Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Development of PANI/ $Fe(NO_3)_2$ Nanomaterial for Reactive Orange 16 (RO16) Dye Removal

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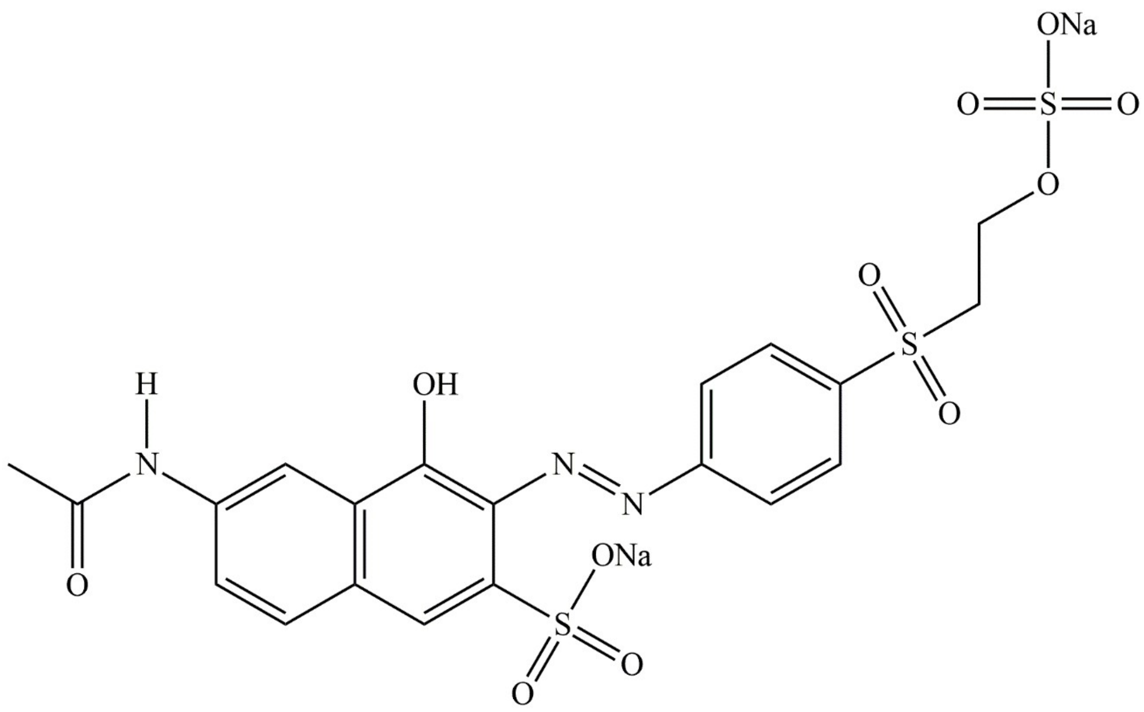


Fig. S1 Molecular structure of RO16

Table S1: General characteristics of RO16 dye

Characteristics	Description
IUPAC Name	disodium (3Z)-6-acetamido-4-oxo-3-[[4-(2-sulfonatooxyethylsulfonyl)phenyl]hydrazinylidene]naphthalene-2-sulfonate
Common Name	Remazol brilliant orange 3R
CAS number	12225-83-1
Color index number	17757
Ionization	Reactive
λmax (nm)	494 nm
Molecular weight (g/mol)	617.54
Dye content	≥ 70%
Chemical formula	$C_{20}H_{17}N_3Na_2O_{11}S_3$
H-Bond Donor	2
H-Bond Acceptor	13

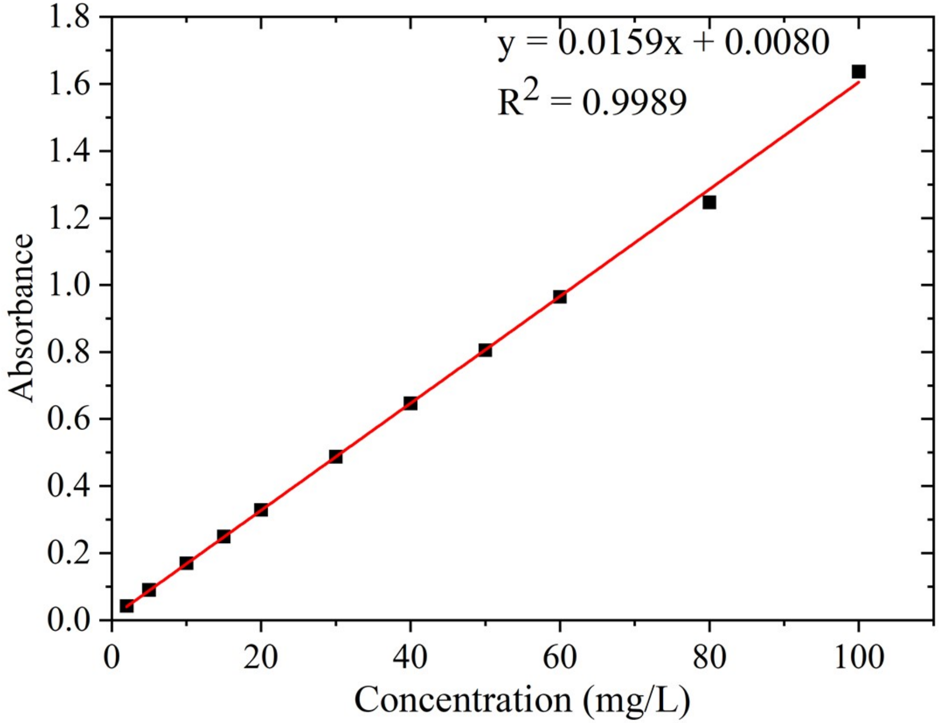


Fig.S2. Calibration curve of absorbance against concentration of RO16 dye

Table S2: Linear and non-linear isotherm equation

Type	Linear Form	Plot	Ref.
Langmuir –I (Hanes-Woolf Linearization)	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ vs. C_e	1
Langmuir –II (Lineweaver-Burk Linearization)	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \times \frac{1}{C_e}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	1
Langmuir – III (Eadie-Hoffsiee Linearization)	$q_e = q_m - \frac{1}{K_L} \times \frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	1
Langmuir –IV (Scatchard Linearization)	$\frac{q_e}{C_e} = q_m K_L - K_L q_e$	$\frac{q_e}{C_e}$ vs. q_e	1
Langmuir - V	$\frac{1}{C_e} = q_m K_L \times \frac{1}{q_e} - K_L$	$\frac{1}{C_e}$ vs. $\frac{1}{q_e}$	1
Langmuir-VI	$C_e = q_m \times \frac{C_e}{q_e} - \frac{1}{K_L}$	C_e vs. $\frac{C_e}{q_e}$	1
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	2
Temkin	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e$	q_e vs. $\ln C_e$	2
Dubinin-Radushkevich	$\ln q_e = \ln q_{DR} - K_{DR} \varepsilon^2$	$\ln q_e$ vs. ε^2	2
Harkins-Jura	$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \left(\frac{1}{A_H}\right) \log C_e$	$\frac{1}{q_e^2}$ vs. $\log C_e$	2
Halsey	$\ln q_e = \left(\frac{1}{n_H}\right) \ln K_H - \left(\frac{1}{n_H}\right) \ln C_e$	$\ln q_e$ vs. $\ln C_e$	2

Elovich	$\ln\left(\frac{q_e}{C_e}\right) = \ln(K_E)(q_m) - \left(\frac{q_e}{q_m}\right)$	$\ln\left(\frac{q_e}{C_e}\right) vs.\, q_e$	2
Jovanovic	$\ln q_e = \ln q_m - k_J C_e$	$\ln q_e \; vs.\, C_e$	2
Redlich-Peterson	$\ln\left(\frac{C_e}{q_e}\right) = \beta \ln C_e - \ln A$	$\ln\left(\frac{C_e}{q_e}\right) vs.\, \ln C_e$	2
Jossens	$\ln\left(\frac{C_e}{q_e}\right) = -\ln H + F q_e^p$	$\ln\left(\frac{C_e}{q_e}\right) vs.\, q_e^p$	2

Table S3: List of error functions

Error functions	Abbreviations	Models	Ref.
Nonlinear chi-square test	χ^2	$\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,\exp}}$	3
Sum of squares of the errors	SSE/ ERRSQ	$SSE = \sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})^2$	3
Average relative error	ARE	$ARE = \frac{100}{n} \sum_{i=1}^{n} \left\| \frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right\|$	3
Residual root mean square error	RMSE	$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{e,\exp} - q_{e,cal})^2}$	4
Coefficient of determination	R^2	$R^2 = \frac{\sum (q_{e,\exp} - \bar{q}_{e,cal})^2}{\sum (q_{e,\exp} - \bar{q}_{e,cal})^2 + \sum (q_{e,\exp} - q_{e,cal})^2}$	3
Standard deviation of relative errors	SRE	$S_{RE} = \sqrt{\frac{\sum_{i=1}^{n} [(q_{e,\exp} - q_{e,cal}) - ARE]^2}{n-1}}$	3
Marquardt's percentage standard deviation	MPSD	$MPSD = 100\sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right)^2}$	3
Normalized standard deviation	NSD	$NSD = \Delta q(\%) = 100\sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right)^2}$	5

Hybrid functional error	HYBRID	$HYBRID = \frac{100}{(n-p)} \sum_{i=1}^{n} \frac{(q_{e,\exp} - q_{e,cal})}{q_{e,\exp}}$	3
Average absolute error	EABS	$EABS = \frac{1}{n} \sum_{i=1}^{n} \left| q_{e,\exp} - q_{e,cal} \right|$	3
Sum of the absolute error	SAE	$SAE = \sum_{i=1}^{n} \left| q_{e,\exp} - q_{e,cal} \right|$	4
Average relative standard error	ARSE	$ARSE = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right)^2}$	4

$q_{e,\exp} (mg\ g^{-1})$: Value obtained from the experiment, $q_{e,cal} (mg\ g^{-1})$: Calculated value from the isotherm for corresponding, $q_{e,\exp}\overline{q}_{cal} (mg\ g^{-1})$: Mean of $q_{e,cal}$, n: Number of experiment

Table S4: Kinetics models of adsorption

Type	Linear Form	Plot	Ref.
Pseudo-first order	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	$\ln(q_e - q_t)\ vs.\ t$	6
Type-1 pseudo-second order	$\frac{t}{q_t} = \left(\frac{1}{q_e}\right)t + \left(\frac{1}{k_2 q_e^2}\right)$	$\frac{t}{q_t}\ vs.\ t$	6
Type-II pseudo-second order	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right)\left(\frac{1}{t}\right) + \left(\frac{1}{q_e}\right)$	$\frac{1}{q_t}\ vs.\ \frac{1}{t}$	6
Type-III pseudo-second order	$q_t = -\left(\frac{1}{k_2 q_e}\right)\left(\frac{q_t}{t}\right) + q_e$	$q_t\ vs.\ \frac{q_t}{t}$	6
Type-IV pseudo-second order	$\frac{q_t}{t} = -k_2 q_e q_t + k_2 q_e^2$	$\frac{q_t}{t}\ vs.\ q_t$	6
Type-V pseudo-second order	$\frac{1}{t} = k_2 q_e^2\left(\frac{1}{q_t}\right) - k_2 q_e^2\left(\frac{1}{q_e}\right)$	$\frac{1}{t}\ vs.\ \left(\frac{1}{q_t}\right)$	6

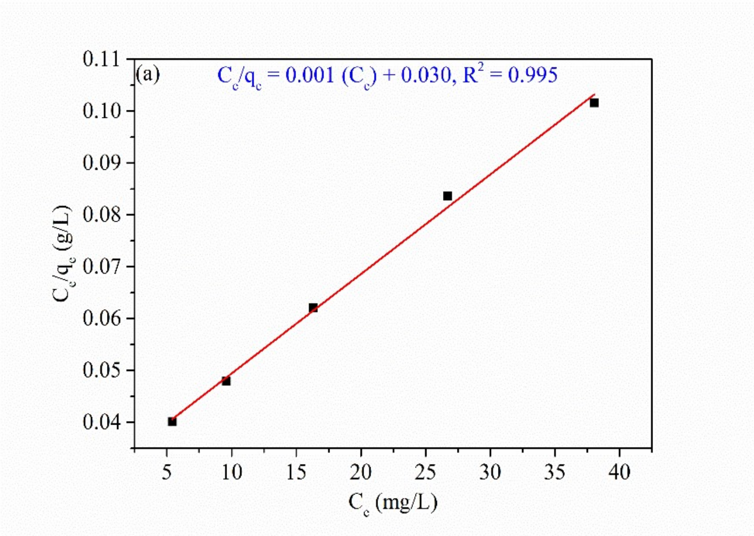
Type-VI pseudo-second order	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$	$\frac{1}{q_e - q_t}\ vs.\ t$	6
Intra-particle diffusion	$q_t = k_i \sqrt{t} + C_i$	$q_t\ vs.\ \sqrt{t}$	7
Elovich	$q_t = A + B \ln t$	$q_t\ vs.\ \ln t$	7
Bangham	$\log\left[\log\left(\frac{C_0}{C_0 - q_t m}\right)\right] = \log\left(\frac{k_0 m}{2.303V}\right) + \sigma \log t$	$\log\left[\log\left(\frac{C_0}{C_0 - q_t m}\right)\right] vs.\ \log t$	7
Boyd	$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right)$	$B_t\ vs.\ t$	7

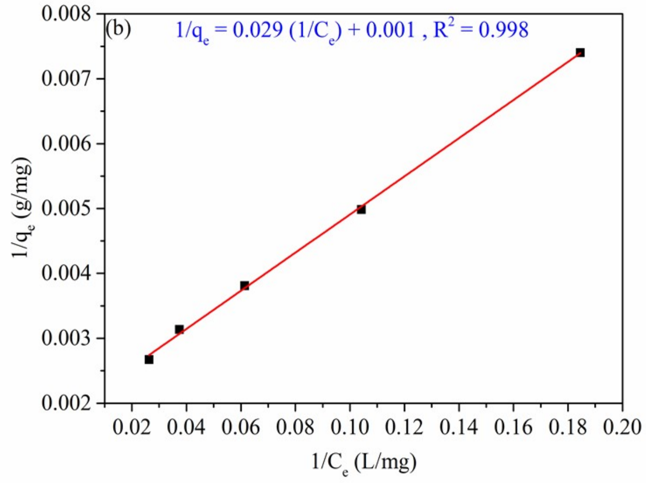
Study of adsorption thermodynamics

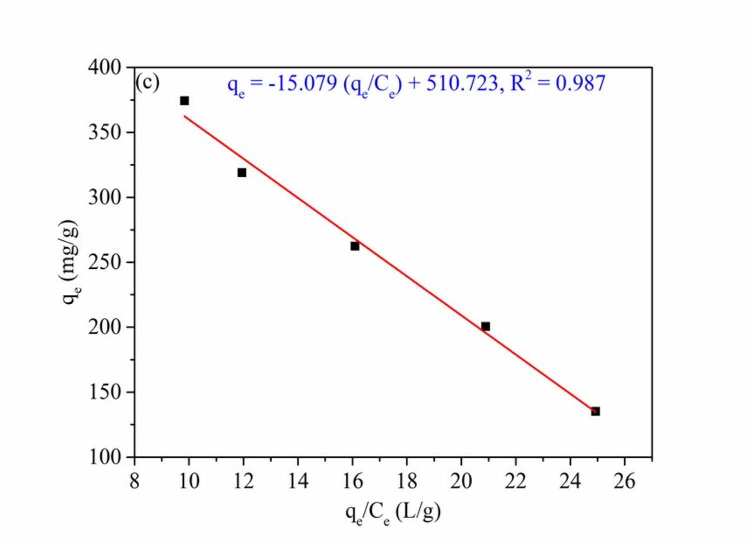
During environmental engineering, entropy and energy are considered adequately for accurately determining the continuous process occurring rapidly. The thermodynamic studies are sufficiently taken into account for scientifically investigating the adsorption process's economic feasibility and accurately estimating exothermic and endothermic nature. Excellent result of thermodynamic parameters acts as a critical indicator for practical use.

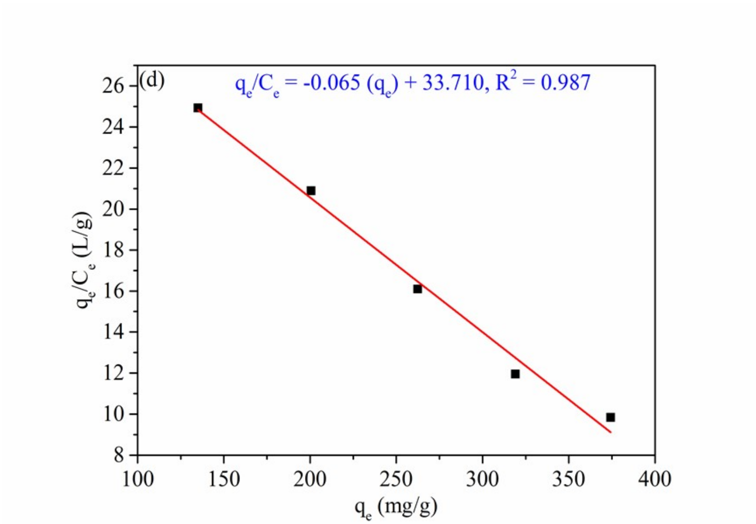
Table S5: Thermodynamic relationship for the adsorption of RO16 onto PANI/$Fe(NO_3)_2$

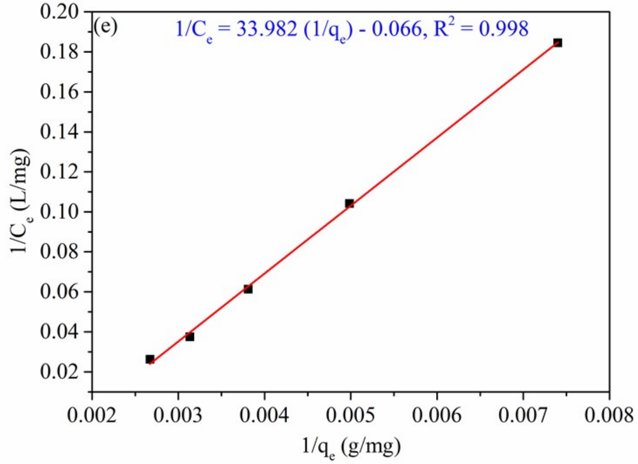
Thermodynamic relations	$\ln K_D = \frac{\Delta S^\circ}{R} + \frac{-\Delta H^\circ}{RT}$ (Van't Hoff equation)	(7)
	$K_D = \frac{q_e}{C_e}$	(8)
	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	(9)
	$\Delta G^\circ = -RT \ln K_D$	(10)

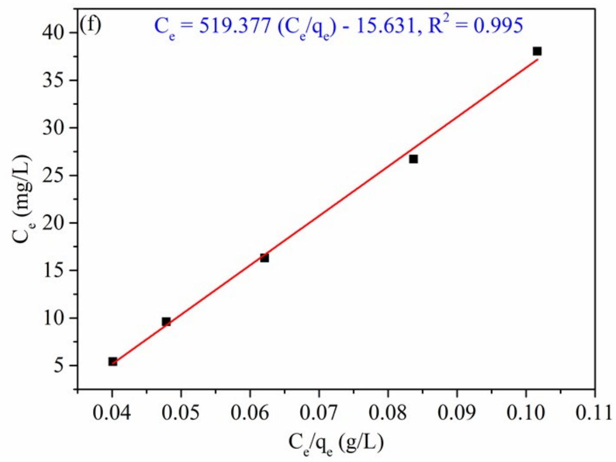

(a)
C_e/q_e = 0.001 (C_e) + 0.030, R^2 = 0.995
C_e/q_e (g/L)
C_e (mg/L)

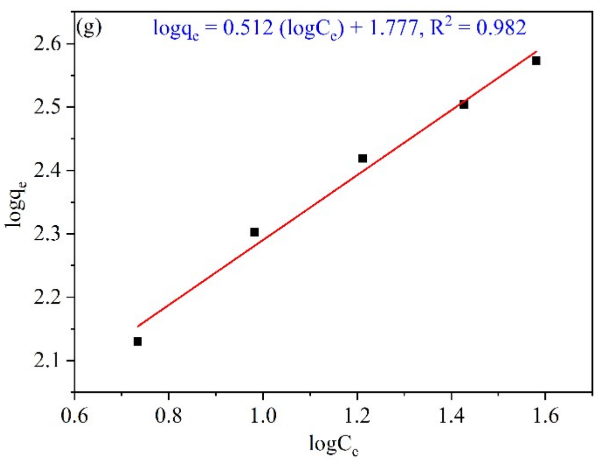

(b)
1/q_e = 0.029 (1/C_e) + 0.001 , R^2 = 0.998
1/q_e (g/mg)
1/C_e (L/mg)

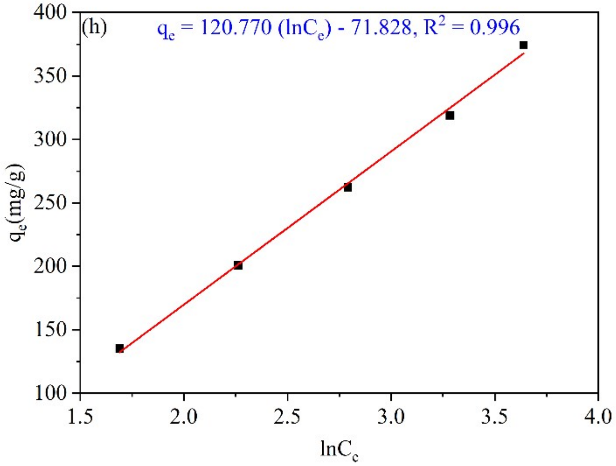

(c)
q_e = -15.079 (q_e/C_e) + 510.723, R^2 = 0.987
q_e (mg/g)
q_e/C_e (L/g)

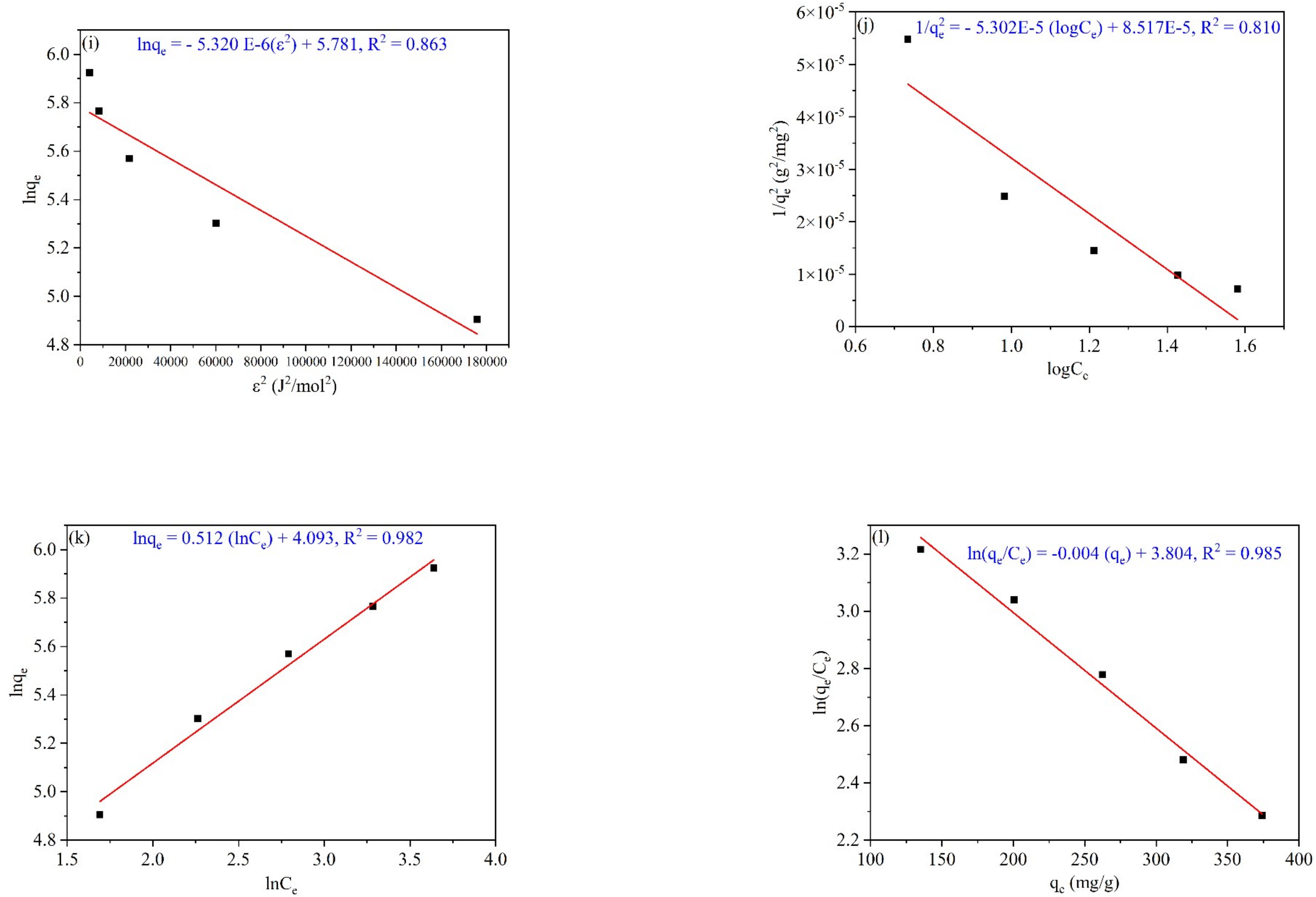

(d)
q_e/C_e = -0.065 (q_e) + 33.710, R^2 = 0.987
q_e/C_e (L/g)
q_e (mg/g)

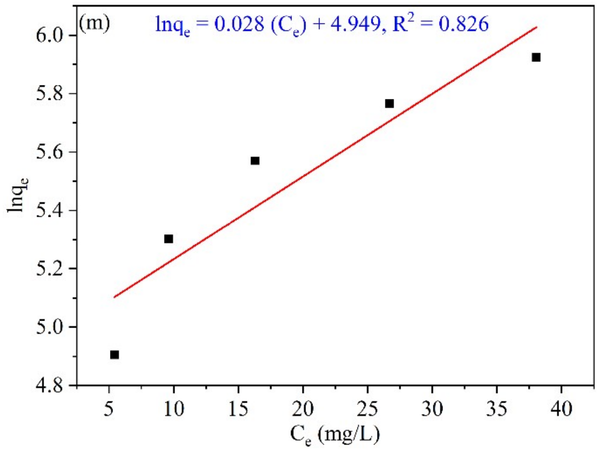

(e)
1/Ce = 33.982 (1/qe) - 0.066, R2 = 0.998
1/Ce (L/mg)
1/qe (g/mg)
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.002
0.003
0.004
0.005
0.006
0.007
0.008

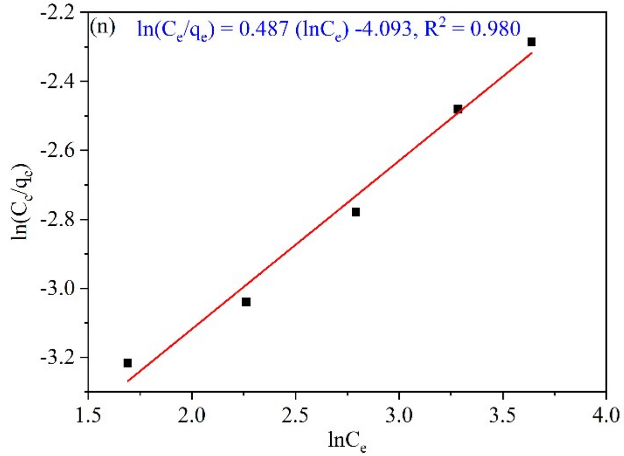

(f)
Ce = 519.377 (Ce/qe) - 15.631, R2 = 0.995
Ce (mg/L)
Ce/qe (g/L)
5
10
15
20
25
30
35
40
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11


(g)
logqe = 0.512 (logCe) + 1.777, R2 = 0.982
logqe
logCe
2.1
2.2
2.3
2.4
2.5
2.6
0.6
0.8
1.0
1.2
1.4
1.6


(h)
qe = 120.770 (lnCe) - 71.828, R2 = 0.996
qe(mg/g)
lnCe
100
150
200
250
300
350
400
1.5
2.0
2.5
3.0
3.5
4.0


(i)
lnq_e = - 5.320 E-6(ε^2) + 5.781, R^2 = 0.863
lnq_e
ε^2 (J^2/mol^2)
(j)
1/q_e^2 = - 5.302E-5 (logC_e) + 8.517E-5, R^2 = 0.810
1/q_e^2 (g^2/mg^2)
logC_e
(k)
lnq_e = 0.512 (lnC_e) + 4.093, R^2 = 0.982
lnq_e
lnC_e
(l)
ln(q_e/C_e) = -0.004 (q_e) + 3.804, R^2 = 0.985
ln(q_e/C_e)
q_e (mg/g)


(m)
lnq$_e$ = 0.028 (C$_e$) + 4.949, R^2 = 0.826
lnq$_e$
C$_e$ (mg/L)
6.0
5.8
5.6
5.4
5.2
5.0
4.8
5
10
15
20
25
30
35
40


(n)
ln(C$_e$/q$_e$) = 0.487 (lnC$_e$) -4.093, R^2 = 0.980
ln(C$_e$/q$_e$)
lnC$_e$
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
1.5
2.0
2.5
3.0
3.5
4.0

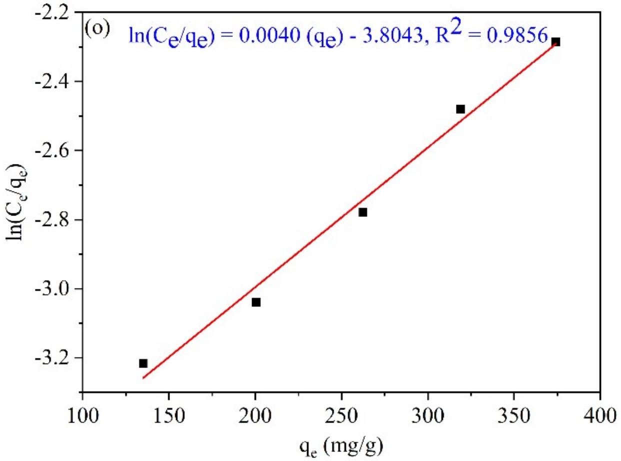

(o)
ln(C$_e$/q$_e$) = 0.0040 (q$_e$) - 3.8043, R^2 = 0.9856
ln(C$_e$/q$_e$)
q$_e$ (mg/g)
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
100
150
200
250
300
350
400

Fig.S3 Adsorption isotherms for the adsorption of dyes on: PANI/ $Fe(NO_3)_2$ (a) Langmuir –I, (b) Langmuir –II, (c) Langmuir –III, (d) Langmuir –IV, (e) Langmuir –V, (f) Langmuir –VI, (g) Freundlich, (h) Temkin, (i) Dubinin-Radushkevich, (j) Harkins-Jura, (k) Halsey, (l) Elovich, (m) Jovanovich, (n) Redlich-Peterson, (o) Jossens. Reaction conditions: (the initial concentration, contact time, pH, volume of solution, amount of adsorbent and temperature was 100 mg/L, 80 min, 4, 100 mL, 70 mg and 298K respectively).

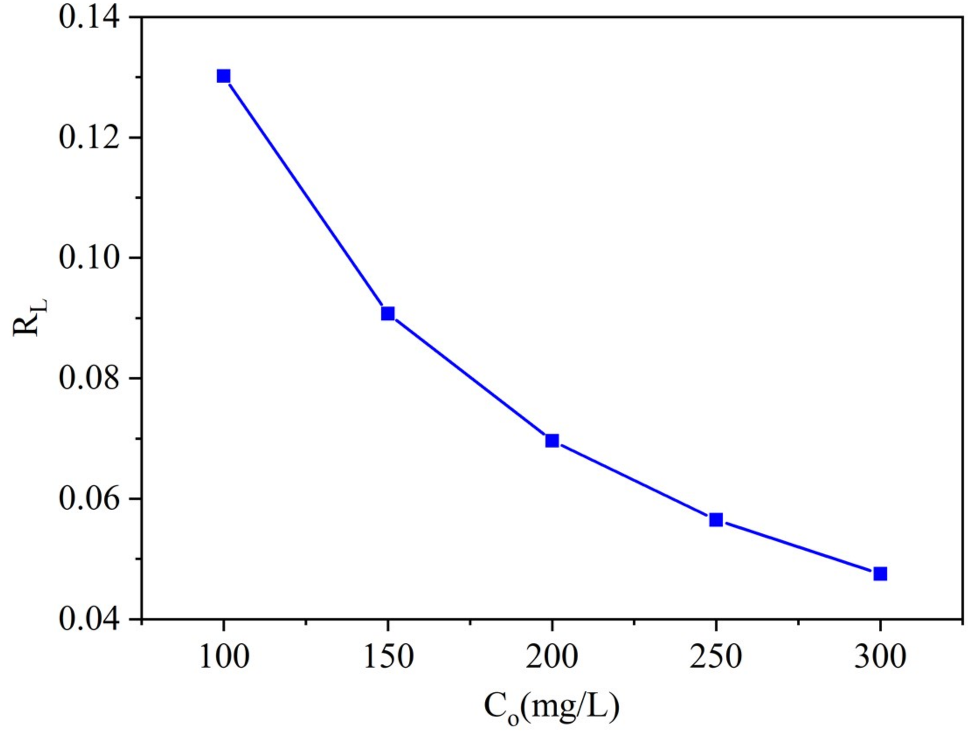
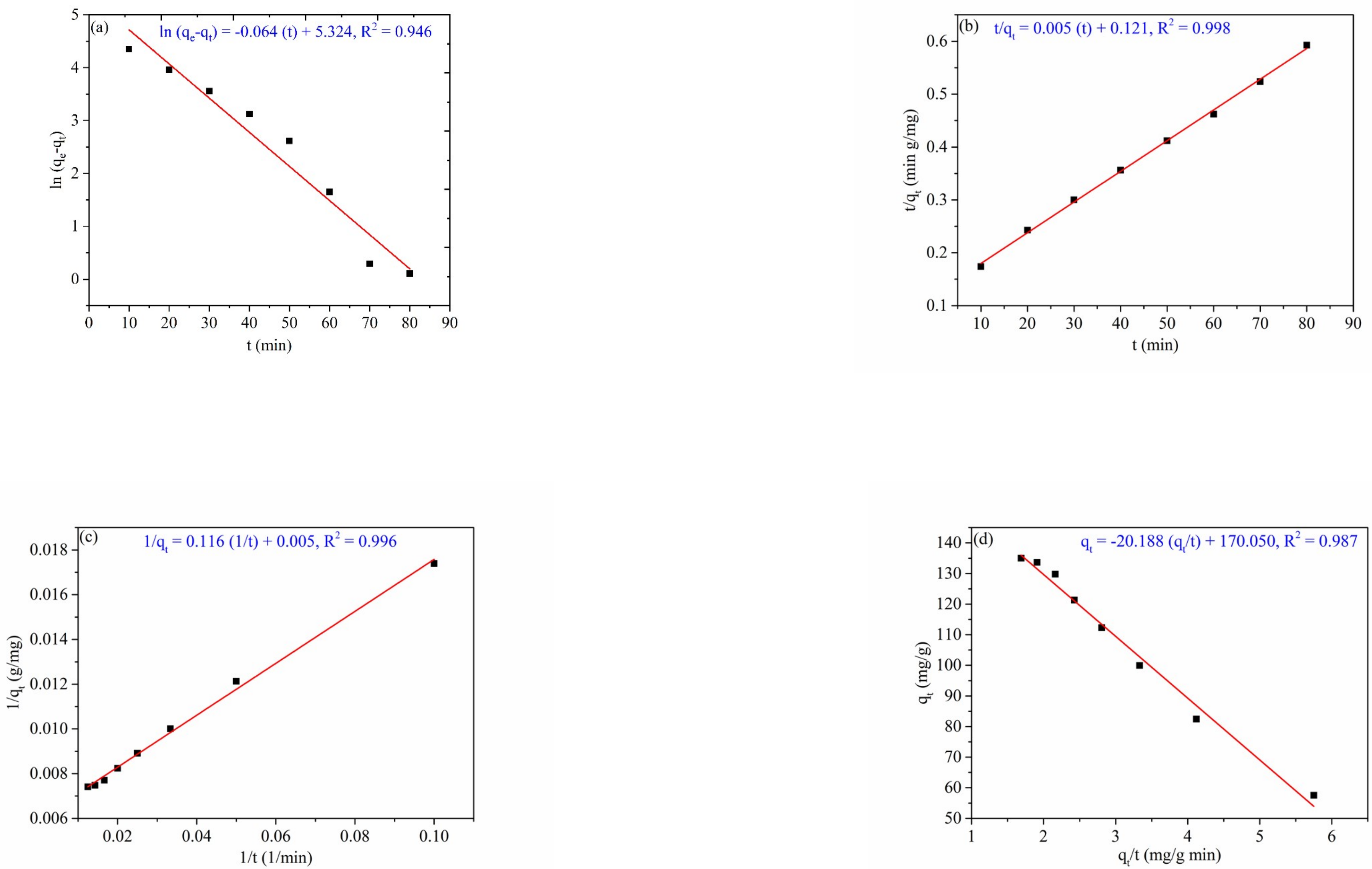
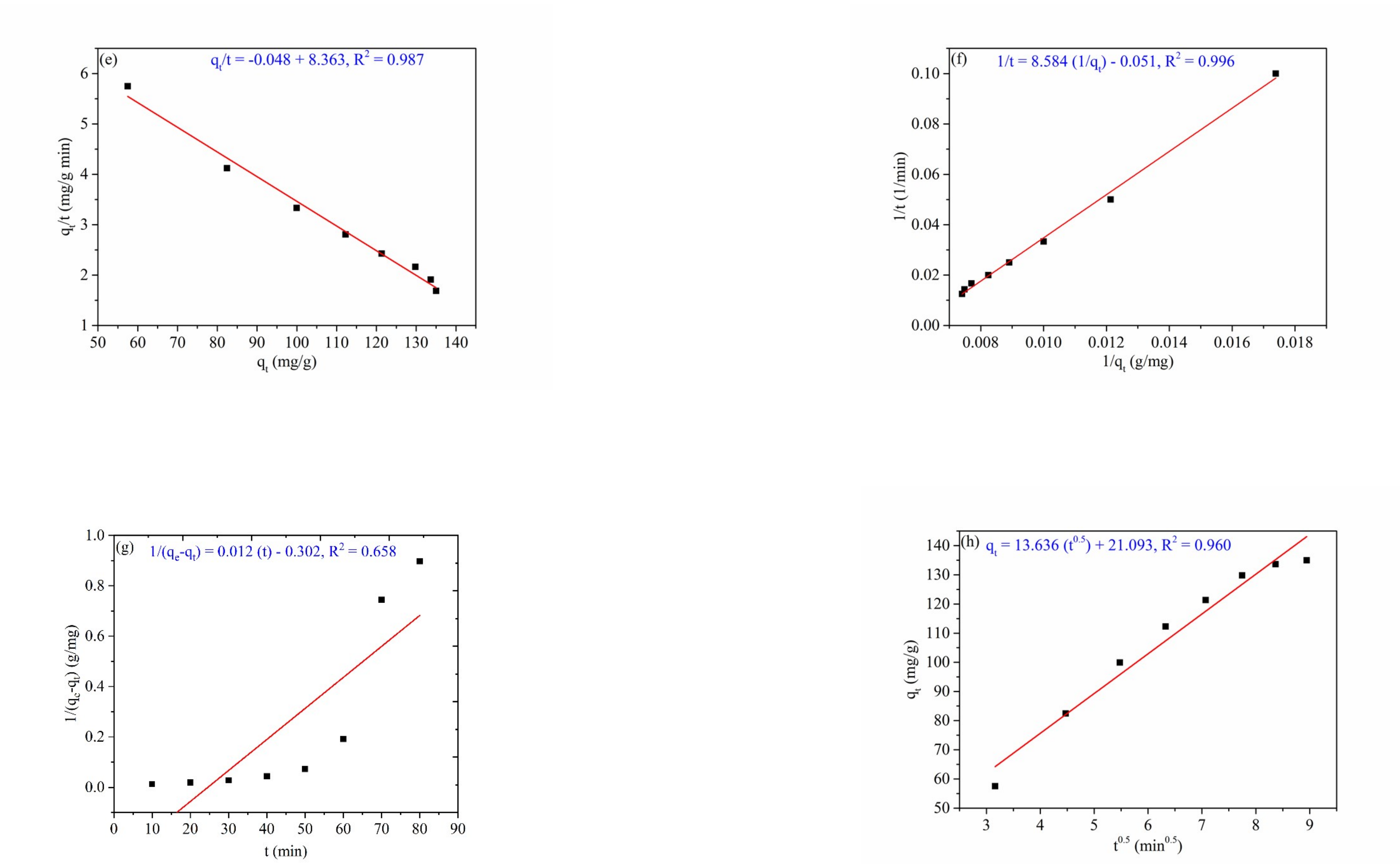


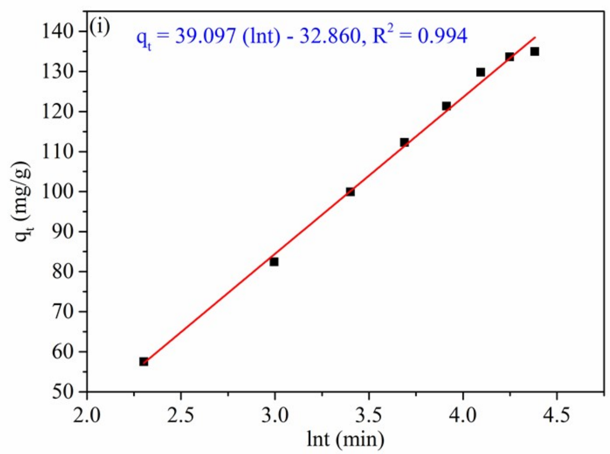
Fig.S4. Effect of initial concentration on the separation factor with: PANI/ $Fe(NO_3)_2$ (pH, volume of solution and amount of adsorbent was 4, 100 mL, and 70 mg, respectively).

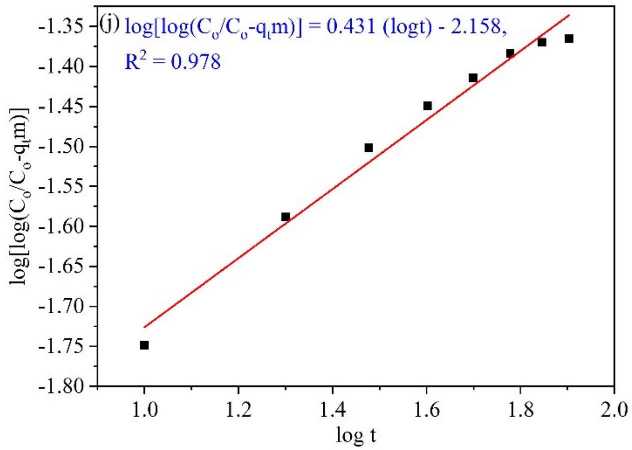
Table S6: Values of twelve different error analyses of isotherm models for RO16 adsorption onto PANI/ $Fe(NO_3)_2$ nanocomposite. Reaction conditions: (the initial concentration, contact time, pH, volume of solution, amount of adsorbent and temperature was 100 mg/L, 80 min, 4, 100 mL, 70 mg and 298K respectively).

Isotherms	**Error**											
	SSE/ ERRSQ	**χ^2**	**R^2**	**ARE**	**RMSE**	**HYBRID**	**MPSD**	**SAE**	**EABS**	**ARSE**	**SRE**	**NSD**
Langmuir –I	8.619E-06	1.07E-04	0.9955	0.1759	1.467E-03	0.2199	1.9805	7E-05	1.4E-05	0.0190	0.0467	1.9085
Langmuir –II	1.18E-08	3.73E-06	0.9988	0.0642	5.431E-05	0.0803	1.7543	8.673E-19	1.734E-19	0.0175	0.0283	1.7543
Langmuir –III	339.3743	1.065	0.9877	0.0053	9.2110	0.0067	2.9489	0.4631	0.0926	0.0290	0.3401	2.9489
Langmuir –IV	1.4185	0.1197	0.9877	0.1029	0.5955	0.1286	5.1296	0.0213	0.0042	0.0512	0.0636	5.1296
Langmuir –V	1.376E-05	0.0003	0.9988	0.3601	0.0018	0.4501	5.3889	0.0001	3.2E-05	0.0538	0.0673	5.3889
Langmuir –VI	0.0015	0.0006	0.9955	0.0154	0.0199	0.0193	0.8701	0.0008	0.0001	0.0087	0.0029	0.8701
Freundlich	8.611E-06	0.0001	0.9823	0.1759	0.0014	0.2199	1.9805	7E-05	1.4E-05	0.0190	0.0467	1.9085
Temkin	97.1229	0.3259	0.9964	0.0766	4.9275	0.0958	1.7688	0.4435	0.0887	0.0176	0.3344	1.7688
Dubinin-Radushkevich	0.0662	0.0119	0.8631	0.0318	0.1286	0.0398	2.3184	0.0018	0.0003	0.0231	0.0291	2.3184
Harkins-Jura	2.133E-10	1.146E-05	0.8104	4.5932	7.303E-06	5.7415	49.4243	8.464E-08	1.692E-08	0.4942	0.2396	49.4243
Halsey	0.0084	0.0015	0.9823	0.0155	0.0460	0.0194	0.8700	0.0018	0.0003	0.0087	0.0166	0.8700
Elovich	0.0063	0.0021	0.9856	0.0149	0.0397	0.0186	1.3737	0.0013	0.0002	0.0137	0.0227	1.3737
Jovanovic	0.0838	0.0159	0.8264	0.07319	0.1448	0.0914	2.7558	0.0019	0.0003	0.0275	0.0208	2.7558
Redlich-Peterson	0.0087	-0.0030	0.9805	0.0246	0.0466	0.0307	1.6196	0.0018	0.0003	0.0161	0.0119	1.6196
Jossens	0.0063	-0.0021	0.9856	0.0149	0.0397	0.0186	1.3737	0.0013	0.0002	0.0137	0.0120	1.3737


(a)
ln (qe-qt) = -0.064 (t) + 5.324, R2 = 0.946
ln (qe-qt)
t (min)
(b)
t/qt = 0.005 (t) + 0.121, R2 = 0.998
t/qt (min g/mg)
t (min)
(c)
1/qt = 0.116 (1/t) + 0.005, R2 = 0.996
1/qt (g/mg)
1/t (1/min)
(d)
qt = -20.188 (qt/t) + 170.050, R2 = 0.987
qt (mg/g)
qt/t (mg/g min)


(e)
q_t/t = -0.048 + 8.363, R^2 = 0.987
q_t/t (mg/g min)
q_t (mg/g)
(f)
1/t = 8.584 (1/q_t) - 0.051, R^2 = 0.996
1/t (1/min)
1/q_t (g/mg)
(g)
1/(q_e-q_t) = 0.012 (t) - 0.302, R^2 = 0.658
1/(q_e-q_t) (g/mg)
t (min)
(h)
q_t = 13.636 (t^0.5) + 21.093, R^2 = 0.960
q_t (mg/g)
t^0.5 (min^0.5)


(i)
q_t = 39.097 (lnt) - 32.860, R^2 = 0.994
q_t (mg/g)
lnt (min)


(j)
log[log(C_o/C_o-q_tm)] = 0.431 (logt) - 2.158,
R^2 = 0.978
log[log(C_o/C_o-q_tm)]
log t

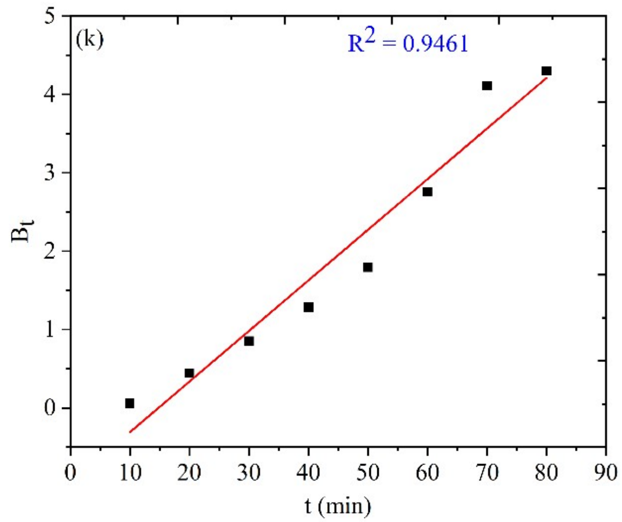

(k)
R^2 = 0.9461
B_t
t (min)

Fig.S5 Adsorption kinetics for the adsorption of dyes on: PANI/ $Fe(NO_3)_2$ (a) Pseudo-first order, (b) Type-I pseudo-second order, (c) Type-II pseudo-second order, (d) Type-III pseudo-second order, (e) Type-IV pseudo-second order, (f) Type-V pseudo-second order, (g) Type-VI pseudo-second order, (h) Intra-particle diffusion, (i) Elovich, (j) Bangham, (k) Boyd. Reaction conditions: (the initial concentration, contact time, pH, volume of solution, amount of adsorbent and temperature was 100 mg/L, (10-80) min, 4, 100 mL, 70 mg and 298K respectively).

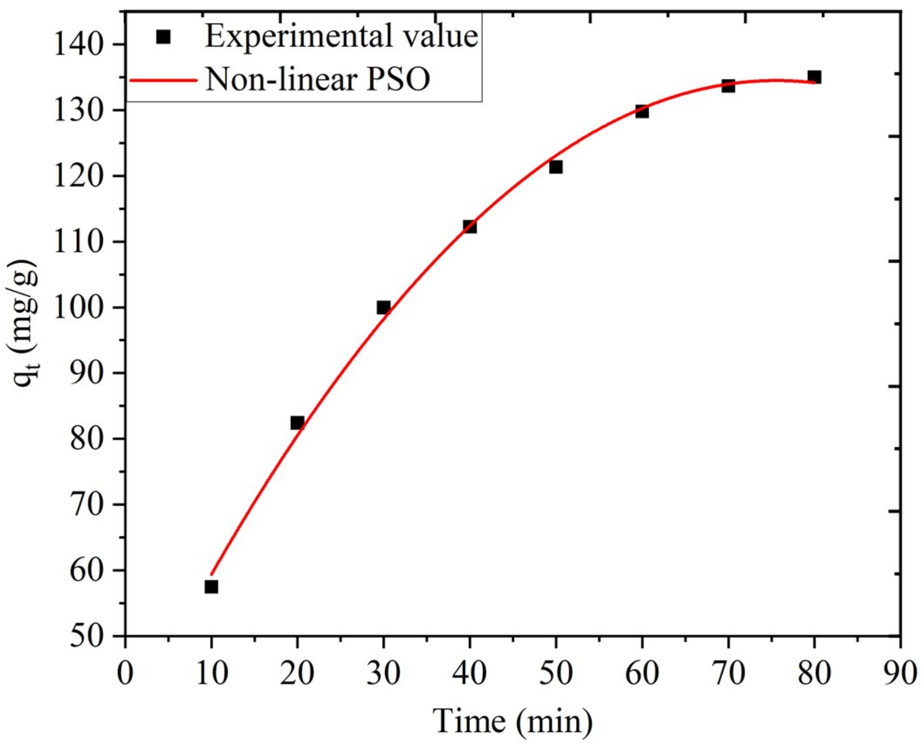


Fig.S6 PSO kinetics obtained by the nonlinear method

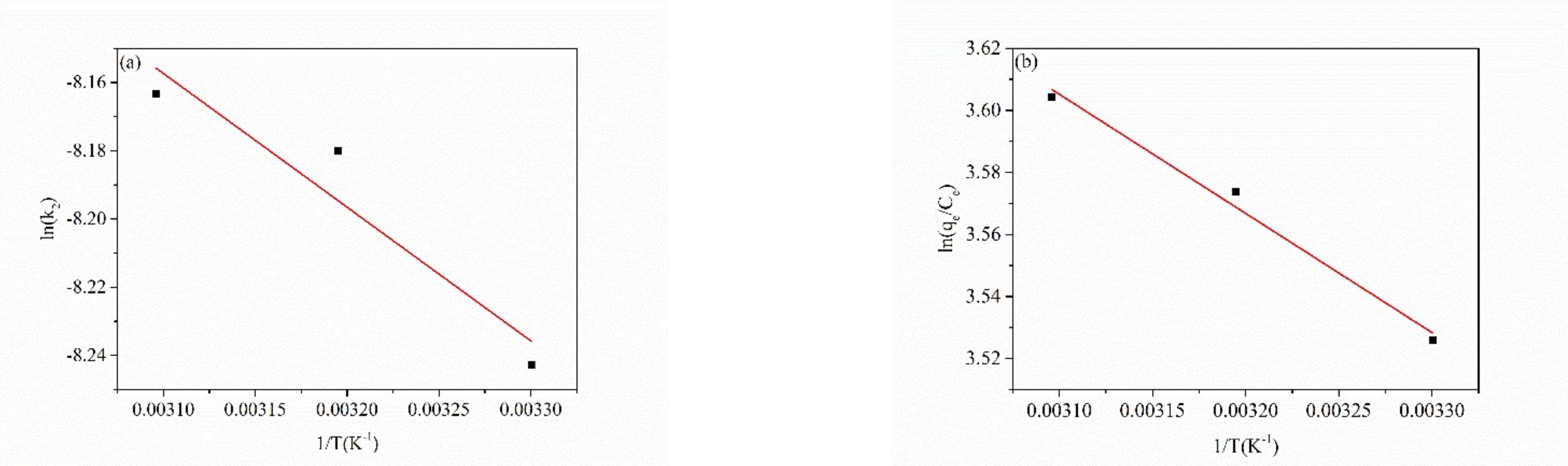
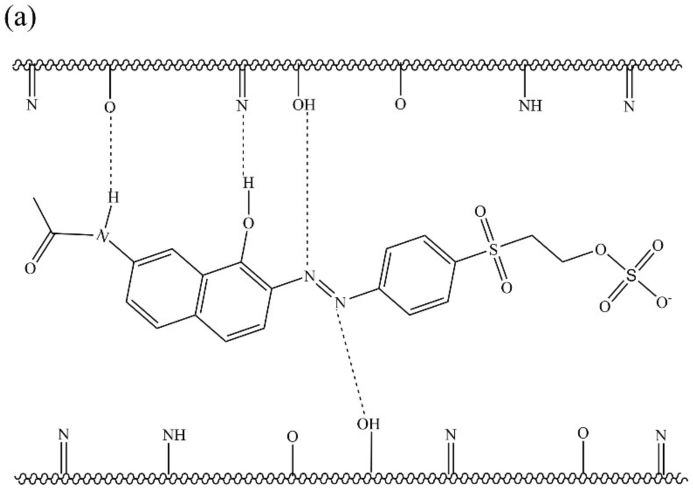


Fig.S7 (a) Arrhenius plot for the activation energy and (b) Van't Hoff regression (thermodynamics) of adsorption of RO16 dye onto PANI/ $Fe(NO_3)_2$. (the initial concentration, contact time, volume of solution and amount of adsorbent was 100 mg/L, 80 min, 100 mL and 70 mg, respectively).



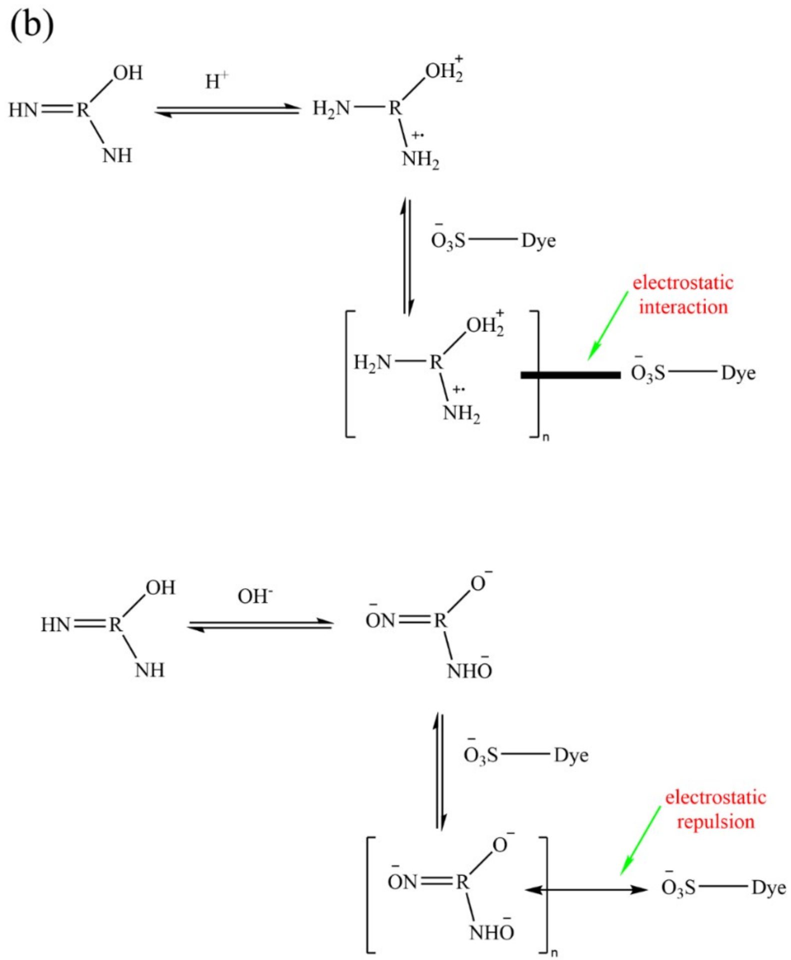


Fig.S8 (a) Proposed mechanism for the adsorption of RO16 onto PANI/ $Fe(NO_3)_2$ surface. =N, -NH, and –OH representing the functional groups present onto the PANI/ $Fe(NO_3)_2$ composite. and (b) Electrostatic interaction and repulsion.

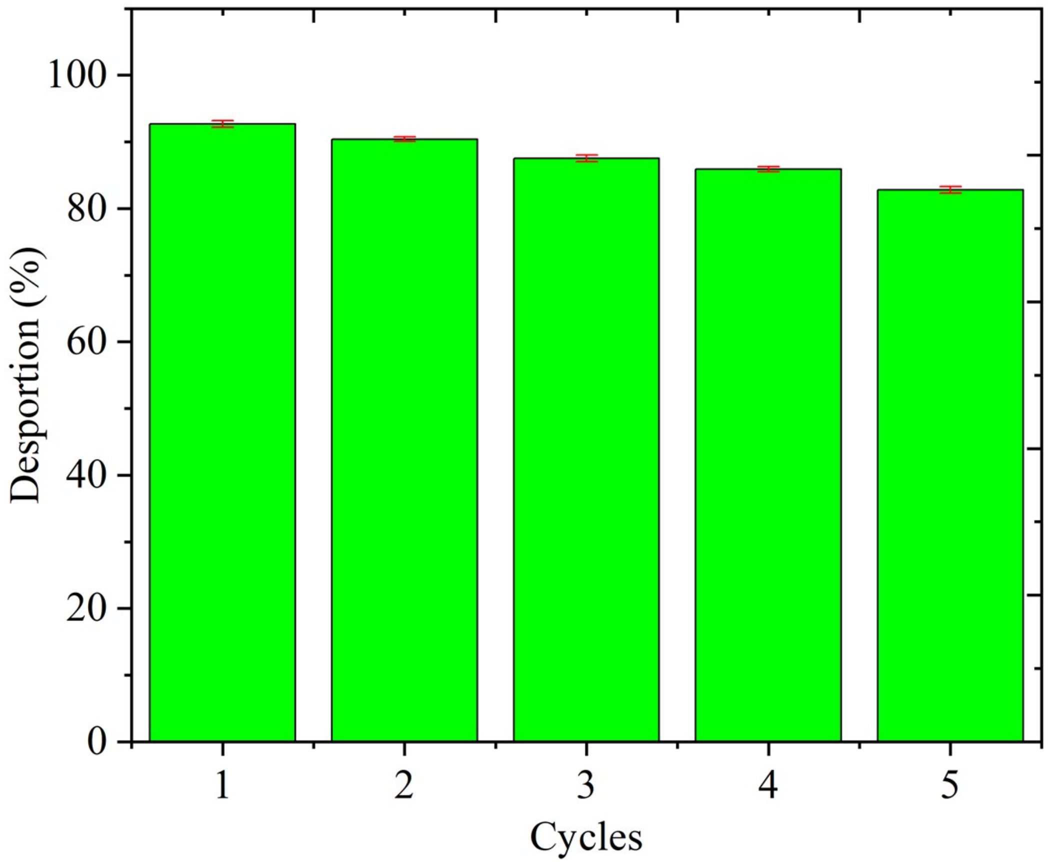


Fig.S9 Cycles of reuse (Adsorption/desorption) on the removal efficiency with PANI/ $Fe(NO_3)_2$ (the initial concentration, pH, contact time, volume of solution and amount of adsorbent was 100 mg/L, 4, 80 min, 100 mL, and 70 mg, respectively).

Table S7: The water quality parameters of different water samples

Water Quality Parameters	**Units**	**Water Sample**		
		Tap water	**Raw water**	**Waste water**
pH		7.00	6.20	7.70
$C_{Ca^{2+}}$	$(mg\ L^{-1})$	12.8	54.3	12.5
$C_{Mg^{2+}}$	$(mg\ L^{-1})$	1.8	17.7	3.9
$C_{Na^{+}}$	$(mg\ L^{-1})$	21.5	186.5	47.5
$C_{K^{+}}$	$(mg\ L^{-1})$	2.3	20.2	4.7

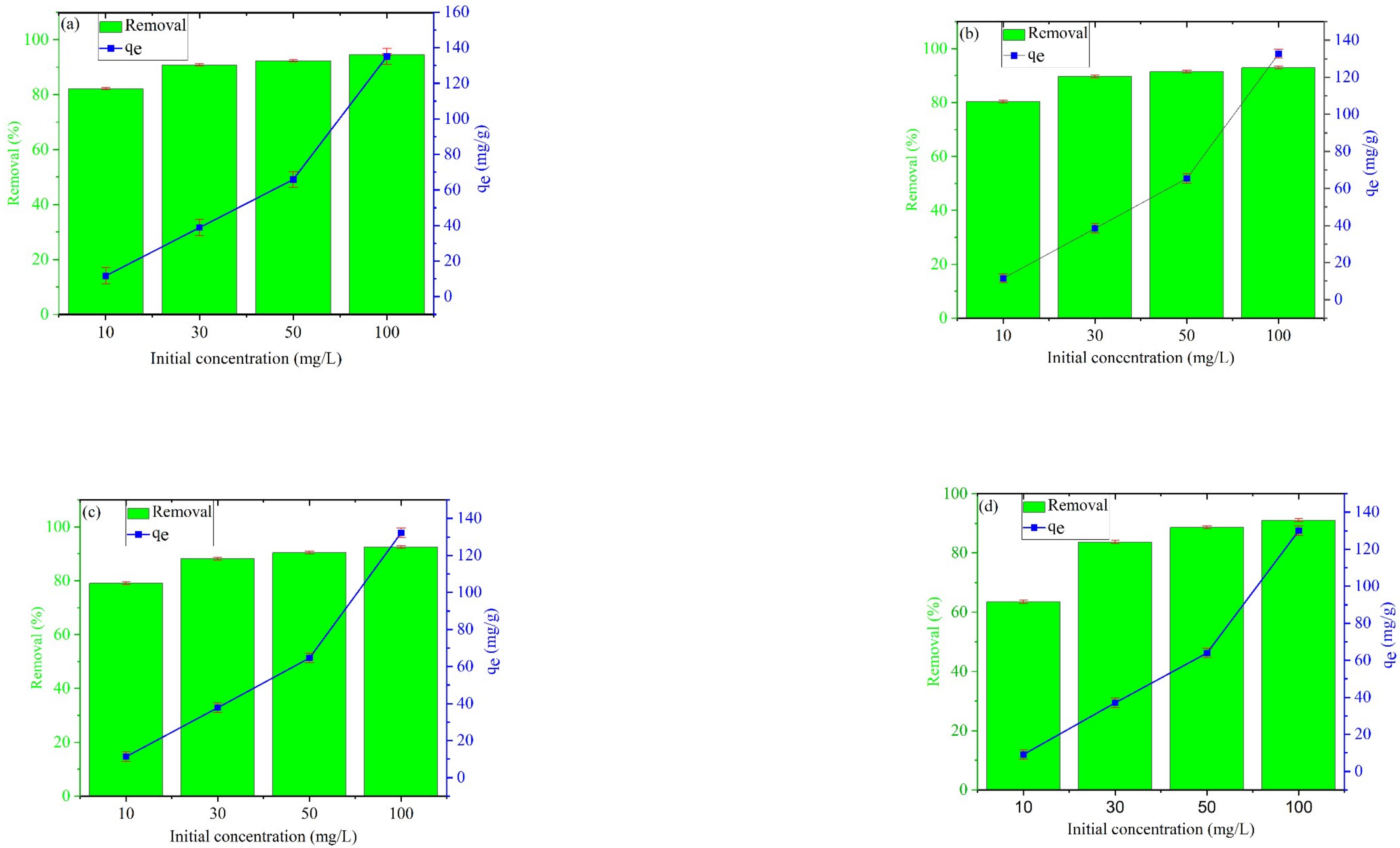

(a)
Removal
qe
Removal (%)
qe (mg/g)
Initial concentration (mg/L)
(b)
Removal
qe
Removal (%)
qe (mg/g)
Initial concentration (mg/L)
(c)
Removal
qe
Removal (%)
qe (mg/g)
Initial concentration (mg/L)
(d)
Removal
qe
Removal (%)
qe (mg/g)
Initial concentration (mg/L)

Fig.S10 Adsorption removal of RO16 dye from real water samples' PANI/ $Fe(NO_3)_2$ (the initial concentration, pH, contact time, volume of solution and amount of adsorbent was 10, 30, 50, 100 mg/L, 4, 80 min, 100 mL, and 70 mg, respectively).

Notes and references

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