Eco-Engineered Electrospun La/Rb–MOF/Chitosan–PCL Nanofibrous Membrane for High-Performance, Recyclable, and Sustainable Cr(VI) Removal from Water

Table S1. Chemical name, formula, and company

Chemical name	Formula	Company
Chitosan	$C_{56}H_{103}N_9O_3$	Sigma-Aldrich, Germany
polycaprolactone	$(C_6H_{10}O_2)_n$	Sigma-Aldrich, Germany
Lanthanum nitrate hexahydrate	$La(NO_3)_3.6H_2O$	Sigma-Aldrich, Germany
Rubidium chloride	RbCl	Sigma-Aldrich, Germany
benzene-1,3,5-tricarboxylic acid	$C_6H_3(CO_2H)_3$	Sigma-Aldrich, Germany
Methanol	CH_3OH	LOBA CHEMIE PVT.LTD, India
Ethanol	C_2H_6O	Sigma-Aldrich, Germany
Sodium hydroxide (99%, AR)	NaOH	Chimmed, Russia
Hydrochloric acid (37%, AR)	HCl	LOBA CHEMIE PVT.LTD, India

Table S2. Instruments and equibments.

Test name	Abbrevation	Instrument name	Company	Illustration
Fourier transformer infrared	FT-IR	A Nicolet IS10 Fourier transform infrared (FTIR) spectrometer	Thermo Fisher Scientific, Waltham, MA, USA	equipped with an attenuated total reflectance accessory and which ran in the 4000-400 cm^{-1} range was used to gather FTIR spectra
Powered X-ray diffraction	PXRD	Siemens diffractometer (model D500, Germany)	Germany	patterns were captured from powder samples through the use of a Siemens diffractometer (model D500, Germany) that was fitted with a Cu-K radiation source (wavelength 1.54 Angstroms (Å)) operating at 30 kV and 20 mA.
Scanning Electron Microscope	SEM	(JSM-6510LV, JEOL Ltd., Tokyo, Japan)	JEOL Ltd., Tokyo, Japan	The morphology of the investigated sorbents was analyzed with the use of a scanning electron microscope
X-ray photoelectron spectroscopy	XPS	K-ALPHA (Themo Fisher Scientific, USA)	Themo Fisher Scientific, USA	Used for determination the elemental analysis for the compound
Braunnar Emmet Teller	BET	Quantachrome Instruments, Anton Paar Quanta Tec, Inc., Boynton Beach, FL,	Quanta Tec, Inc., Boynton Beach, FL, USA	was utilised for surface and pore analysis (Brunauer Emmett-Teller (BET) surface area, porous volume, and pore size), and NovaWin Software (v11.0) was used for data interpretation.

		USA		The BET surface area of material adsorbents was obtained by the application of nitrogen adsorption-desorption isotherms at 77K through the use of a specific analyser (Quadrasorb–EVO, Quantachrome, USA).
UV-visible spectrophotometer	UV spectrophotometer	HACH LANGE DR5000	HACH LANGE Germany	Measuring the concentration of the adsorbate soulution via using bear lambert law
Energy Dispersive X-ray	EDX	Leo1430VP microscope	Carl Zeiss AG, Jena, Germany	Elemntal analysis of the material
Transmission electron microscopy	TEM	TEM, FEI Teanci G2 F20, USA	FEI Teanci G2 F20, USA	Determination the morphology of the material and size
pH meter	pH	HANNA (model 211)	USA	Measuring the acidity or basicity of the solution
Sonication	Ultrasonic	Elmasonic P300H ultrasonic bath, continuous mode, power 380 W	Elma Schmidbauer GmbH, Singen, Germany	Sonication of the material as well as used ton disperse material on the solution as it decrease the particle size of the material
Water bath	Shaking	GFL Orbital Shaker 3017		
Atomic	atomic absorption spectrometer	SIMAA 6000		Determination metal concentration

Table S3. True variables, codes, and their BBD levels.

Code	Variables	-1	0	+1
A	pH	2	5	8
B	Dose (g)	0.02	0.25	0.5
C	Time (min.)	5	55.5	100

Table S4. Equations used in this work to fit the data of adsorption experiments.

Serial	Equation	Nmae	Description	Ref.
1	$q_e = \frac{q_m}{1 + K_L C_e}$	Langmuir	q_e (mg.g^{-1}) Adsorption capacity, C_e equilibrium concentration, q_m (mg.g^{-1}) is the monolayer saturation capacity constant and K_L (L/mg) is the Langmuir constant associated with the free adsorption energy. The favorability of the adsorption process in the Langmuir model is determined by means of the R_L dimensionless factor ($R_L = 1/(1 + k_L \cdot C_0)$) as follows: $R_L = 0$, $0 < R_L < 1$, $R_L = 1$, and $R_L > 1$ indicating irreversible, favorable, linear, and unfavorable adsorption isotherms, respectively.	[1]
2	$q_e = K_F C_e^{\frac{1}{n}}$	Freundlich	K_F Freundlich isotherm constants [(mg/g)/(mg/L)$^{1/n}$], and $1/n$ represents the exponent of non-linearity (i.e., C-type, L-type, and S-type isotherms). n is the Freundlich constants, and $n < 1$ indicates poor adsorption while $n = 1$–2 and $n = 2$–10 indicate average and good adsorptions, respectively. The values of n and k_f are calculated, respectively	[2]
3	$q_e = q_m \exp(-\beta\varepsilon^2)$ $\varepsilon = RTln\left(1 + \frac{1}{C_e}\right)$ $E_{DR} = \sqrt{\frac{1}{2K_{DR}}}$	Dubinin–Radushkevich	q_D is the maximum monolayer adsorption capacity (mg/g), B_D is the activity coefficient related to the apparent free energy of adsorbate adsorption onto the adsorbent (mol^2/kJ^2), ε_D is the Polanyi potential which is related to the equilibrium concentration, and E is the mean adsorption energy.	[3]
4	$q_e = Q_{max} \frac{RT}{b} \ln(K_T C_e)$	Temkin	K_T is the Temkin isotherm constant or equilibrium binding constant (L/mg) corresponding to the maximum binding energy, and b_T is the Temkin isotherm constant related to the heat of adsorbate adsorption onto the adsorbent due to adsorbent-adsorbate interaction (J/mol), R is the gas constant (8.314 J/mol/K), and T is the absolute temperature (herein 298 K).	[4]

	$q_e = \frac{q_m k_T c_e}{(1 + (K_L C_e)t)1/t}$	Toth	q_e: amount of adsorbate adsorbed at equilibrium (mg/g), Ce:equilibrium concentration of adsorbate in solution (mg/L) q_{max}: theoretical maximum adsorption capacity (mg/g) K_T: Toth isotherm constant related to affinity (L/mg) t t: heterogeneity parameter (dimensionless)	[5]
5	$q_t = q_e\left(1 - e^{K_1 t}\right)$	Pseudo-First-order kinetic	q_e and q_t are the adsorption capacities at equilibrium and time t (mg/g), and k_1 is the rate constant (min^{-1}), respectively.	[6]
6	$q_t = \frac{tK_2 q_e^2}{1 + q_e K_2 t}$	Pseudo-Second-order kinetic	k_2 is the pseudo-second order constant (mg/(g.min))	[7]
7	$q_t = K_i t^{1/2} + X$	Intraparticle diffusion	q_t is the adsorption capacity at time t in (mg/g), k_{int} is the intraparticle diffusion rate constant ($mg \cdot g^{-1} \cdot min^{-1/2}$), and C is a constant related to the the thickness of the boundary layer (mg/g).	[8]
8	$q_t = \frac{1}{\beta} \ln(\alpha\beta t + 1)$	Elovich	The constants α chemical adsorption rate ($mg.g^{-1}min^{-1}$), and β Coefficient in relation with extension of covered surface	[9]
9	$\Delta G^o = \Delta H^o - T\Delta S^o$	Gibbs free energy	ΔG°: Gibbs free energy change; Kd: equilibrium constant; R: gas constant; T: temperature.	[10]
10	$LnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$	Van't Hoff	ΔS°: entropy change; ΔH°: enthalpy change.	[11]
11	$LnK_d = lnA - (\frac{Ea^0}{R})\frac{1}{T}$	Arhinus	Ea was the activation energy, A Arhinus constant, R ideal gas constant 8.314 J/mol K, T (K) is the absolute solution temperature	[12]

Table S5: Identification of the peaks of La 3d

La-Rb-MOF/CS-PCL			Cr@La-Rb-MOF/CS-PCL		
Bending energy	%	Identification	Bending energy	%	Identification
835.93	25.68	La $3d_{5/2}$—La(III)–O (MOF lattice)	831.91	17.76	La $3d_{5/2}$—La(III)–O (coordination altered after Cr adsorption)
838.36	2.34	La $3d_{5/2}$—Satellite/shake-up	836.32	10.84	La $3d_{5/2}$—Satellite/shake-up due to ligand/electron transfer
839	26.55	La $3d_{5/2}$—La(III)–O–C (carboxylate)	840	17.23	La $3d_{5/2}$—La(III)–O–C (carboxylate, chelated ligand)
846.45	22.96	La $3d_{3/2}$—La(III)–O (MOF lattice)	846.21	17.16	La $3d_{3/2}$—La(III)–O (coordination altered after Cr adsorption)
849.33	3.41	La $3d_{3/2}$—Satellite/shake-up	850.88	15.62	La $3d_{3/2}$—Satellite/shake-up due to ligand/electron transfer
851.87	15.31	La $3d_{3/2}$—La(III)–O–C (chelated)	855.79	18.72	La $3d_{3/2}$—La(III)–O–C (carboxylate, chelated ligand)
853.39	3.77	La $3d_{3/2}$—Satellite/shake-up	856.04	2.67	La $3d_{3/2}$—Satellite/shake-up due to ligand/electron transfer

Table S6. List of abbreviation.

Symbol	Definition
q_e	the adsorbed amount of dye at equilibrium concentration ($mg.g^{-1}$)
q_{mL}	the maximum sorption capacity (corresponding to the saturation of the monolayer, ($mg.g^{-1}$)
K_L	Langmuir binding constant which is related to the energy of sorption (L/mg)
C_e	is the equilibrium concentration of dyes in solution
K_F	Freundlich constants related to the sorption capacity (mg/g) $(L/mg)^{1/n}$
n	intensity
K_{DR}	constant related to the sorption energy ($mol^2k\ J^{-2}$)
q_{DR}	theoretical saturation capacity (mg/g)
ε	Polanyi potential (J^2mol^{-2})
R	Gas constant (8.314 $J.mol^{-1}K^{-1}$)
T	temperature where the adsorption occurs
A_T	Temkin isotherm constant
b_T	Temkin constant in relation to heat of adsorption ($J.mol^{-1}$)
q_t	is the amount of dye adsorbed ($mmol.g^{-1}$)
K_1	Rate constant for Pseudo first order constant for the adsorption processes (min^{-1})
q_2	Maximum adsorption capacity for pseudo second order
K_2	Rate constant for Pseudo first order constant for the adsorption processes ($g.mg^{-1}min^{-1}$)
α	Chemical adsorption rate ($mg.g^{-1}min^{-1}$)
β	Coefficient in relation with extension of covered surface
ΔG^o	Free Gibb's energy
ΔH^o	Enthalpy
ΔS^o	Entropy
K_c	distribution coefficient
C_{eq}	Concentration at equilibrium (mg/L)

Table S7. The parameter of the adsorption isotherm for Cr(VI) ions on La-Rb-MOF/CS-PCL

Isotherm	Value of parameters	
Langmuir	$q_{m\ exp}$ (mg/g)	449.2
	q_m (mg/g)	451.8
	K_L (L/mg)	0.064
	R_L	0.075
	Reduced Chi-Sqr	51.37029
	Residual Sum of Squares	821.92458
	R-Square (COD)	0.99755
	R^2	0.99739
Freundlich	n	2.96
	K_F (mg/g) $(L/mg)^{1/n}$	92.66
	Reduced Chi-Sqr	902.91751
	Residual Sum of Squares	14446.68013
	R-Square (COD)	0.95689
	R^2	0.9542
Dubin–Radushkevich	$Q_{DR}(mg.g^{-1})$	387.04
	K_{DR} ($mol^2k\ J^{-2}$)	1.0234E-5
	Ea (kJ/mol)	31.4
	Reduced Chi-Sqr	2720.32832
	Residual Sum of Squares	43525.25312
	R-Square (COD)	0.87013
	R^2	0.86201
Temkin	b_T (J/mol)	25.2
	K_T (L/mol)	0.807
	Reduced Chi-Sqr	130.51897
	Residual Sum of Squares	2088.30349
	R-Square (COD)	0.99377
	R^2	0.99338
Jossens	K	35.16

	J	0.092
	Reduced Chi-Sqr	40.9289
	Residual Sum of Squares	613.93353
	R-Square (COD)	0.99817
	R^2	0.99792
Toth	q_m	528.62
	K_T (L/mg)	9.2
	t	0.844
	Reduced Chi-Sqr	37.29076
	Residual Sum of Squares	559.36138
	R-Square (COD)	0.99833
	R^2	0.99811

Table S8: Models of adsorption kinetic parameters of Cr(VI)ions on La-Rb-MOF/CS-PCL.

Model	Value of parameters	
Pseudo-First-order kinetic	K_1 (min^{-1})x10^{-2}	0.969
	Reduced Chi-Sqr	15.16423
	Residual Sum of Squares	288.12032
	R-Square (COD)	0.99921
	R^2	0.99916
Pseudo-second-order kinetic	K_2 (g $mg^{-1}min^{-1}$)x10^{-2}	3.97E-5
	q_e (mg/g)	452.4
	Reduced Chi-Sqr	743.43356
	Residual Sum of Squares	14125.23764
	R-Square (COD)	0.96629
	R^2	0.96452
Intraparticle diffusion	K_i ($mgg^{-1}min^{1/2}$)	48.72
	X (mg/g)	68.6

	Reduced Chi-Sqr	461.41148
	Residual Sum of Squares	460950.06723
	R-Square (COD)	0.96461
	R^2	0.96461
Elovich	β (g/mg)	142.05
	α ($mgg^{-1}.min^{-1}$)	0.00179
	Reduced Chi-Sqr	148.89259
	Residual Sum of Squares	2828.95928
	R-Square (COD)	0.9922
	R^2	0.99179
Experimental data	q_e (exp) (mmol/g)	453.6

Table S9: The thermodynamic parameters.

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)
293	-0.5582		
298	-2.11708	90.8	311.75
303	-3.67595		
308	-5.23483		
313	-6.7937		
318	-8.35258		

Table S10: Analyzing similar adsorbents for the absorption of Cr(VI) ions.

Adsorbent	Adsorption capacity (mg/g)	Initial Cr(VI) Conc. (mg/L)	Dosage (g/L)	Contact Time (min)	Ref.
3D hierarchical GO-NiFe LDH	53.6	50	1	60	[13]
NiFe-LDHs	26.78	25	1	120	[14]
Fe3O4/GO composite	32.3	50	2	150	[15]
mFeOOH@AC	27.2	100	1	60	[16]
α-FeOOH/carbon microspheres	55.4	20	1	30	[17]
NiO nanosheets	49	25	1	100	[18]
Two-dimensional (2D) Ti3C2Tx	104	50	0.5	120	[19]
Polyethyleneimine	243.7	100	0.25	60	[20]
$Cu_{0.1}Ni_{0.05O}$-MX	321.02	100	0.2	120	[21]
NH_2-Ag-MOF@CSC composite sponge	382.9	50	1	120	[22]
La-Rb/CS/PCL	449.5	400	0.8	100	This search

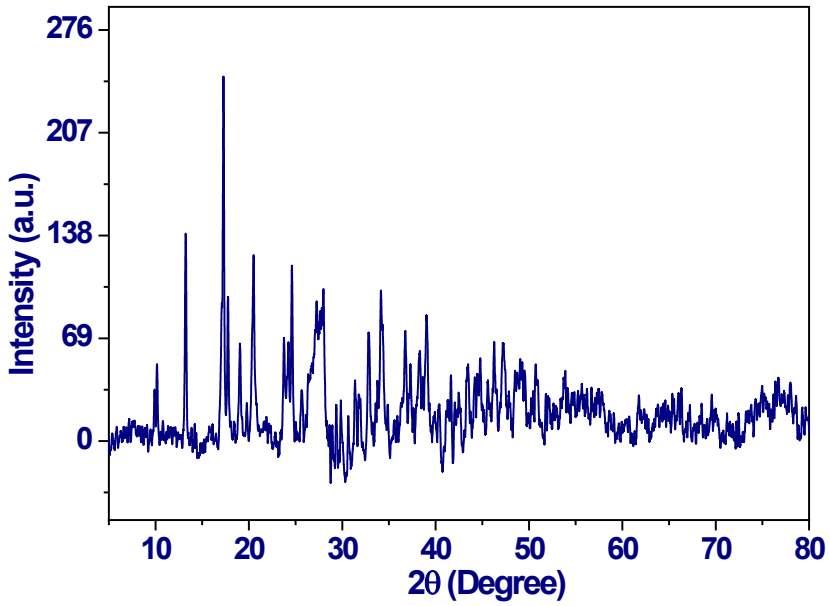

Fig.S1: XRD of La-Rb-MOF

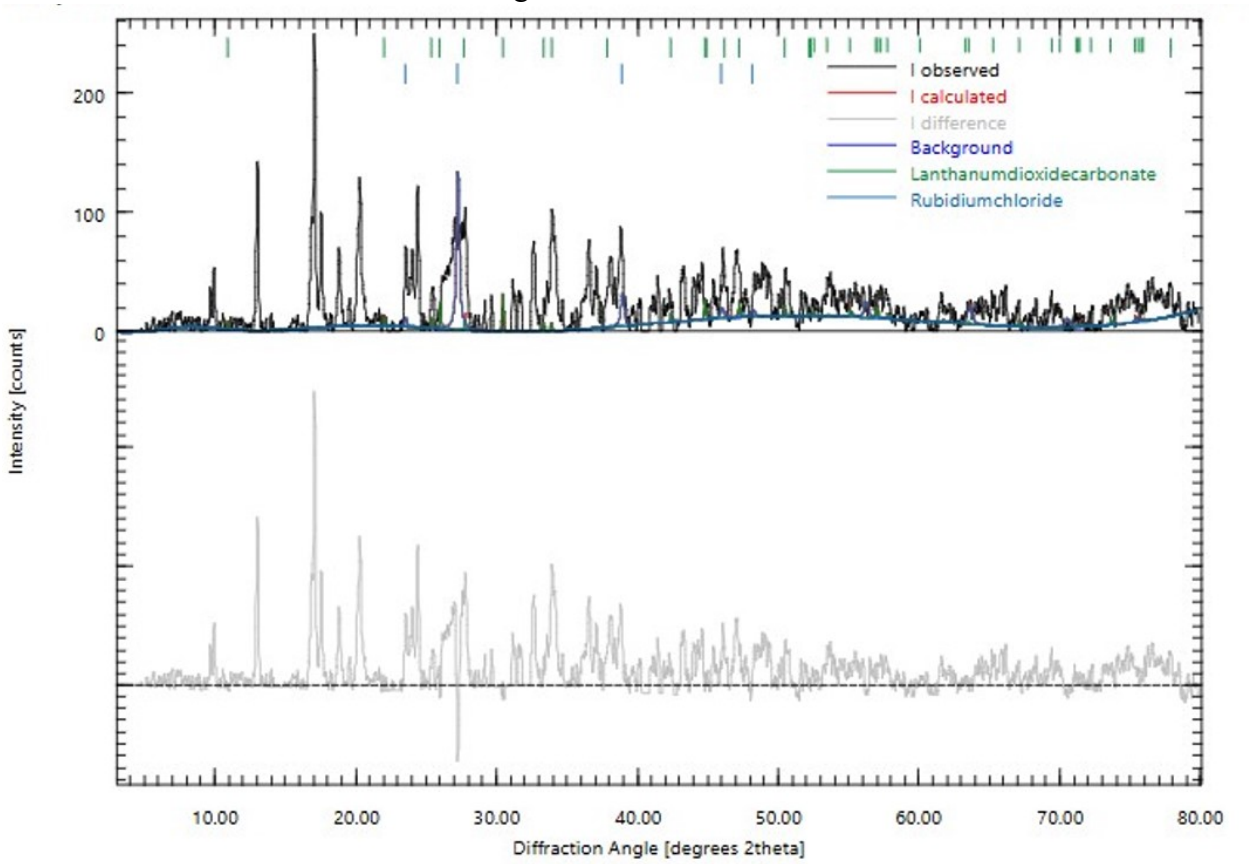

Fig.S2: Powder X-ray Diffraction Pattern and Pawley/Le Bail Refinement Comparison for La-Rb MOF: Experimental versus Simulated Profiles with Phase Assignment

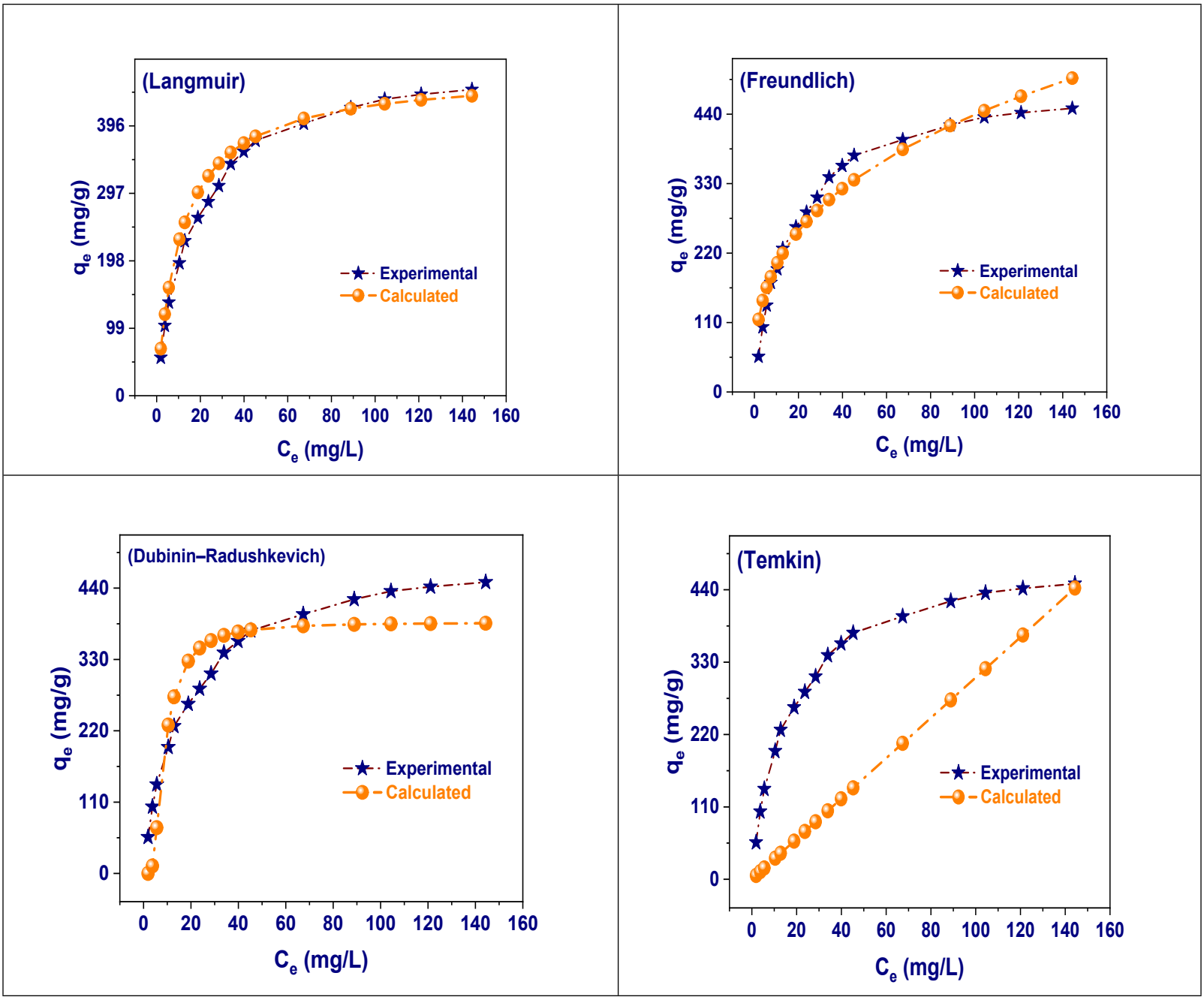

Fig. S3: Adsorption capacity of adsorption iostherm models experimental and calculated

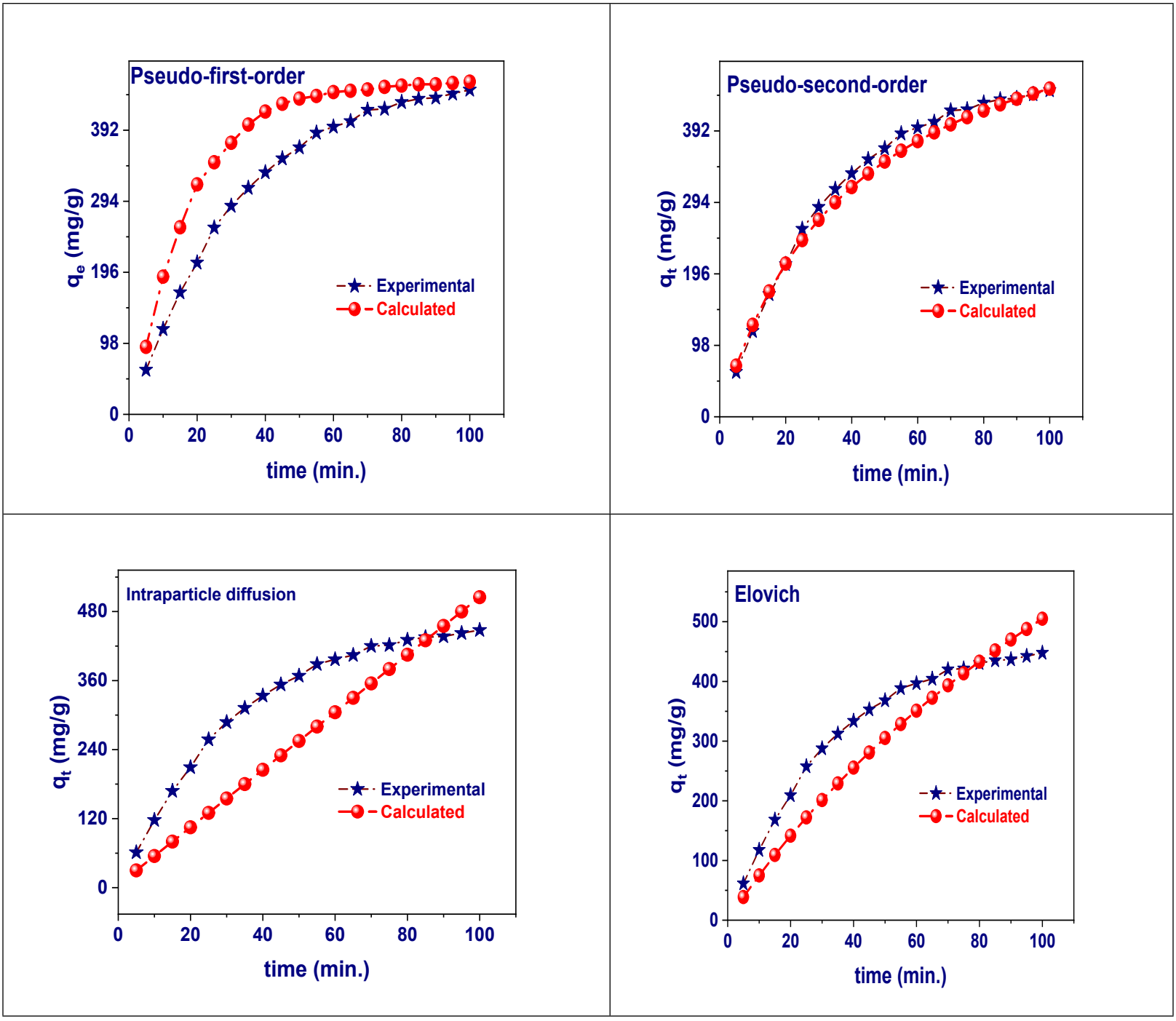

Fig. S4: Adsorption capacity of adsorption kinetic models experimental and calculated

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