materials

MDPI

Supplementary materials

Fabrication, Characterization and Evaluation of an Alginate-Lignin Composite for Rare-Earth Elements Recovery

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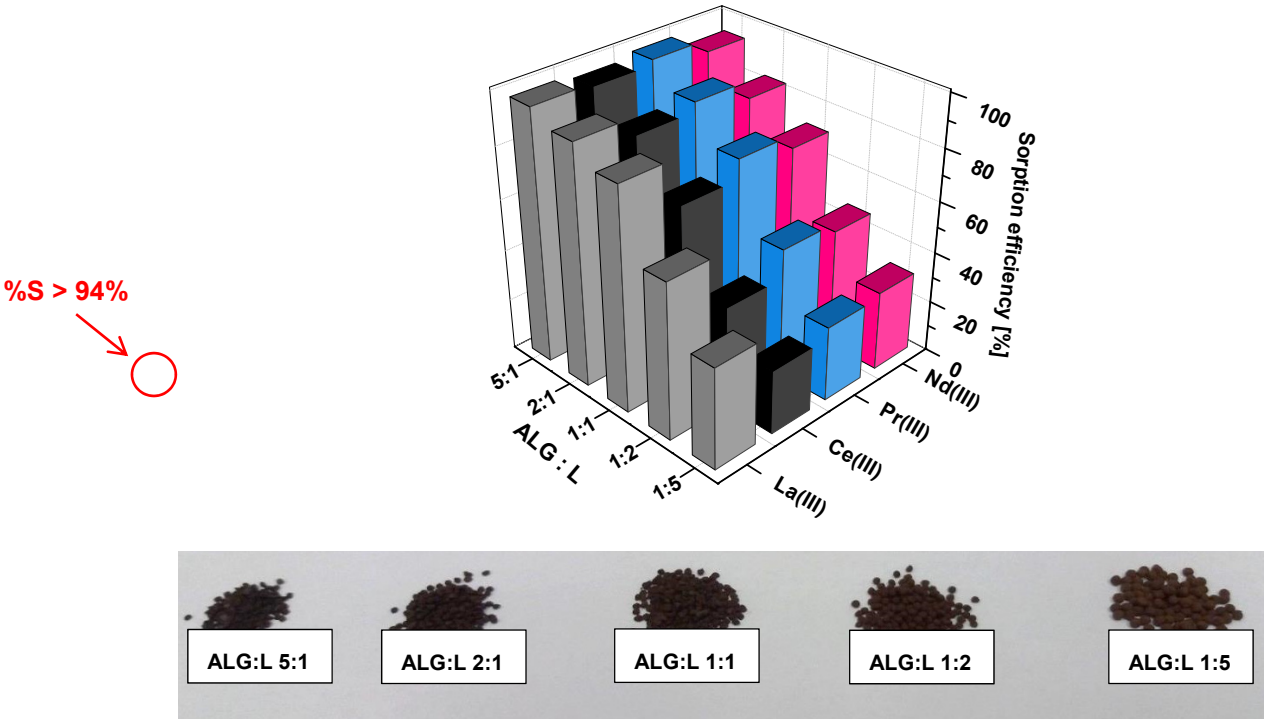


Figure S1. Sorption effectiveness results depending on the ALG:L ratios (conditions: C_0 = 100 mg/dm^3, pH = 5, m = 0.05 g, V = 20 cm^3, t = 480 min, T = 293 K).

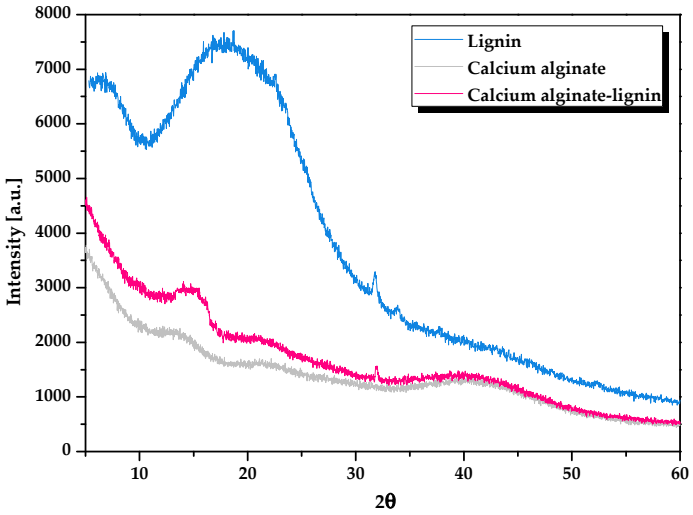
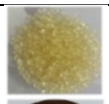


Figure S2. XRD patterns of calcium alginate, lignin, and calcium alginate-lignin composite.

Table S1. Textural parameters of the studied biosorbents.

Biosorbent		*Textural parameters*		
		S_{BET} [m²/g]	D [nm]	V_{total} [cm³/g]
Calcium alginate		4.707	3.144	0.773×10^{-2}
Lignin		1.918	6.107	$0.385\ 10^{-2}$
Calcium alginate-lignin (ALG_5L_1)		8.018	2.975	1.070×10^{-2}

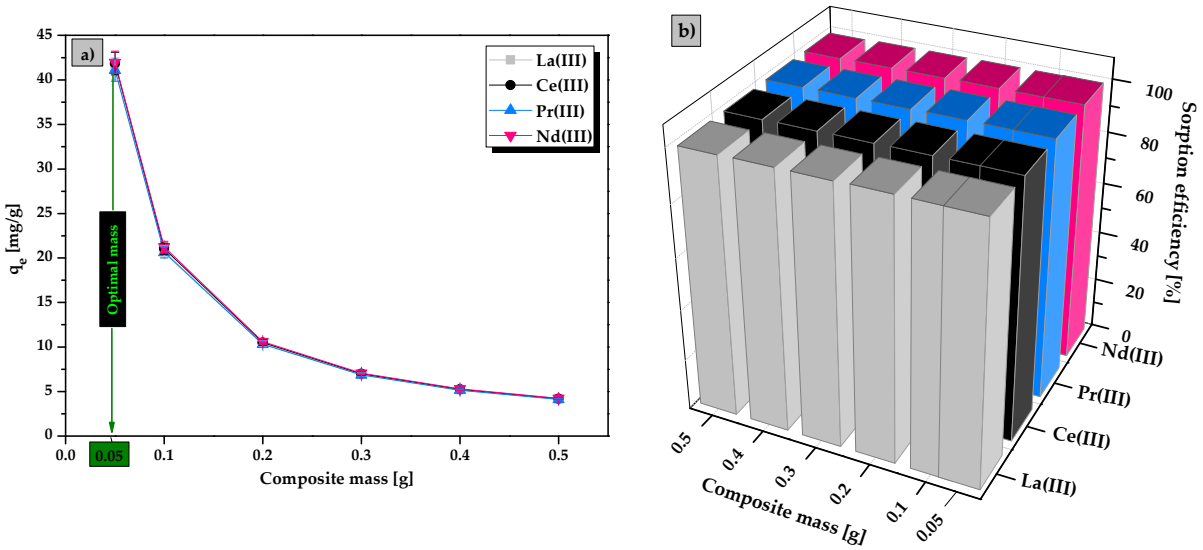


Figure S3. Influence of composite mass on La(III), Ce(III), Pr(III), and Nd(III) ions sorption by the ALG_5L_1 composite (conditions: C_0 = 100 mg/dm³, pH = 5, m = 0.05-0.5 g, V = 20 cm³, t = 480 min, T = 293 K).

Table S2. Calculated thermodynamic parameters for the La(III), Ce(III), Pr(III), and Nd(III) ions sorption onto ALG_5L_1 composite.

ALG_5L_1 + sorbed metal ions	***ΔH°* [kJ/mol]**	***ΔS°* [J/mol·K]**	R^2	***ΔG°* [kJ/mol]**		
				293 K	**313 K**	**333 K**
ALG_5L_1 + La(III)	7.31	32.27	0.985	-18.94	-20.83	-22.52
ALG_5L_1 + Ce(III)	7.76	33.79	0.973	-18.93	-20.89	-22.56
ALG_5L_1 + Pr(III)	6.11	25.39	0.974	-18.19	-19.74	-21.51
ALG_5L_1 + Nd(III)	8.45	32.20	0.934	-17.89	-19.45	-21.50

Table S3. Calculated thermodynamic parameters for La(III), Ce(III), Pr(III), and Nd(III) ions sorption onto lignin.

Lignin + sorbed metal ions	***ΔH°* [kJ/mol]**	***ΔS°* [J/mol·K]**	R^2	***ΔG°* [kJ/mol]**		
				293 K	**313 K**	**333 K**
Lignin + La(III)	3.98	1.03	1.000	-13.15	-14.32	-15.49
Lignin + Ce(III)	6.79	7.70	0.995	-12.30	-13.54	-14.90
Lignin + Pr(III)	9.27	18.20	0.998	-12.91	-14.38	-15.93
Lignin + Nd(III)	4.65	0.71	0.999	-11.98	-13.10	-14.25

Table S4. Calculated kinetic parameters for Ce(III) ions sorption onto the ALG_5L_1 composite.

Kinetic model	Equations	Parameter	ALG_5L_1				
		C_0 [mg/dm³]	25	50	100	150	200
		q_{exp} [mg/g]	9.56	19.85	40.65	61.04	86.13
PFO	$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} \times t$	q_1 [mg/g]	5.50	17.08	38.62	48.57	76.94
		$k_1 \times 10^{-2}$ [1/min]	2.15	2.18	1.02	0.37	0.26
		R^2	0.883	0.967	0.996	0.936	0.985
PSO	$\frac{t}{q_t} = \frac{1}{k_2 \times q_2^2} + \frac{1}{q_2} \times t$	q_2 [mg/g]	10.14	23.20	42.88	65.88	91.62
	$h = k_2 \times q_2^2$	$k_2 \times 10^{-2}$ [g/mg·min]	0.49	0.076	0.045	0.014	0.007
		h [mg/g·min]	0.50	0.41	0.83	0.61	0.62
		R^2	0.997	0.997	0.998	0.992	0.984
IPD	$q_t = k_i \times t^{1/2} + C_i$	k_{i1} [mg/g·min$^{1/2}$]	0.92	1.59	2.05	3.28	1.80
		C_1	0.45	0.68	1.18	3.30	0.37
		R^2	0.974	0.953	0.986	0.988	0.904
		k_{i2} [mg/g·min$^{1/2}$]	0.89	1.96	2.50	2.78	3.33
		C_2	0.70	1.30	0.85	1.73	3.15
		R^2	0.859	0.955	0.980	0.981	0.996
		k_{i3} [mg/g·min$^{1/2}$]	0.003	0.013	0.17	0.45	1.41
		C_3	9.49	19.57	35.16	44.38	33.63
		R^2	0.978	0.939	0.568	0.925	0.980
Boyd	$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt)$	B	6.24	6.75	4.52	2.79	1.98
	$F = \frac{q_t}{q_e}$	R^2	0.891	0.971	0.992	0.873	0.997
DW	$\log(1 - F^2) = -\frac{K}{2.303t}$	K	0.020	0.020	0.009	0.003	0.002
		R^2	0.896	0.973	0.990	0.972	0.997

Table S5. Calculated kinetic parameters for Pr(III) ions sorption onto the ALG_5L_1 composite.

Kinetic model	Equations	Parameter	ALG_5L_1				
		C_0 [mg/dm³]	25	50	100	150	200
		q_{exp} [mg/g]	9.15	19.10	39.33	60.06	74.65
PFO	$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} \times t$	q_1 [mg/g]	5.25	17.06	39.37	50.67	63.91
		$k_1 \times 10^{-2}$ [1/min]	2.46	2.36	1.05	0.39	0.28
		R^2	0.899	0.987	0.995	0.965	0.978
PSO	$\frac{t}{q_t} = \frac{1}{k_2 \times q_2^2} + \frac{1}{q_2} \times t$	q_2 [mg/g]	9.64	20.84	42.22	64.86	79.26
	$h = k_2 \times q_2^2$	$k_2 \times 10^{-2}$ [g/mg·min]	0.58	0.15	0.035	0.014	0.010
		h [mg/g·min]	0.54	0.66	0.62	0.59	0.62
		R^2	0.998	0.995	0.996	0.996	0.991
IPD	$q_t = k_i \times t^{1/2} + C_i$	k_{i1} [mg/g·min$^{1/2}$]	1.15	1.63	1.24	2.16	4.03
		C_1	0.80	1.11	0.51	1.66	4.09
		R^2	0.970	0.901	0.993	0.821	0.912
		k_{i2} [mg/g·min$^{1/2}$]	0.80	1.78	2.24	2.57	2.75
		C_2	1.13	0.27	2.14	2.26	2.78
		R^2	0.871	0.953	0.995	0.988	0.981
		k_{i3} [mg/g·min$^{1/2}$]	0.001	0.015	0.21	0.49	1.06
		C_3	9.12	18.79	32.88	42.42	35.53
		R^2	0.974	0.735	0.482	0.858	0.975
Boyd	$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt)$	B	7.10	7.46	4.40	3.05	2.21
	$F = \frac{q_t}{q_e}$	R^2	0.905	0.989	0.985	0.913	0.998
DW	$\log(1 - F^2) = -\frac{K}{2.303t}$	K	0.023	0.022	0.009	0.003	0.002
		R^2	0.909	0.990	0.982	0.985	0.998

Table S6. Calculated kinetic parameters for Nd(III) ions sorption onto the ALG$_5$L$_1$ composite.

Kinetic model	Equations	Parameter	ALG$_5$L$_1$				
		C_0 [mg/dm^3]	25	50	100	150	200
		q_{exp} [mg/g]	8.43	20.13	42.62	65.71	78.16
PFO	$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} \times t$	q_1 [mg/g]	6.20	16.75	41.06	51.20	64.59
		$k_1 \times 10^{-2}$ [1/min]	2.22	2.12	1.00	0.35	0.26
		R^2	0.954	0.955	0.978	0.938	0.966
PSO	$\frac{t}{q_t} = \frac{1}{k_2 \times q_2^2} + \frac{1}{q_2} \times t$	q_2 [mg/g]	9.01	22.59	44.23	68.38	80.20
	$h = k_2 \times q_2^2$	$k_2 \times 10^{-2}$ [g/mg·min]	0.46	0.11	0.058	0.019	0.013
		h [mg/g·min]	0.38	0.54	1.13	0.90	0.81
		R^2	0.997	0.992	0.997	0.997	0.986
IPD	$q_t = k_i \times t^{1/2} + C_i$	k_{i1} [mg/g·min$^{1/2}$]	0.87	1.65	2.40	2.29	3.89
		C_1	0.58	1.40	1.63	0.34	1.38
		R^2	0.929	0.986	0.880	0.797	0.939
		k_{i2} [mg/g·min$^{1/2}$]	0.74	2.00	2.10	2.53	2.80
		C_2	0.71	1.47	4.68	7.98	4.02
		R^2	0.910	0.931	0.983	0.971	0.985
		k_{i3} [mg/g·min$^{1/2}$]	0.005	0.016	0.31	0.52	1.09
		C_3	8.32	19.79	32.88	46.53	37.21
		R^2	0.709	0.745	0.472	0.889	0.977
Boyd	$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt)$	B	6.62	6.21	4.43	2.70	1.96
	$F = \frac{q_t}{q_e}$	R^2	0.960	0.959	0.959	0.876	0.994
DW	$\log(1 - F^2) = -\frac{K}{2.303t}$	K	0.020	0.019	0.009	0.003	0.002
		R^2	0.962	0.960	0.955	0.971	0.995

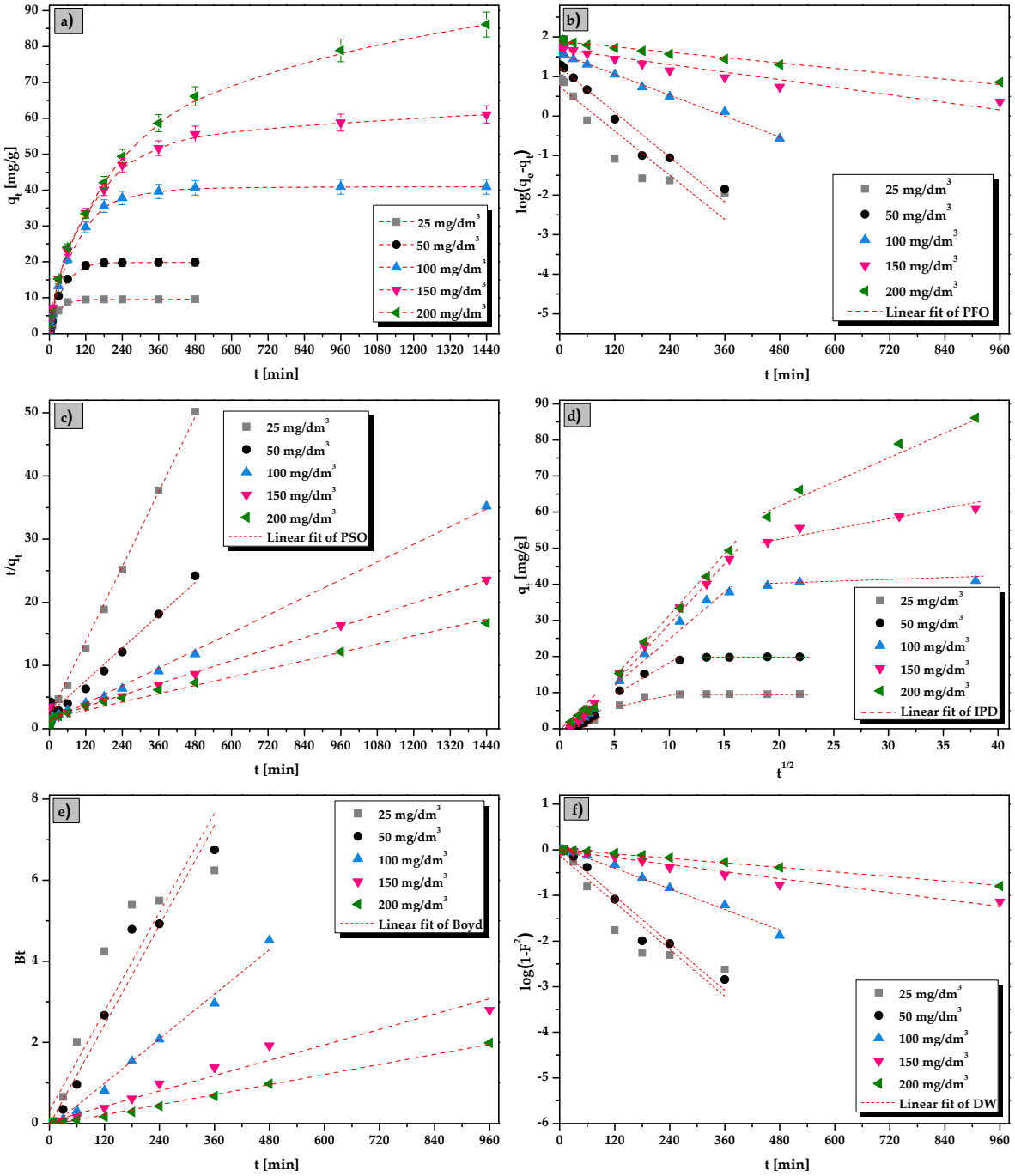


Figure S4. (**a**) Influence of interaction time and linear fitting of kinetic models: (**b**) PFO, (**c**) PSO, (**d**) IPD, (**e**) Boyd, and (**f**) DW for Ce(III) ions sorption on the ALG$_5$L$_1$ composite.

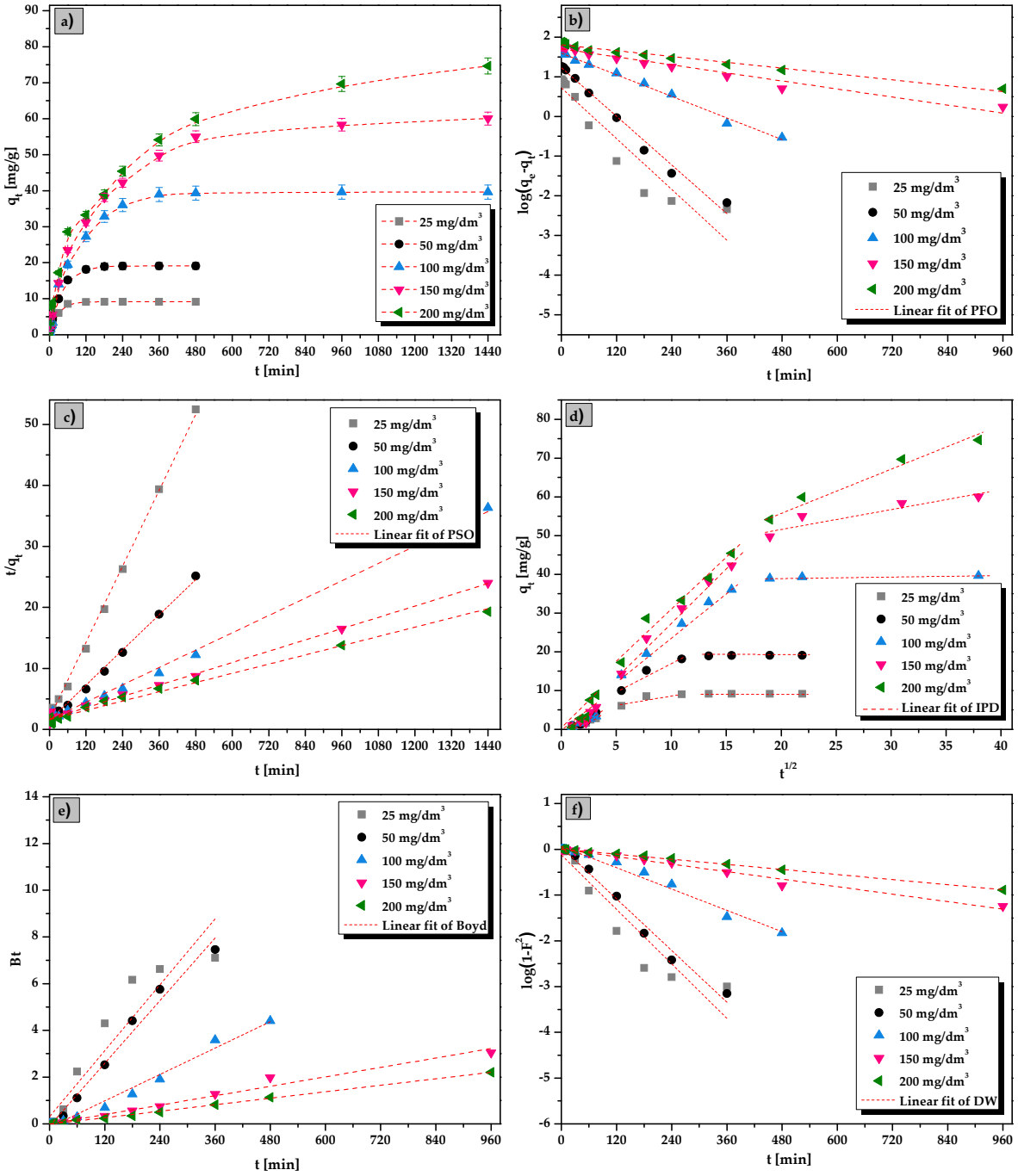


Figure S5. (**a**) Influence of interaction time and linear fitting of kinetic models: (**b**) PFO, (**c**) PSO, (**d**) IPD, (**e**) Boyd, and (**f**) DW for Pr(III) ions sorption on the ALG_5L_1 composite.

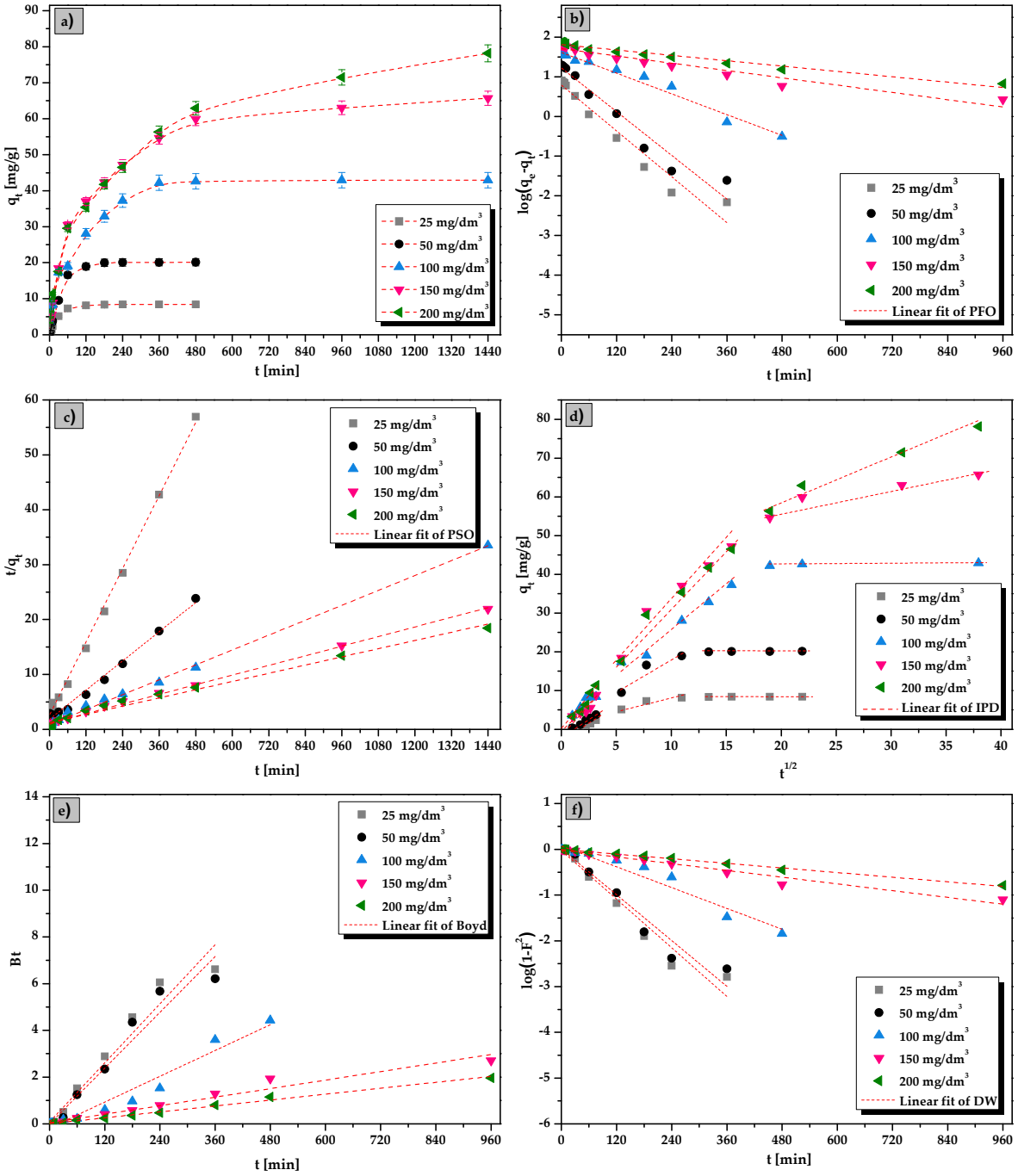


Figure S6. (**a**) Influence of interaction time and linear fitting of kinetic models: (**b**) PFO, (**c**) PSO, (**d**) IPD, (**e**) Boyd, and (**f**) DW for Nd(III) ions sorption on the ALG$_5$L$_1$ composite.

Table S7. Calculated kinetic parameters for La(III), Ce(III), Pr(III), and Nd(III) ions sorption onto raw lignin for C_0 =100 mg/dm^3.

Kinetic model	Equations	Parameter	Lignin			
		Ions	**La(III)**	**Ce(III)**	**Pr(III)**	**Nd(III)**
		q_{exp} **[mg/g]**	22.72	23.66	20.27	18.85
PFO	$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} \times t$	q_1 **[mg/g]**	7.87	13.05	7.74	7.11
		$k_1 \times 10^{-2}$ **[1/min]**	1.60	1.87	1.98	1.38
		R^2	0.946	0.957	0.899	0.962
PSO	$\frac{t}{q_t} = \frac{1}{k_2 \times q_2^2} + \frac{1}{q_2} \times t$	q_2 **[mg/g]**	22.83	24.03	20.49	18.93
	$h = k_2 \times q_2^2$	$k_2 \times 10^{-2}$ **[g/mg·min]**	1.25	0.60	1.20	1.11
		h **[mg/g·min]**	5.97	3.46	5.04	4.00
		R^2	0.999	0.999	1.000	0.999
IPD	$q_t = k_i \times t^{1/2} + C_i$	k_{i1} **[mg/g·min$^{1/2}$]**	4.10	3.56	4.33	2.53
		C_1	5.37	2.76	1.24	5.86
		R^2	0.937	0.955	0.963	0.986
		k_{i2} **[mg/g·min$^{1/2}$]**	0.47	0.95	0.65	0.54
		C_2	16.57	12.53	13.42	12.01
		R^2	0.938	0.911	0.918	0.965
		k_{i3} **[mg/g·min$^{1/2}$]**	0.19	0.24	0.09	0.19
		C_3	19.30	19.42	18.75	15.49
		R^2	0.928	0.923	0.770	0.940
Boyd	$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt)$	B	4.53	4.94	4.76	3.69
	$F = \frac{q_t}{q_e}$	R^2	0.956	0.963	0.911	0.972
DW	$\log(1 - F^2) = -\frac{K}{2.303t}$	K	0.015	0.017	0.019	0.013
		R^2	0.960	0.960	0.917	0.976

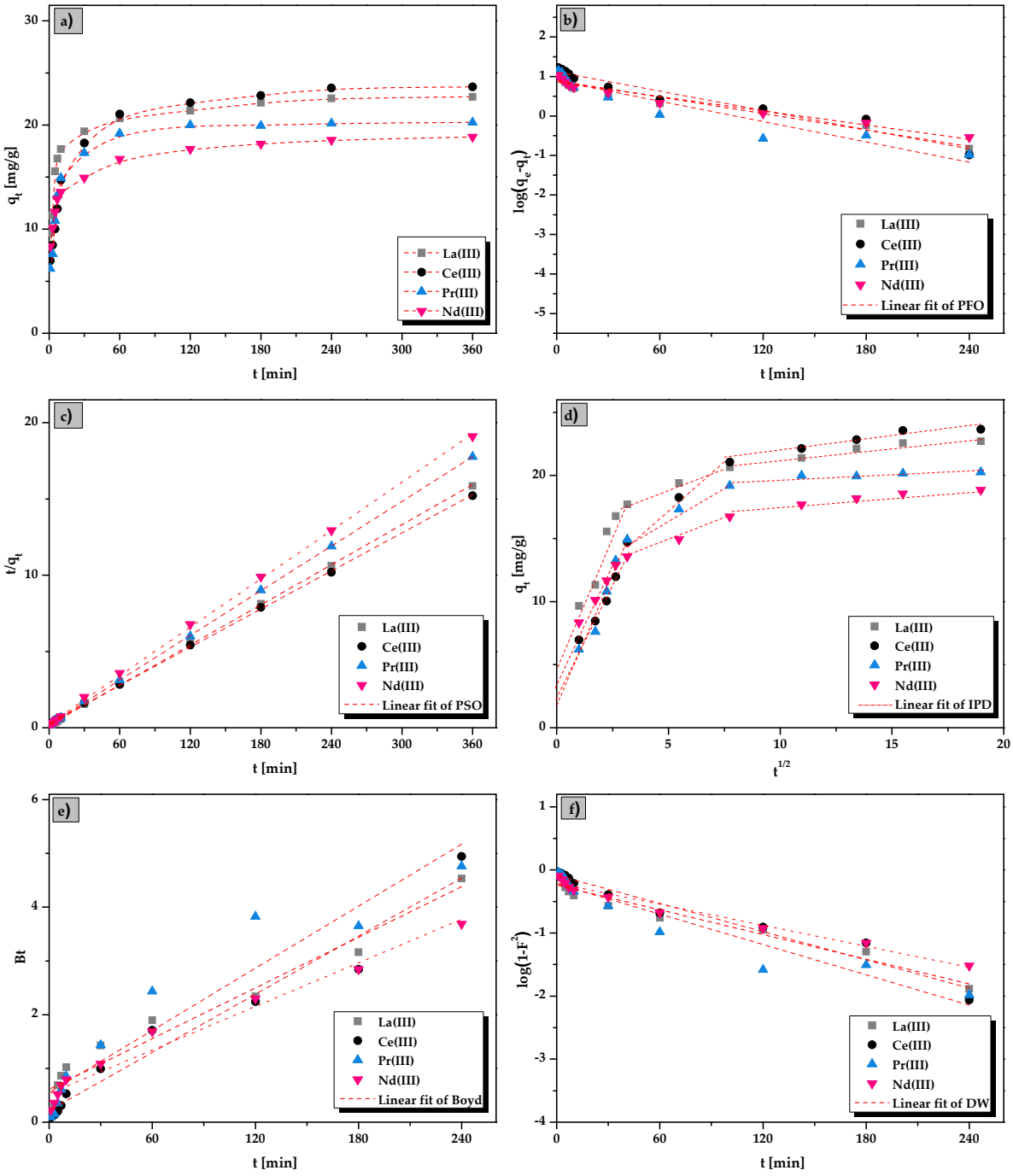


Figure S7. (**a**) Influence of interaction time and linear fitting of kinetic models: (**b**) PFO, (**c**) PSO, (**d**) IPD, (**e**) Boyd, and (**f**) DW for La(III), Ce(III), Pr(III), and Nd(III) ions sorption onto raw lignin for C_0 =100 mg/dm^3.

Table S8. Calculated isotherm parameters for Ce(III), Pr(III), and Nd(III) ions sorption onto the ALG_5L_1 composite.

Isotherm model	**Parameter**	**Ce(III)**			**Pr(III)**			**Nd(III)**		
	***T* [K]**	**293**	**313**	**333**	**293**	**313**	**333**	**293**	**313**	**333**
	q_{exp} **[mg/g]**	93.83	96.58	97.97	92.99	97.85	97.98	96.28	98.46	98.68
Langmuir	q_m **[mg/g]**	94.56	96.68	97.66	92.02	95.71	97.30	94.89	97.43	97.72
	K_L **[dm³/mg]**	0.27	0.32	0.33	0.15	0.17	0.22	0.13	0.16	0.20
	R^2	0.998	0.997	0.998	0.995	0.993	0.997	0.993	0.994	0.996
	χ^2	0.005	0.013	0.024	0.099	0.171	0.050	0.157	0.101	0.073
Freundlich	K_F **[mg/g]**	31.26	34.36	36.54	30.47	29.93	31.61	31.40	28.54	28.75
	n	4.43	4.68	4.83	4.74	4.34	4.38	4.88	4.18	4.10
	R^2	0.876	0.864	0.945	0.934	0.840	0.864	0.965	0.829	0.823
	χ^2	1.973	1.847	2.102	0.724	1.400	2.541	0.169	1.317	2.071
Temkin	$A\times10^2$ **[dm³/g]**	0.89	1.70	3.30	1.82	0.76	0.99	3.02	0.52	0.48
	B **[J/mol]**	9.380	9.036	8.526	8.022	9.423	9.441	7.661	9.885	10.203
	R^2	0.977	0.968	0.991	0.984	0.974	0.985	0.961	0.969	0.976
	χ^2	0.003	0.004	0.036	0.348	0.148	0.012	0.938	0.122	0.022
Dubinin-Radusch-kevich	$X_m\times10^{-3}$ **[mg/g]**	2.42	2.36	2.37	2.11	2.52	2.58	2.00	2.57	2.67
	$\beta\times10^{-3}$ **[mol²/kJ²]**	1.73	1.58	1.49	1.57	1.85	1.80	1.45	1.94	1.98
	E **[kJ/mol]**	16.98	17.78	18.31	17.82	16.44	16.66	18.57	16.07	15.90
	R^2	0.898	0.880	0.981	0.963	0.884	0.911	0.978	0.863	0.858
	χ^2	0.420	0.237	0.310	0.016	0.331	0.833	0.354	0.262	0.613

Table S9. Calculated isotherm parameters for La(III), Ce(III), Pr(III), and Nd(III) ions sorption onto raw lignin.

Isotherm model	Parameter	La(III)			Ce(III)			Pr(III)			Nd(III)		
	T [K]	293	313	333	293	313	333	293	313	333	293	313	333
	q_{exp} [mg/g]	34.69	36.25	37.98	26.41	30.08	37.39	32.22	36.90	40.74	24.07	27.57	30.06
Langmuir	q_m [mg/g]	35.93	37.24	39.08	27.06	30.84	38.89	33.15	37.85	41.89	24.91	28.34	31.00
	K_L [dm³/mg]	0.054	0.060	0.069	0.082	0.084	0.044	0.052	0.055	0.063	0.051	0.042	0.041
	R^2	0.997	0.996	0.997	0.999	0.999	0.997	0.996	0.996	0.999	0.999	0.995	0.994
	χ^2	0.003	0.007	0.002	0.001	0.001	0.004	0.013	0.018	0.008	0.002	0.020	0.029
Freundlich	K_F [mg/g]	10.01	10.14	11.31	8.62	9.54	7.77	6.98	7.30	6.83	5.15	5.97	6.39
	n	4.66	4.51	4.69	5.06	4.91	3.65	3.67	3.41	3.00	3.66	3.80	3.75
	R^2	0.977	0.989	0.989	0.942	0.960	0.942	0.953	0.951	0.904	0.956	0.988	0.986
	χ^2	0.070	0.104	0.154	0.231	0.291	0.343	0.306	0.534	1.410	0.346	0.117	1.286
Temkin	A [dm³/g]	6.30	9.55	15.10	8.03	8.61	1.72	2.69	2.32	1.49	1.66	2.11	2.19
	B [J/mol]	4.37	4.31	4.32	3.34	3.77	5.71	4.63	5.47	6.73	3.78	3.99	4.31
	R^2	0.947	0.952	0.956	0.973	0.990	0.987	0.991	0.995	0.987	0.978	0.991	0.990
	χ^2	0.005	0.014	0.005	0.040	0.039	0.005	0.001	0.001	0.069	0.028	0.007	0.337
Dubinin-Radusch-kevich	$X_m \times 10^{-3}$ [mg/g]	0.81	0.85	0.88	0.65	0.75	1.08	0.92	1.13	1.49	0.71	0.74	0.81
	$\beta \times 10^{-3}$ [mol²/kJ²]	1.95	1.94	1.83	1.95	1.96	2.74	2.61	2.79	3.27	2.74	2.55	2.57
	E [kJ/mol]	16.01	16.07	16.54	15.99	15.96	13.51	13.84	13.38	12.37	13.52	13.99	13.95
	R^2	0.959	0.982	0.985	0.970	0.986	0.964	0.977	0.979	0.944	0.979	0.998	0.998
	χ^2	0.004	0.004	0.001	0.095	0.107	0.105	0.0693	0.156	0.737	0.135	0.006	0.009

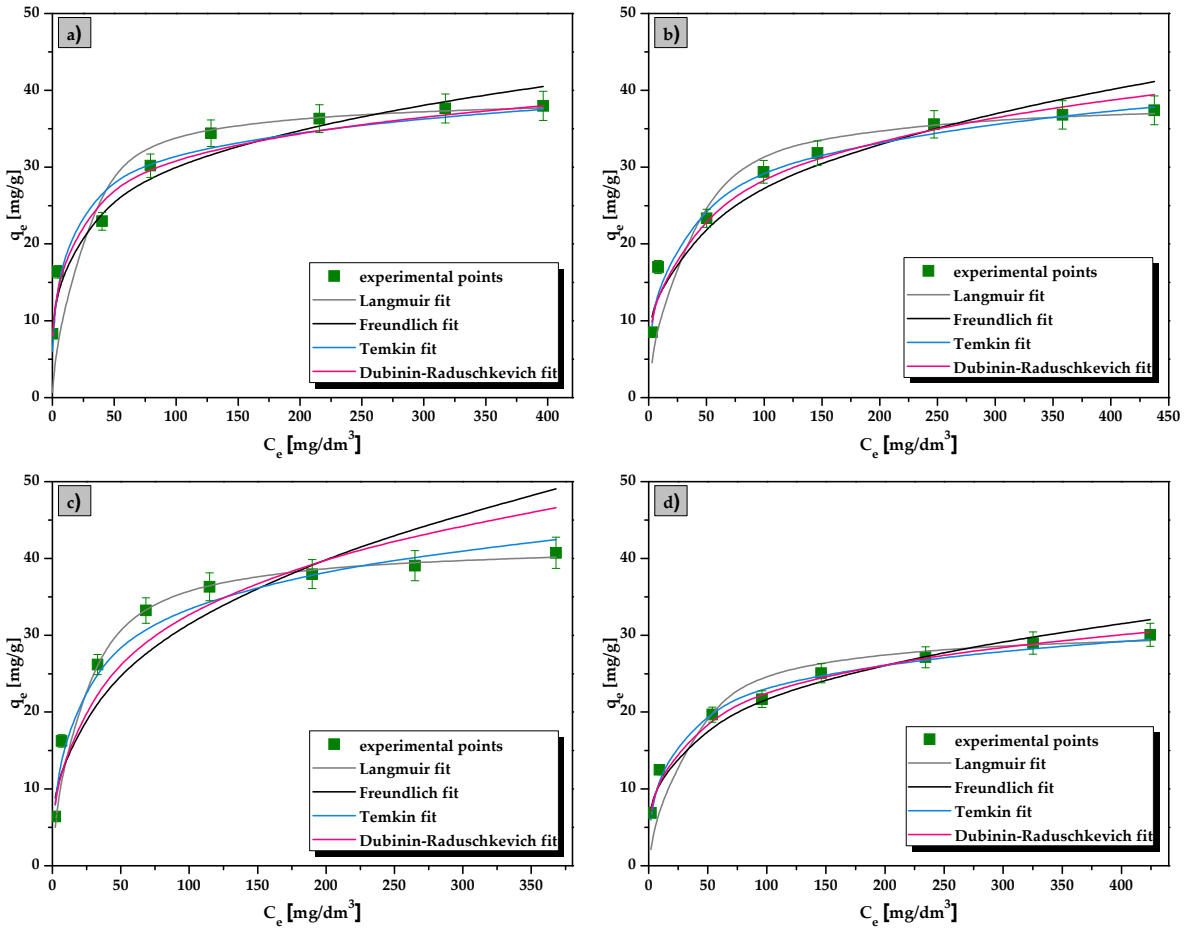


Figure S8. Nonlinear fitting of isotherm models for (**a**) La(III), (**b**) Ce(III), (**c**) Pr(III), and (**d**) Nd(III) ions sorption on raw lignin at 333 K.