\left(\frac{1}{N_2} - 1\right) - 2 \quad \text{(40)}$$

Appendix D: Validation of IRA and HOA for systems 2c, 3a & 4a

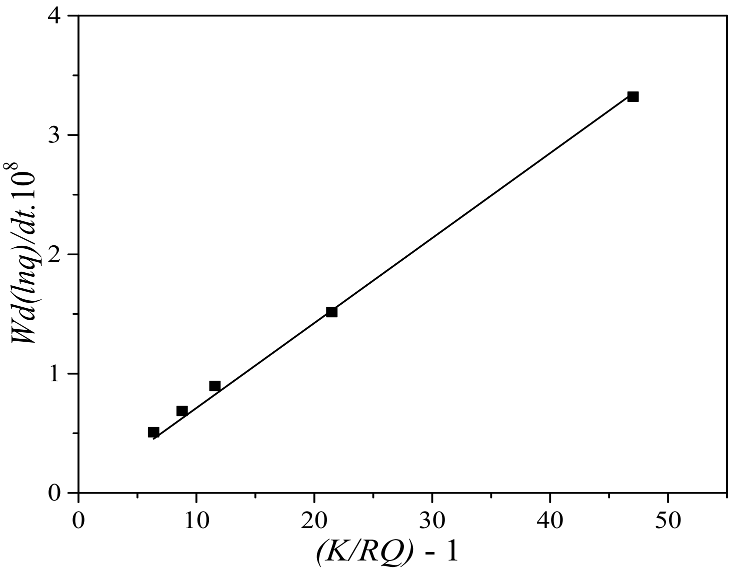

Figure S1: IRA validation (Eq. (17)): $W\frac{dlnq}{dt} vs. \left[\frac{K}{RQ} - 1\right]$ plot for the System 2c

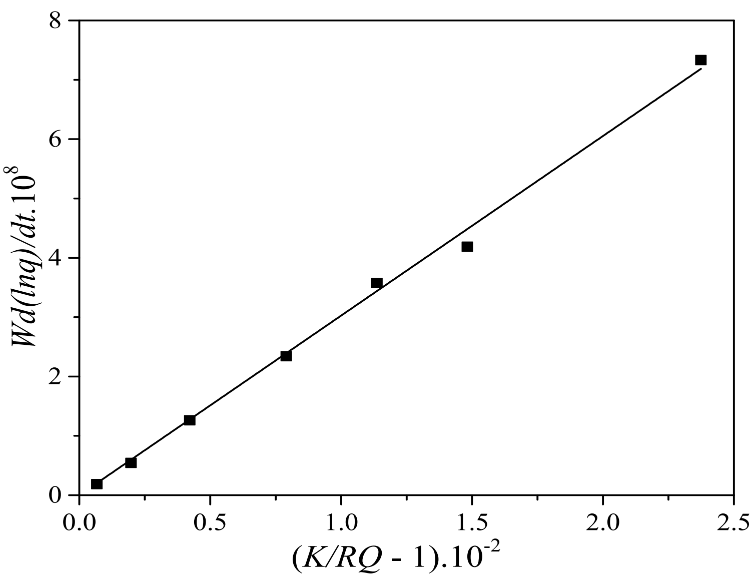

Figure S2: IRA validation (Eq. (17)): $W\frac{dlnq}{dt} vs. \left[\frac{K}{RQ} - 1\right]$ plot for the System 3a

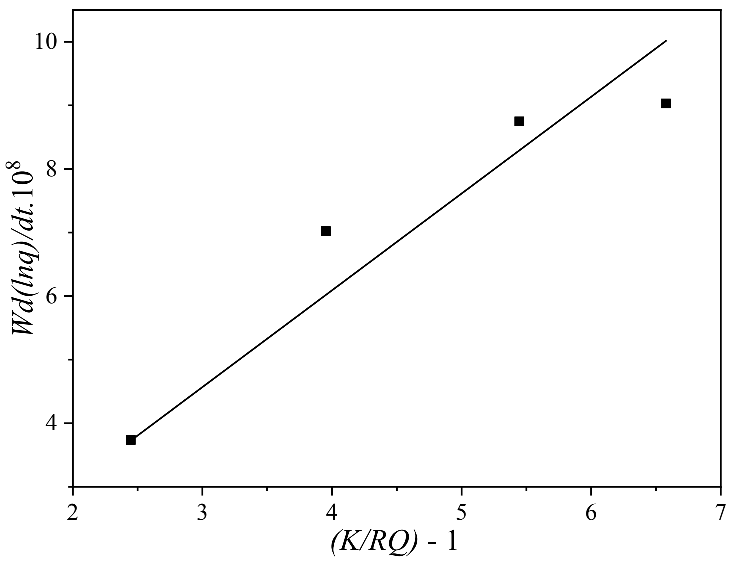

Figure S3: IRA validation (Eq. (17)): $W\frac{dlnq}{dt} vs.\ \left[\frac{K}{RQ} - 1\right]$ plot for the System 4a

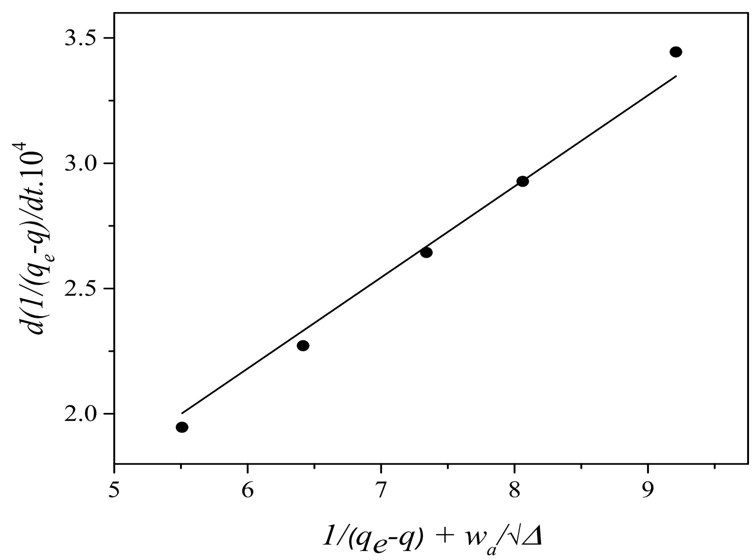

Figure S4:HOA validation (Eq. (26)): $d(1/(q_e\text{-}q))/dt$ vs $\left[\frac{1}{(q_e - q)} + \frac{w_a}{\sqrt{\Delta}}\right]$ plot for the System 2c

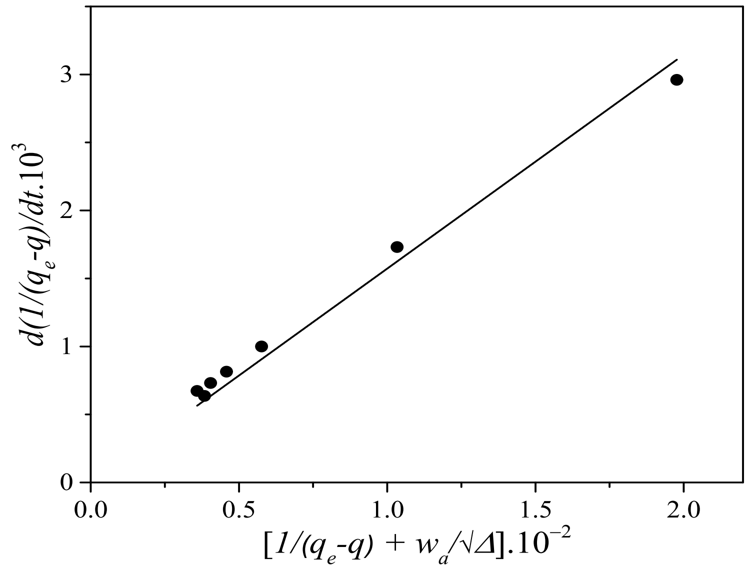

Figure S5: HOA validation (Eq. (26)): $d(1/(q_e\text{-}q))/dt$ vs $\left[\frac{1}{(q_e - q)} + \frac{w_a}{\sqrt{\Delta}}\right]$ plot for the System 3a

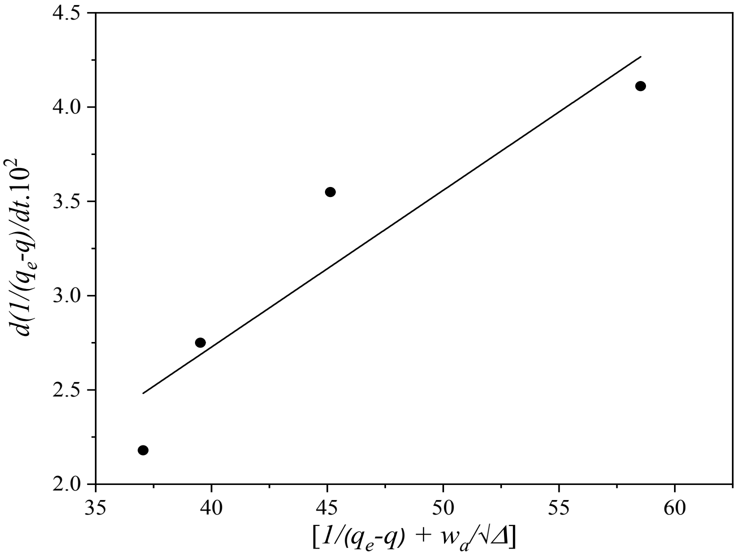

Figure S6: HOA validation (Eq. (26)): $d(1/(q_e\text{-}q))/dt$ vs $\left[\frac{1}{(q_e - q)} + \frac{w_a}{\sqrt{\Delta}}\right]$ plot for the System 4a

Appendix E: Validation of PFO and PSO kinetics in EA for the system 2c , 3a and 4c

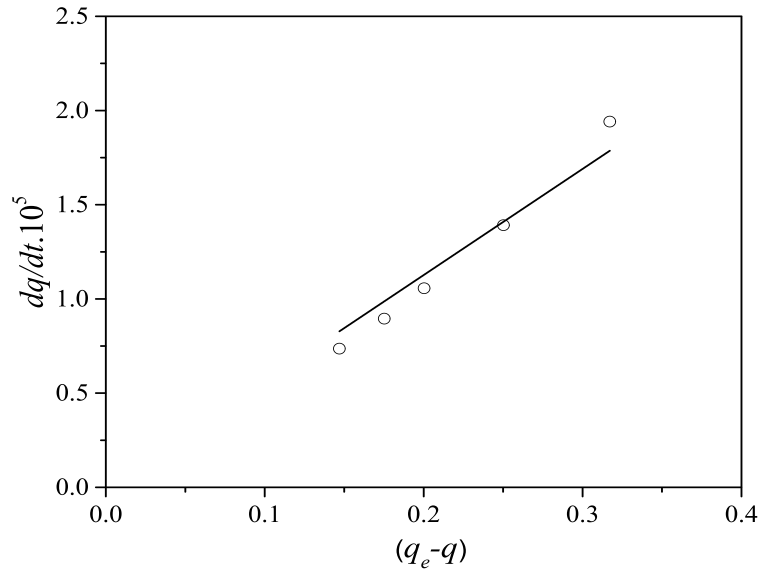

Figure S7:*dq/dt* vs. (q_e –q) plot (Eq. (3)) for the System 2c

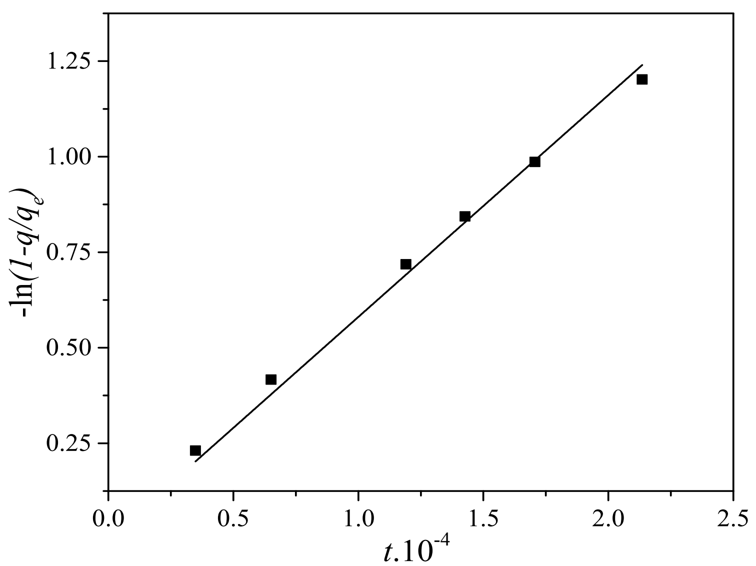

Figure S8:–ln$(1\text{-}q/q_e)$ vs. t plot (Eq. (4))for the System 2c

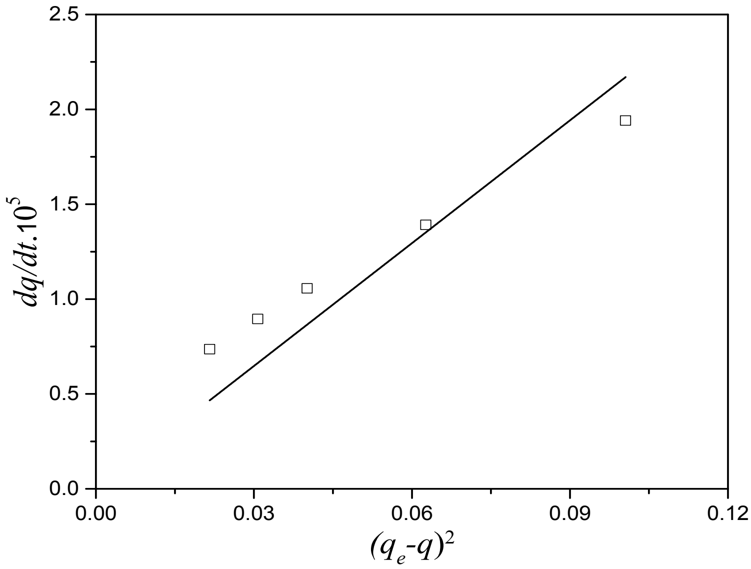

Figure S9:*dq/dt* vs. $(q_e - q)^2$ plot (Eq. (5)) for the System 2c

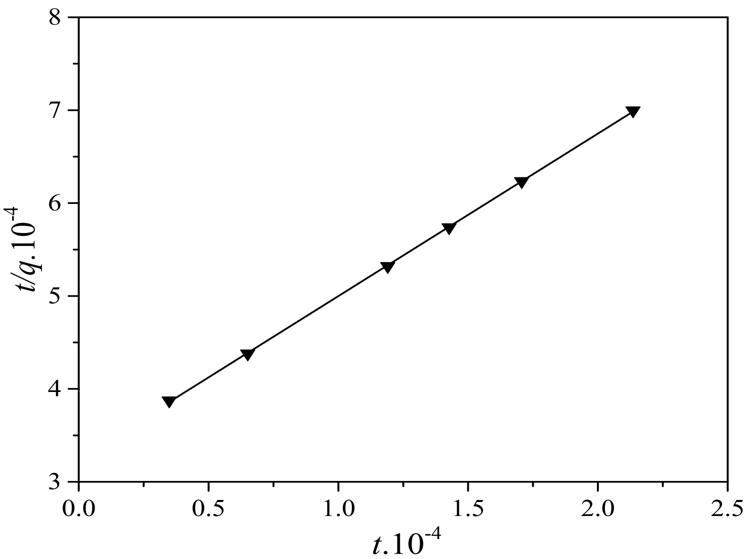

Figure S10: *t/q* vs. *t* plot (Eq. (6)) for the System 2c

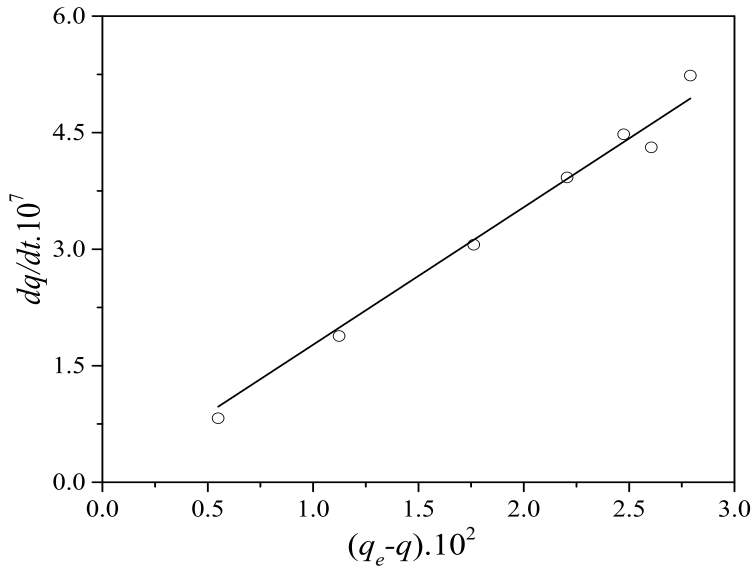

Figure S11: *dq/dt* vs. ($q_e - q$) plot (Eq. (3)) for the System 3a

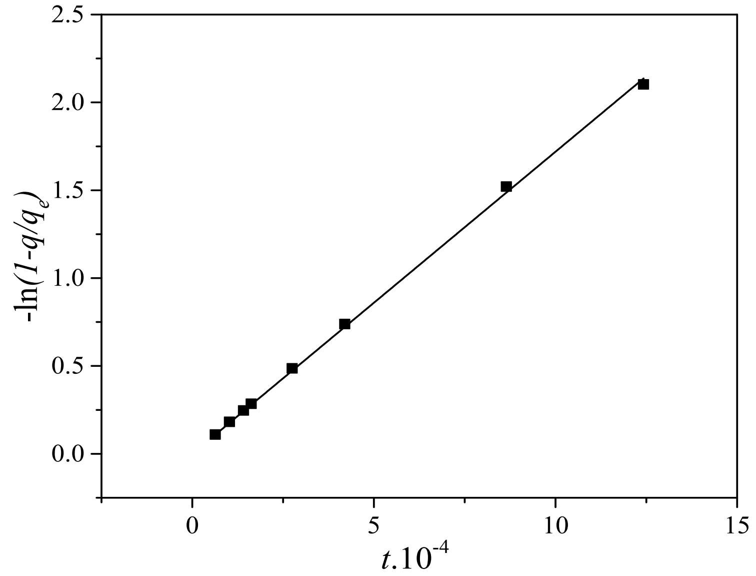

Figure S12: $-\ln(1-q/q_e)$ vs. t plot (Eq. (4)) for the System 3a

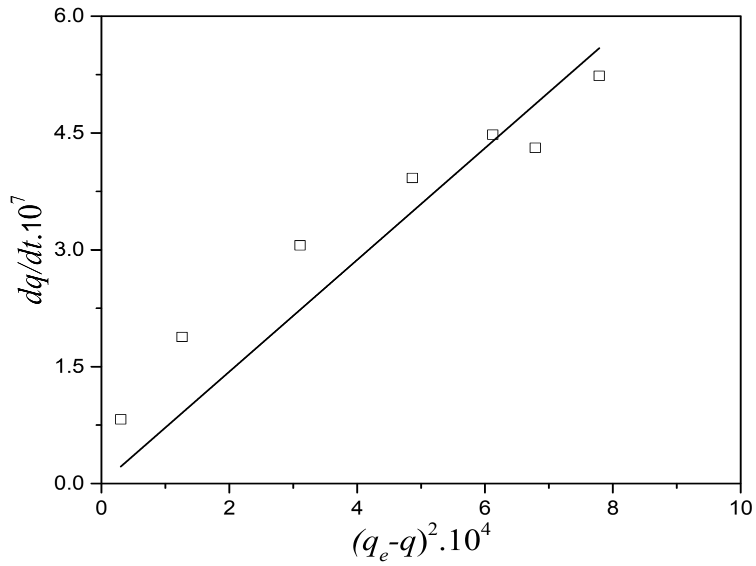

Figure S13: dq/dt vs. $(q_e - q)^2$ plot (Eq. (5)) for the System 3a

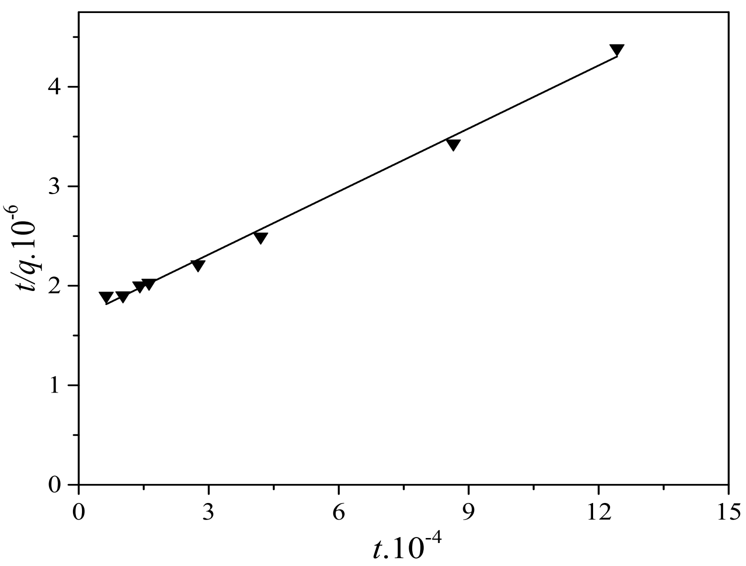

Figure S14: t/q vs. t plot (Eq. (6)) for the System 3a

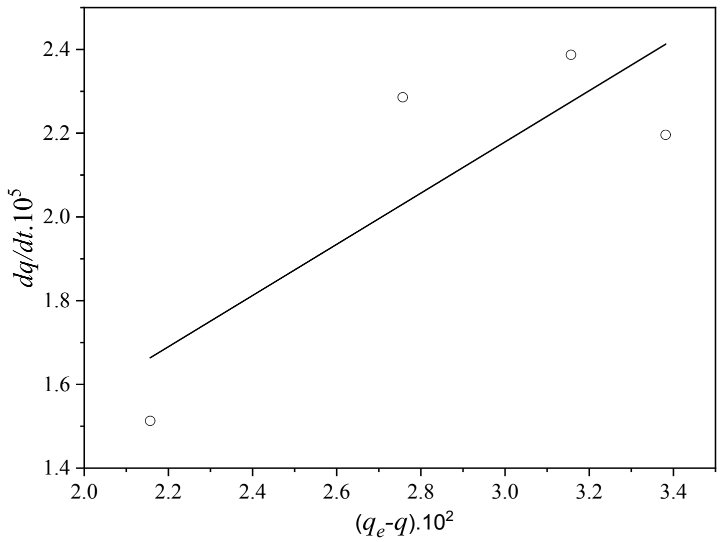

Figure S15: dq/dt vs. $(q_e - q)$ plot (Eq. (3)) for the System 4a

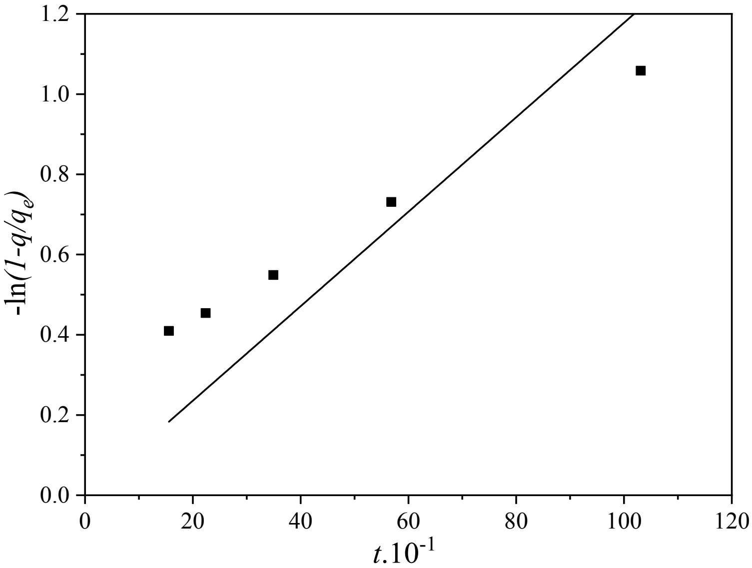

Figure S16: $-\ln(1-q/q_e)$ vs. t plot (Eq. (4)) for the System 4a

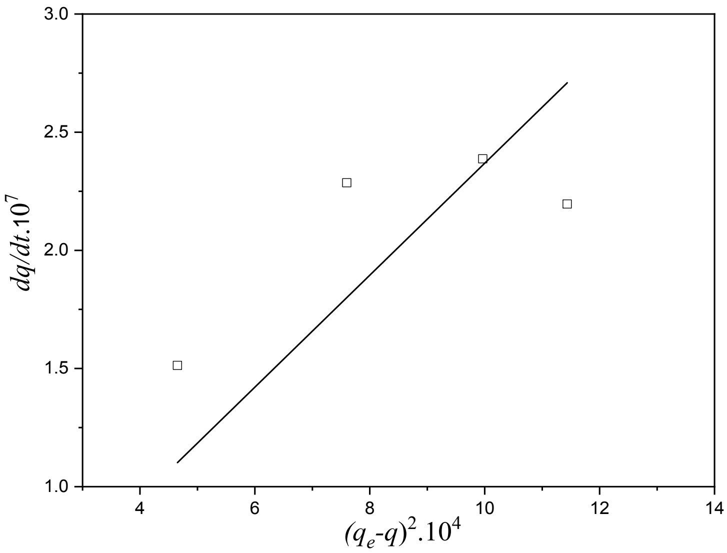

Figure S17: dq/dt vs. $(q_e - q)^2$ plot (Eq. (5)) for the System 4a

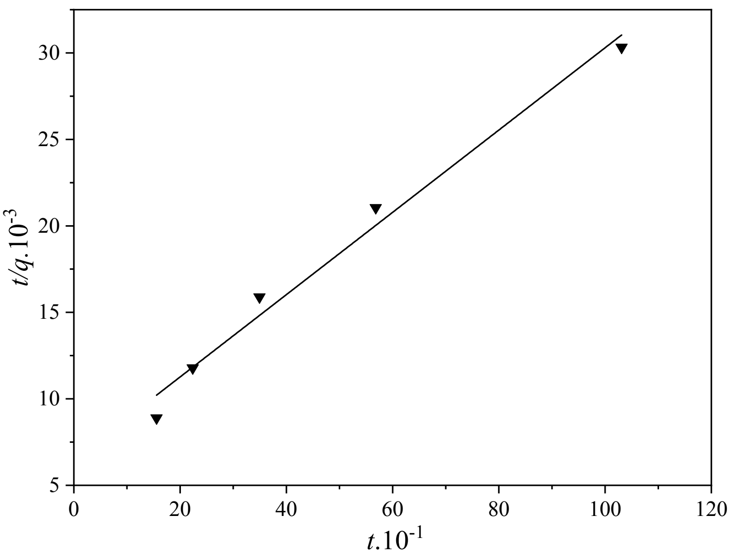

Figure S18: t/q vs. t plot (Eq. (6)) for the System 4a

Table S1: Pseudo-rate constants obtained from linear fit to: i) $-\ln(1-q/q_e)$ vs. t (Eq. (4)) and ii) dq/dt vs. $(q_e - q)$ (Eq. (3)) plots for PFO kinetics, and iii) t/q vs. t (Eq. (6)) and iv) dq/dt vs. $(q_e - q)^2$ (Eq. (5)) plots for PSO kinetics

↓Systems ↓	For PFO kinetics, fit to:			For PSO kinetics, fit to:		
	Eq. (4) (in source)	Eq. (4) (this work)	Eq. (3) (this work)	Eq. (6) (in source)	Eq. (6) (this work)	Eq. (5) (this work)
Parameter→	$K_{E1}\times10^5$ (R^2=)	$K_{E1}\times10^5$ (R^2=)	$K_{E1}\times10^5$ (R^2=)	$K_{E2}\times10^4$ (R^2=)	$K_{E2}\times10^4$ (R^2=)	$K_{E2}\times10^4$ (R^2=)
System 1a	33.3 (0.97)	46.5 (0.99)	39.3 (0.98)	11600 (1.00)	9980 (0.97)	7700 (0.90)
System 1b	31.7 (0.99)	44.7 (0.99)	38.5 (0.99)	6690 (1.00)	4730 (0.99)	4090 (0.88)
System 1c	23.3 (0.99)	37.7 (0.99)	36.6 (0.99)	2730 (1.00)	2515 (0.99)	2980 (0.96)
System 2a	5.43 (0.99)	7.19 (1.00)	7.22 (0.98)	2.55 (0.99)	2.11 (1.00)	6.62 (0.77)
System 2b	4.80 (0.99)	5.79 (1.00)	5.55 (0.98)	1.35 (0.97)	1.32 (1.00)	3.44 (0.67)
System 2c	5.08 (1.00)	5.77 (0.98)	5.63 (0.95)	1.02 (0.99)	0.94 (1.00)	2.16 (0.76)
System 3a	1.73	1.72 (1.00)	1.77 (0.98)	3.08 -	2.21 (1.00)	7.18 (0.82)

System 3b	1.80	1.78 (1.00)	1.74 (0.91)	2.72 -	1.90 (0.99)	5.67 (0.57)
System 3c	1.86	1.83 (1.00)	1.83 (0.81)	2.37	1.87 (0.99)	4.89 (0.50)
System 4a	103 (0.95)	118 (0.94)	72.9 (0.99)	420 (0.99)	670 (0.98)	273 (0.96)
System 4b	96.7 (0.99)	105 (0.98)	97.9 (0.99)	445 (0.99)	344 (0.99)	469 (0.97)
System 4c	88.3 (0.96)	132 (0.98)	141 (0.99)	498 (0.99)	372 (0.99)	921 (0.96)

(R^2 =): correlation coefficient of curve-fitting