Supplementary information

Chitosan glutaraldegyde cryogels for wastewaters treatment and extraction of silver nanoparticles

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Methods

AgNPs Synthesis

Ethanol (70%) tincture of flowers Calendula off. production LLP "Pharmacy 2010", Kazakhstan, Karaganda; silver nitrate 99 % and aqueous solution of ammonia (25 %) LabChemProm(Almaty, Kazakhstan) were used without preliminary treatment. AgNPs were synthesized according to previously reported method with some modifications[1]. A solution of 1 mM silver nitrate was mixed with the ethanol (70%) plant extract of Calendula off. flowers, diluted with purified water in a ratio of 1:50. The plant extract was used as a stabilizer and reducing agent. The final concentration of the reaction mixture was: 1% alcohol tincture of *Calendula off.* and 0.008% silver nitrate and the pH was adjusted to 9 by ammonia solution. Then that reaction mixture was left under sunlight for approximately 48h and the obtained AgNPs suspension was stored at + 4 °C.

Characterization of physical properties of cryogels

Physical properties of the cryogels were evaluated using the following equations.

Swelling ratio:

$$SR = \frac{W_t}{W_d} \times 100\% \qquad \text{eq.S1}$$

Water uptake:

$$WU = \frac{(W_t - W_d)}{W_d} \times 100 \qquad \text{eq.S2}$$

Porosity:

$$P = \left(1 - \frac{d_0}{d_3}\right) \times 100 \qquad \text{eq.S3}$$

- Where $\boldsymbol{W_t}$ and $\boldsymbol{W_d}$ represent the weights of the hydrogel in swollen state at time $\boldsymbol{t}$, and respectively in dried state;
- $\boldsymbol{W_e}$ is the weight of swollen hydrogel at equilibrium;
- d_0 is the density of the dried cross-linked polymer and d_3 is the density of the equilibrium swollen cross-linked polymer.

Results

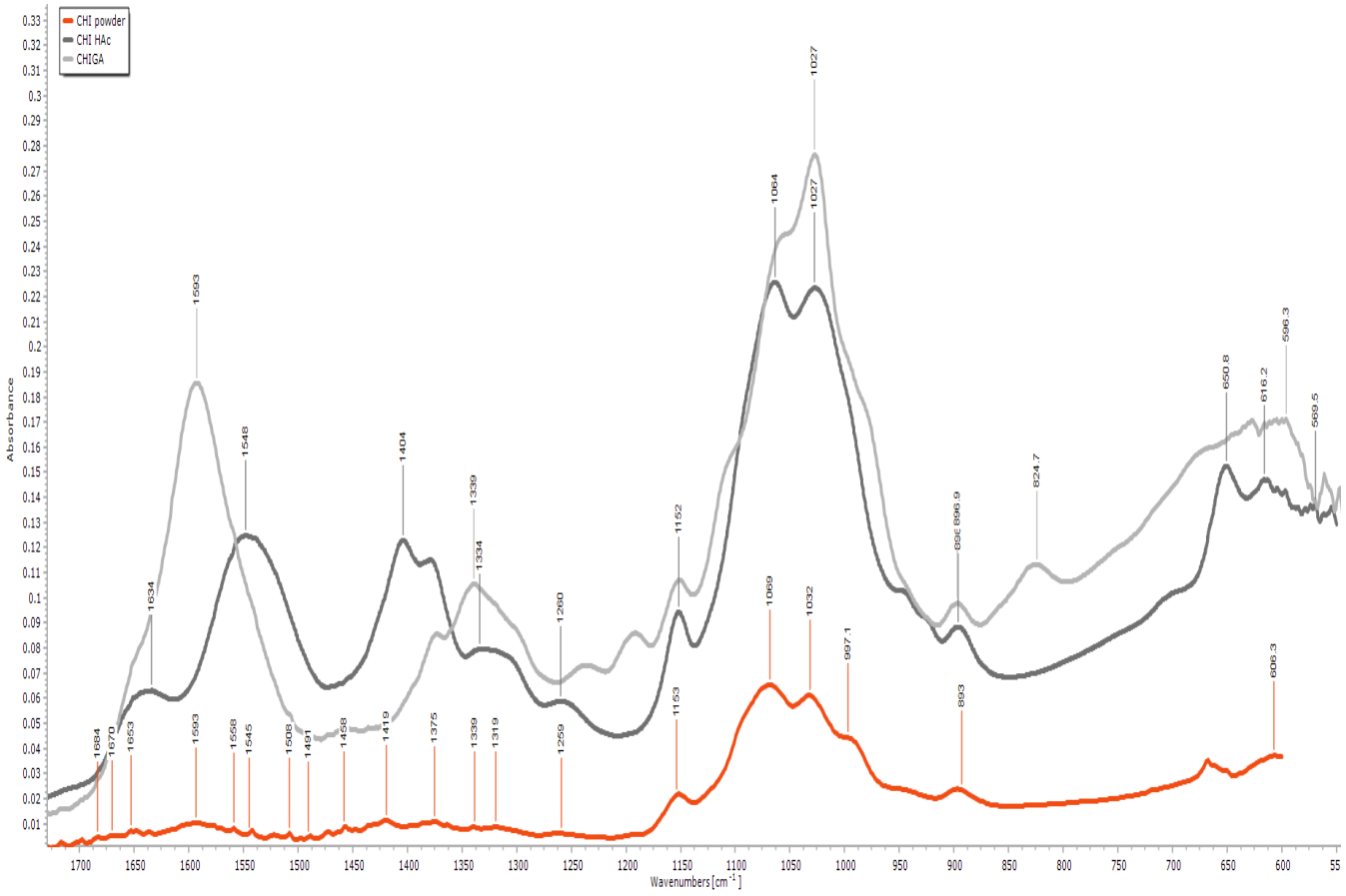


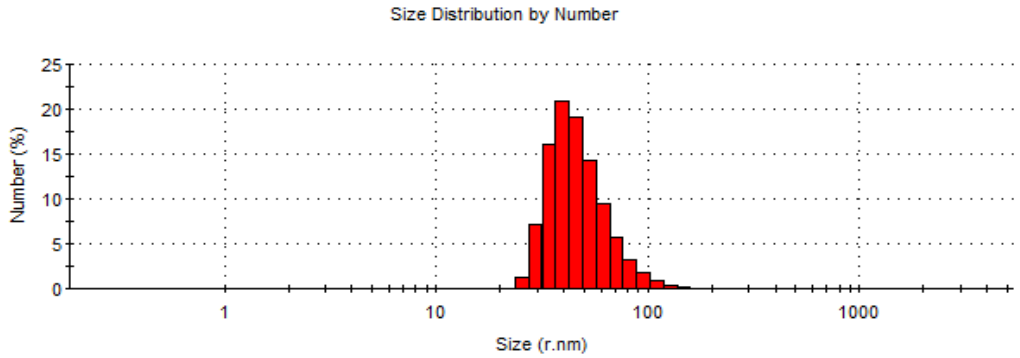
Figure S1 FTIR spectra of dry samples of: CHI in native state, freeze dried CHI dissolved in acetic acid and cryogel CHI-GA.

Record Number:	1	**Dispersant RI:**	1,330
Material RI:	0,54	**Viscosity (cP):**	0,8872
Material Absorbtion:	1,350	**Measurement Date and Time:**	14 января 2021 г. 15

Temperature (°C):	24,9	**Duration Used (s):**	25
Count Rate (kcps):	254,8	**Measurement Position (mm):**	4,65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	8

			Size (r.nm):	**% Number**	**Width (r.nm):**
Z-Average (r.nm):	64,00	**Peak 1:**	47,94	100,0	16,38
PdI:	0,098	**Peak 2:**	0,000	0,0	0,000
Intercept:	0,959	**Peak 3:**	0,000	0,0	0,000

Result quality : Good



Record Number:	19	**Dispersant RI:**	1,330
Date and Time:	14 января 2021 г. 16:22:43	**Viscosity (cP):**	0,8872
		Dispersant Dielectric Constant:	78,5

Temperature (°C):	25,1	**Zeta Runs:**	20
Count Rate (kcps):	173,6	**Measurement Position (mm):**	4,50
Cell Description:	Zeta dip cell	**Attenuator:**	10

			Mean (mV)	**Area (%)**	**Width (mV)**
Zeta Potential (mV):	-36,4	**Peak 1:**	-36,4	100,0	17,1
Zeta Deviation (mV):	17,1	**Peak 2:**	0,00	0,0	0,00
Conductivity (mS/cm):	0,118	**Peak 3:**	0,00	0,0	0,00

Result quality : Good

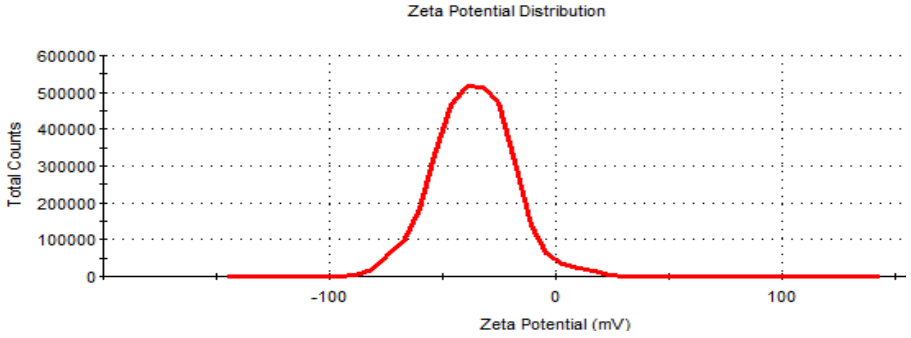


Figure S1. A) Histogram of size distribution of AgNPs stabilized by the *Calendula off flower* extract. B) Zeta potential of AgNPs stabilized by the *Calendula off flower* extract.

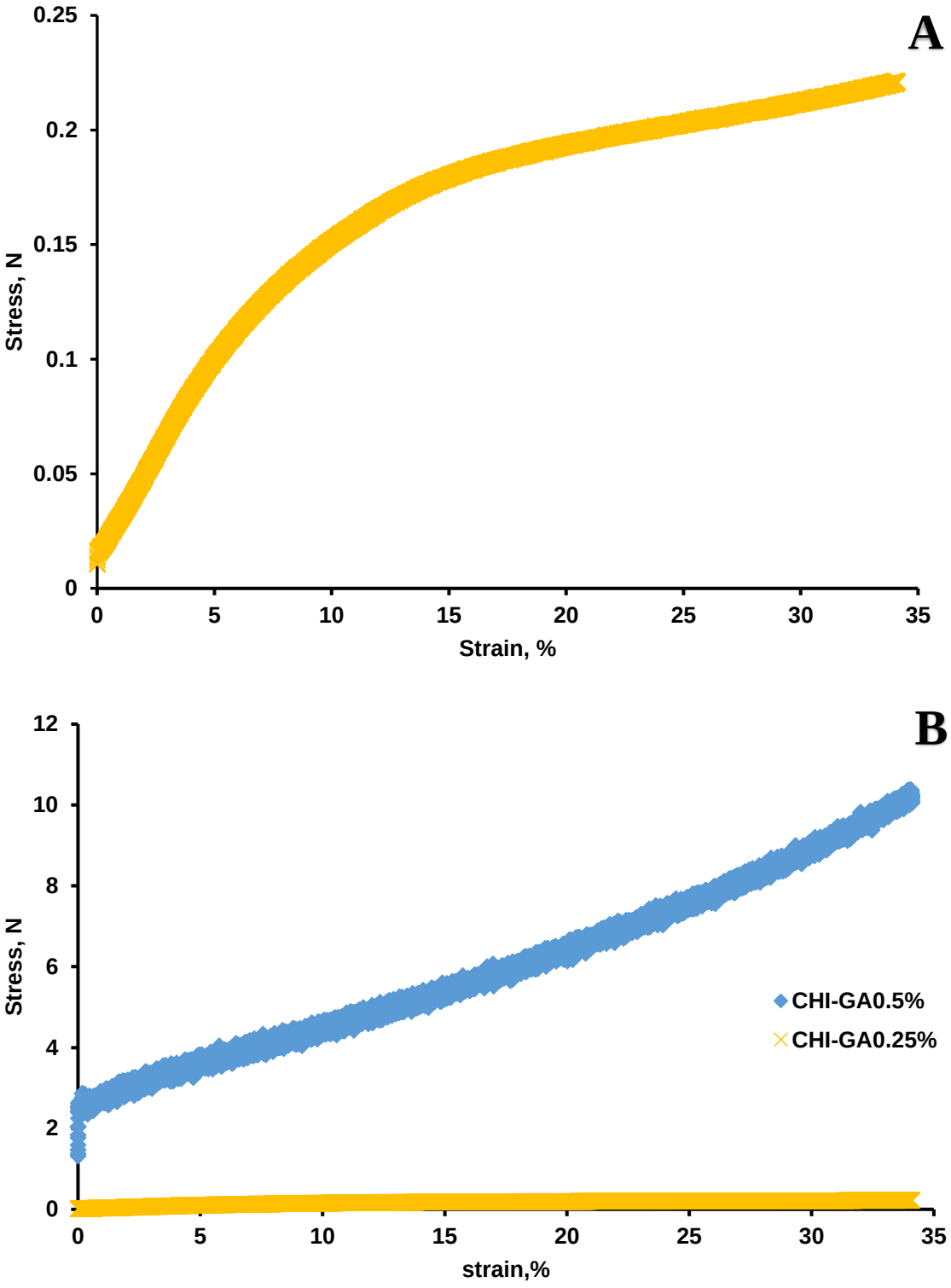


Figure S3. Compression test of cryogels, average data, n=4: A) CHI-GA 0.25%; B) comparison CHI-GA 0.5% and CHI-GA 0.25%;

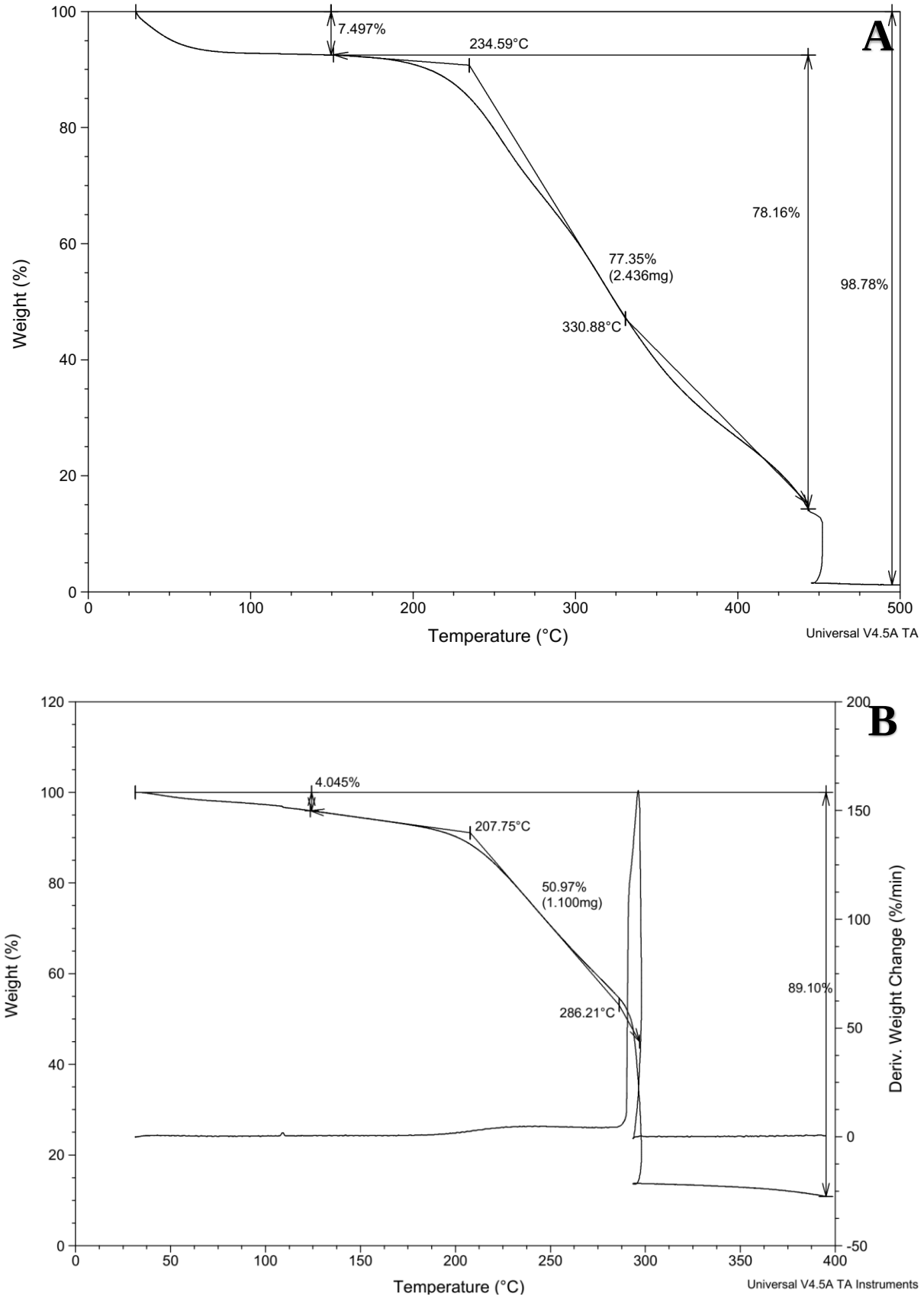


Figure S4. TGA of freeze dried cryogels in an atmosphere of air: a) CHI-GA; CHI-GA reduced by $NaBH_4$.

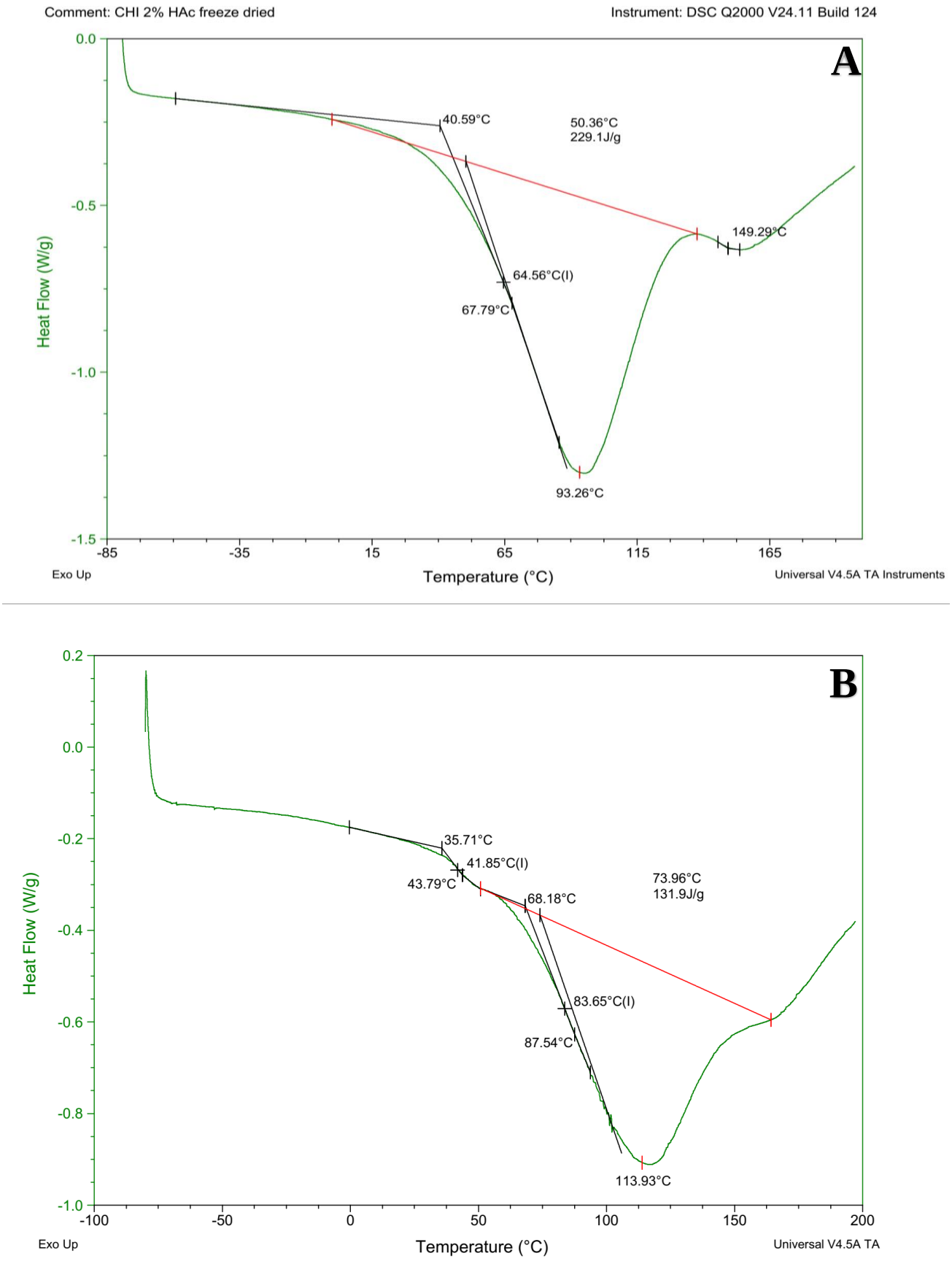


Figure S5 DSC diagram of freeze dried samples: A) solution of CHI*HAc B) cryogel CHI-GA.

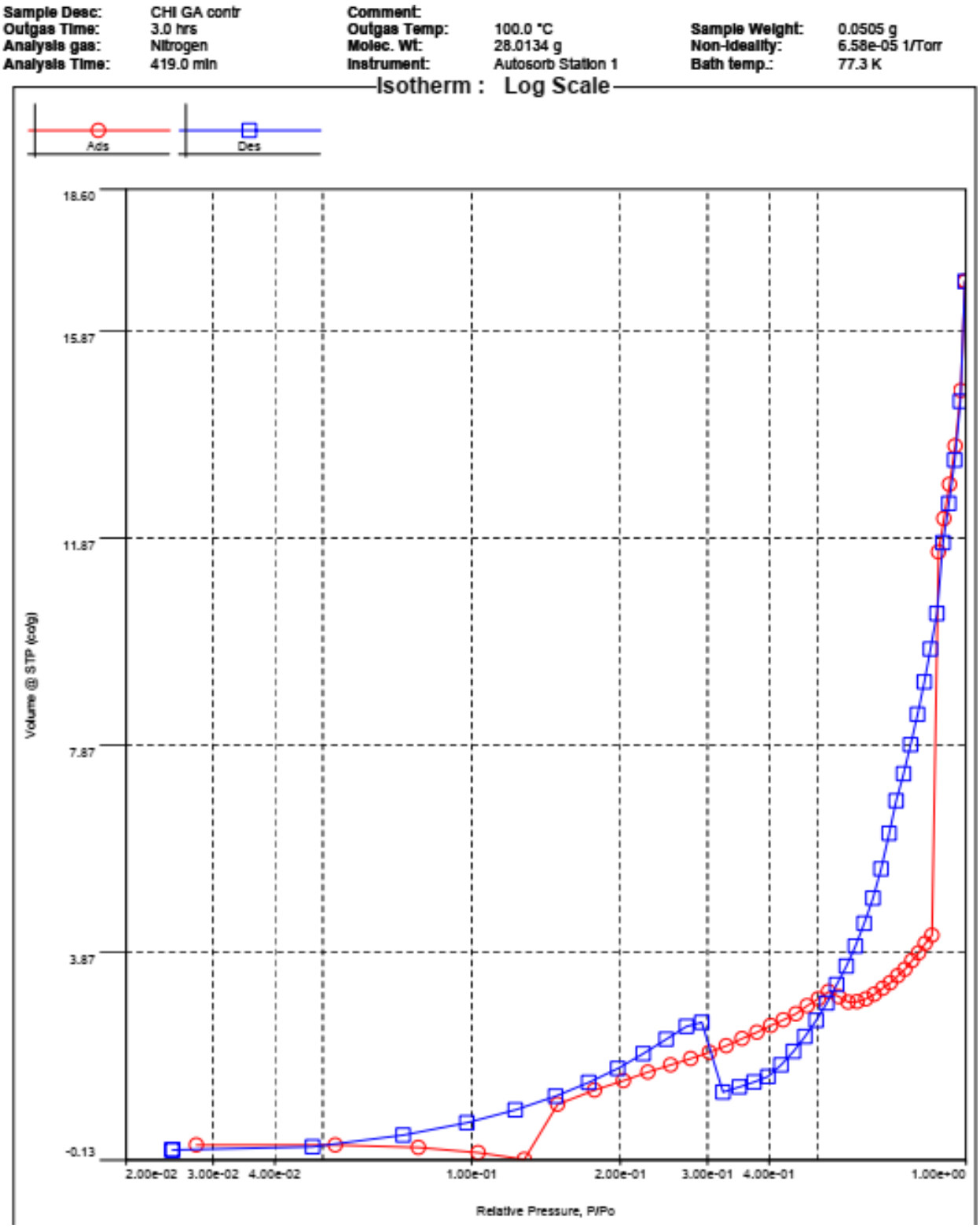


Figure S6 Isotherm of low temperature nitrogen adsorption SBET (red), desorption (blue) by cryogels: A) CHI–GA0.25%.

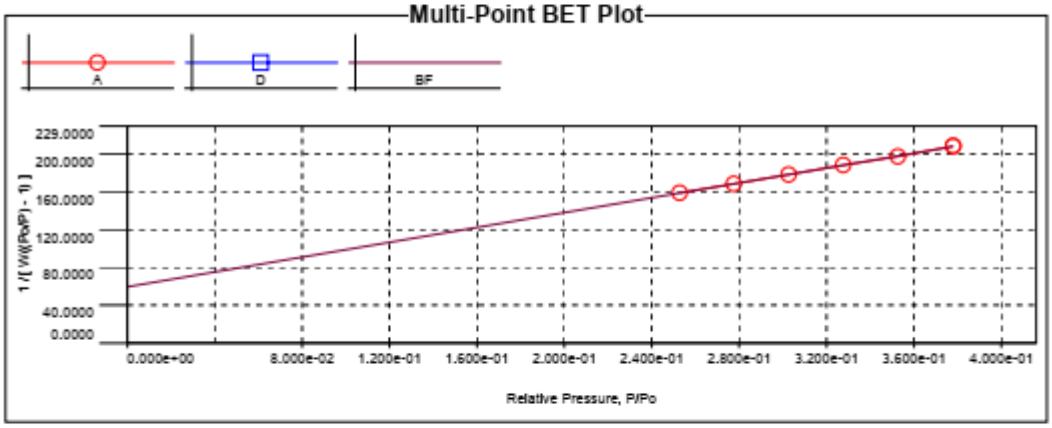
Data Reduction Parameters

	Thermal Transpiration: on	Eff. mol. diameter (D): 4.00 Å	Eff. cell stem diam. (d): 1.0000 mm
t-Method	Calc. method: de Boer		
BJH/DH method	Moving pt. avg.: off	Ignoring P-tags below 0.35 P/Po	
DFT method	Calc. Model: N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)		
	Rel. press. range: 0.0000 - 1.0000		Moving pt. avg: off
Adsorbate	Nitrogen	Temperature 77.350K	
	Molec. Wt.: 28.013	Cross Section: 16.200 Å²	Liquid Density: 0.808 g/cc

MBET summary

Slope =	391.696
Intercept =	5.942e+01
Correlation coefficient, r =	0.999775
C constant=	7.592
Surface Area =	7.720 m²/g

Multi-Point BET Plot



Multi-Point BET

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
2.52806e-01	1.7076	1.5853e+02	3.27711e-01	2.0756	1.8790e+02
2.77659e-01	1.8289	1.6817e+02	3.52633e-01	2.2142	1.9684e+02
3.02688e-01	1.9513	1.7799e+02	3.77971e-01	2.3379	2.0795e+02

Figure S7 Low temperature nitrogen adsorption data using BJH method CHI–GA0.25%.

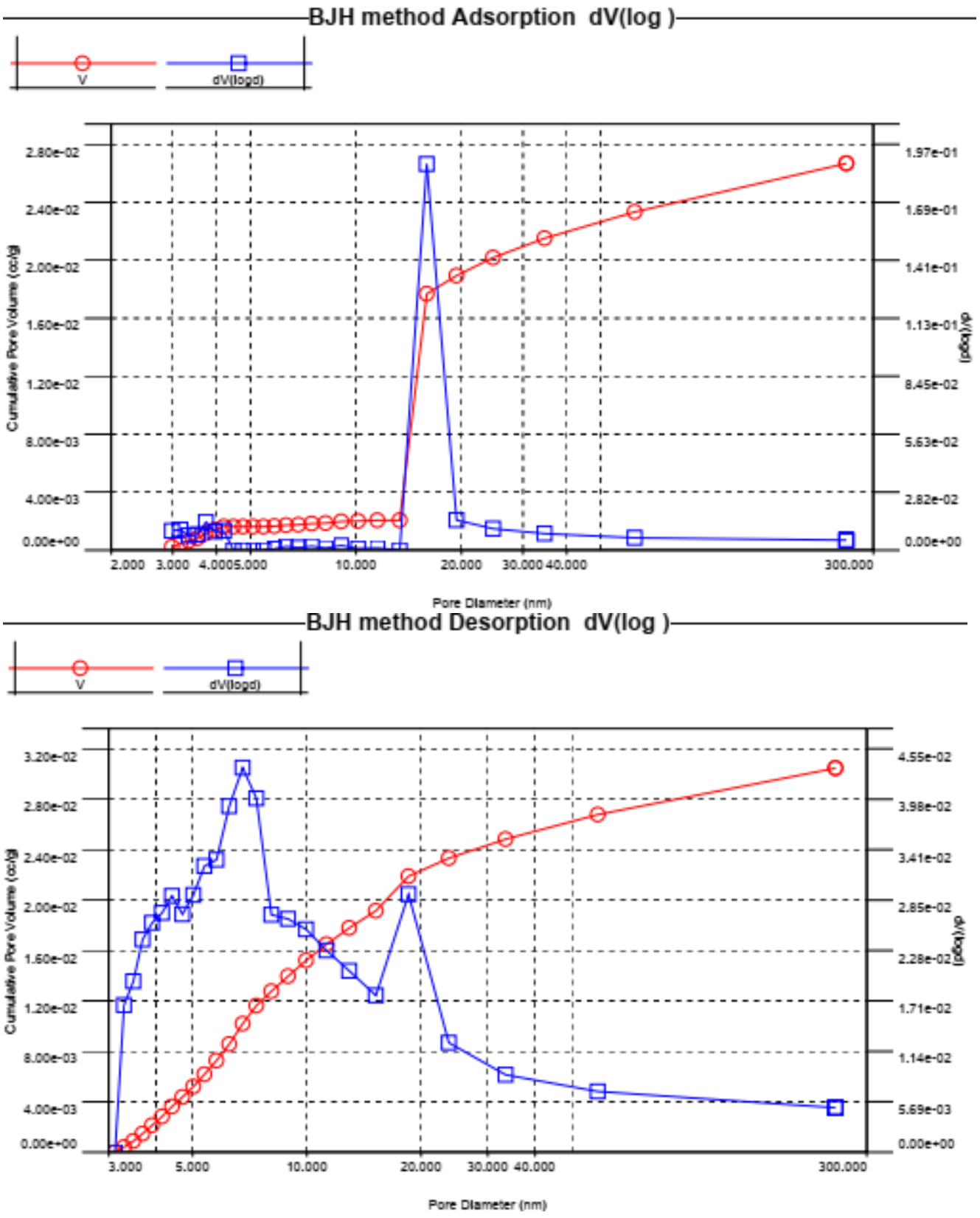
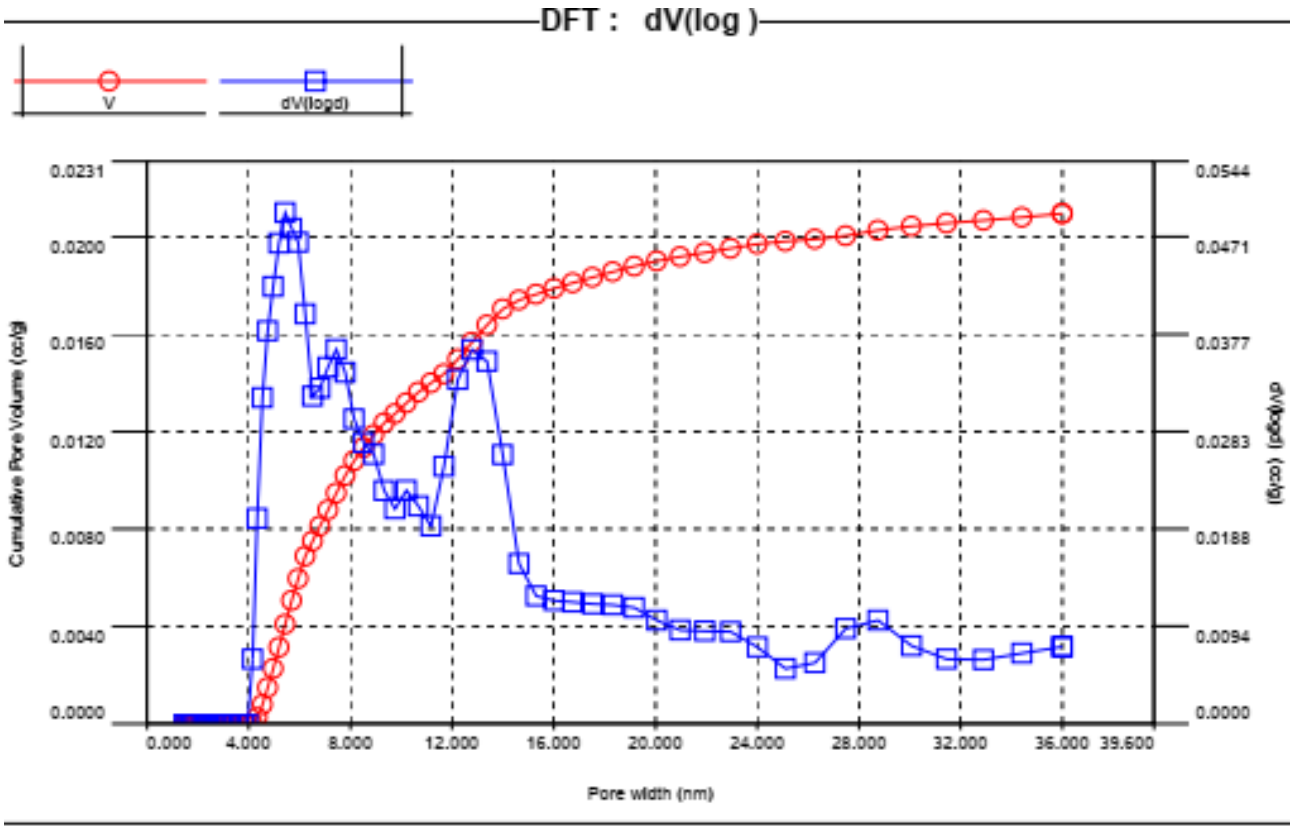


Figure S8 Low temperature nitrogen adsorption data using BJH method CHI–GA0.25%.



MBET summary

Slope =	391.696
Intercept =	5.942e+01
Correlation coefficient, r =	0.999775
C constant=	7.592
Surface Area =	7.720 m²/g

BJH adsorption summary

Surface Area =	6.768 m²/g
Pore Volume =	0.027 cc/g
Pore Diameter Dv(d) =	15.922 nm

BJH desorption summary

Surface Area =	13.117 m²/g
Pore Volume =	0.030 cc/g
Pore Diameter Dv(d) =	3.908 nm

DFT method summary

Pore volume =	0.021 cc/g
Surface area =	5.175 m²/g
Lower confidence limit =	1.475 nm
Fitting error =	4.010 %
Pore width (Mode) =	5.439 nm

Figure S 9 Low temperature nitrogen adsorption data using DFT method CHI–GA 0.25%.

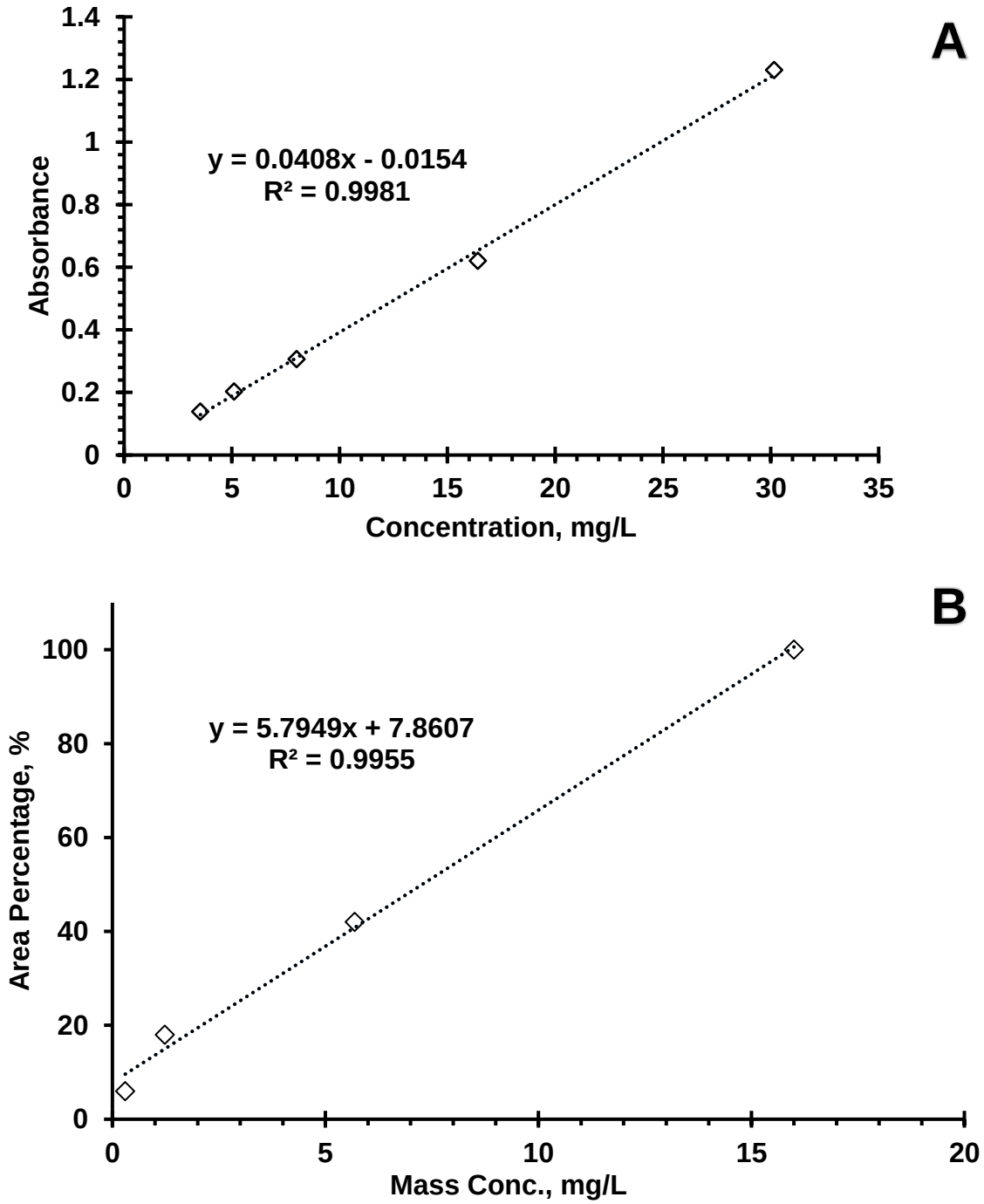
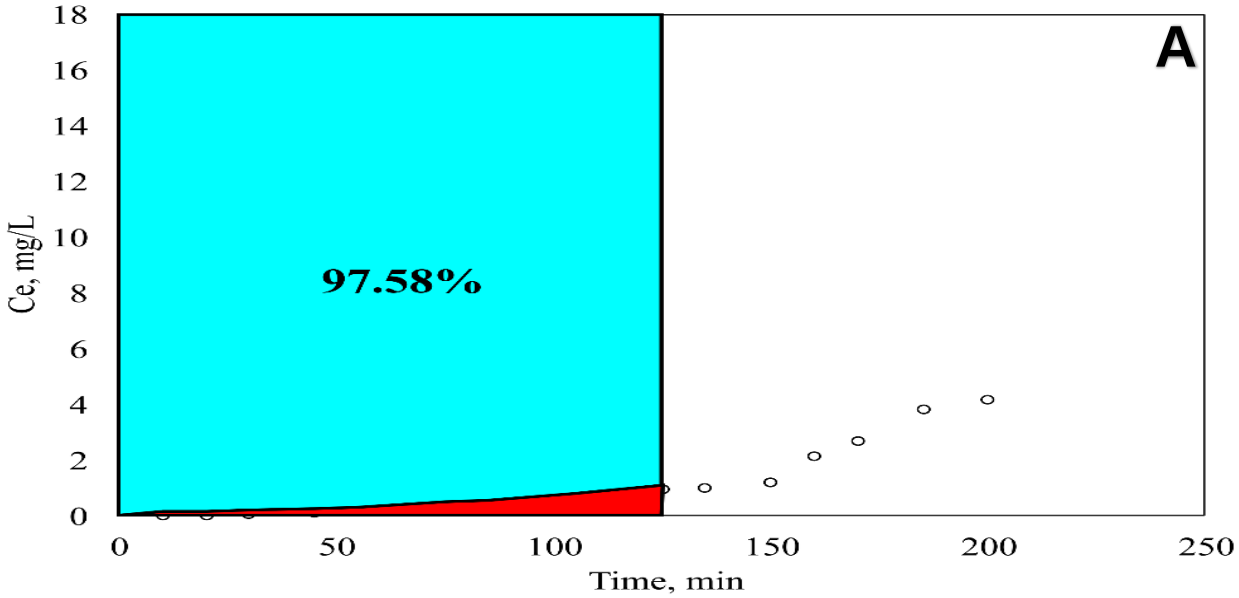
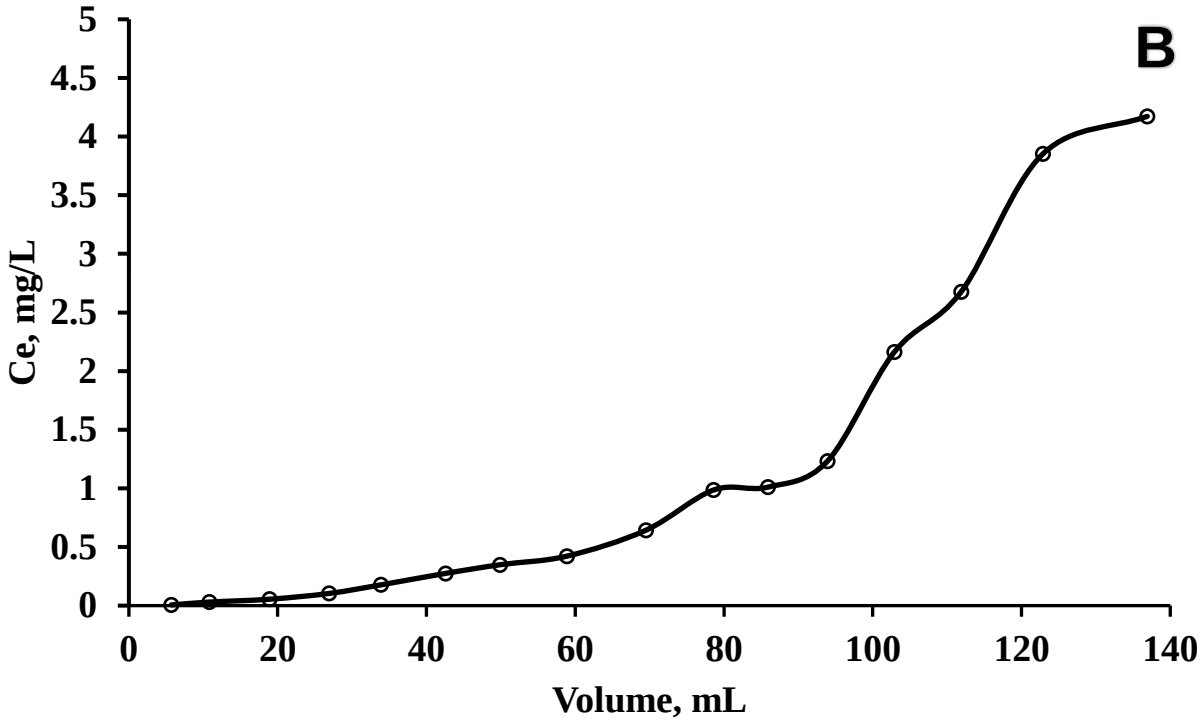


Figure S 10 Calibration curve of: **A)** OD_{420} vs concentration of AgNPs stabilized by *Calendula* extract, concentration confirmed using AAS; B) breakthrough area vs concentration of AgNPs stabilized by *Calendula* extract.


A
97.58%
Ce, mg/L
Time, min
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250


B
Ce, mg/L
Volume, mL
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
20
40
60
80
100
120
140

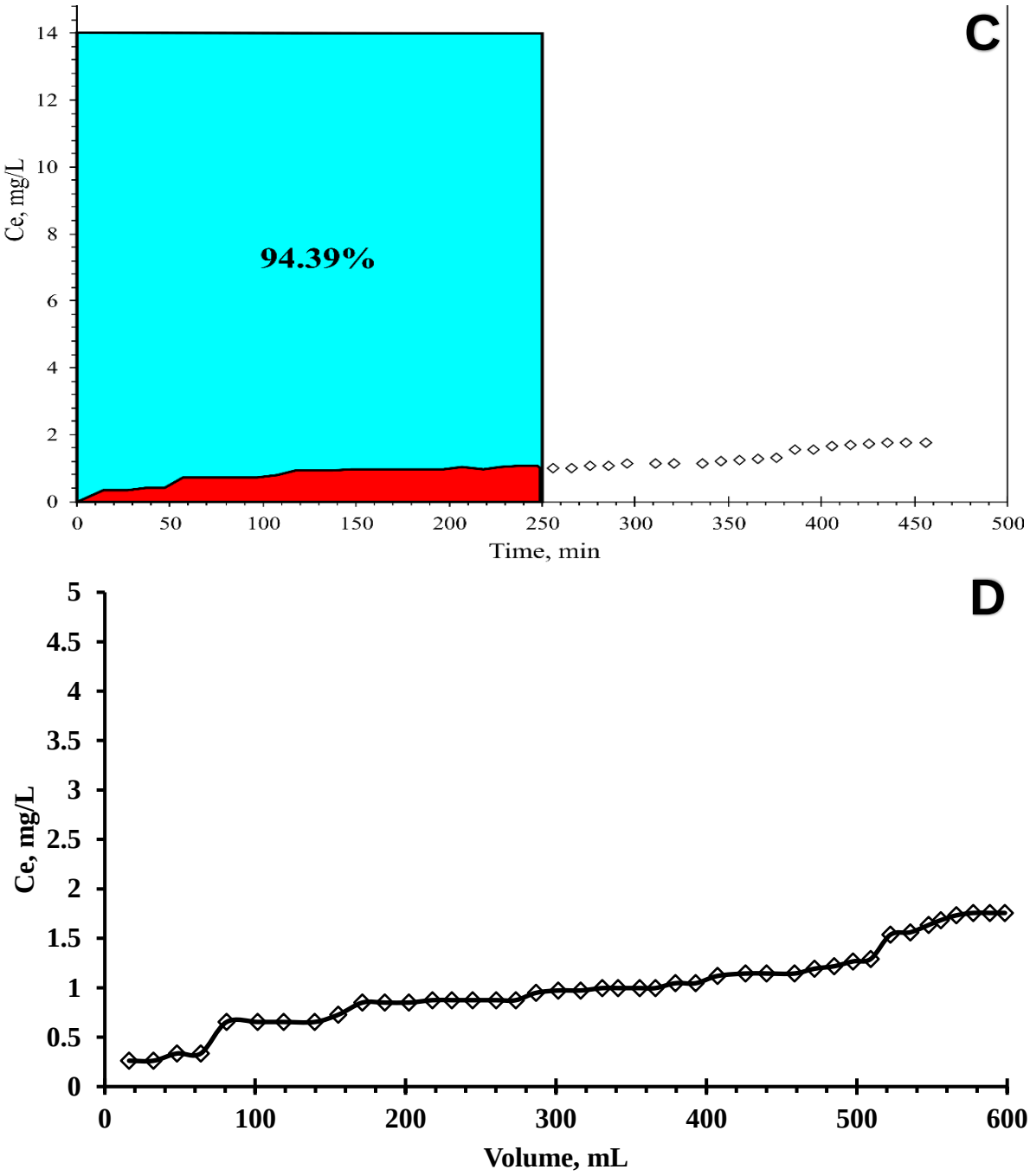


Figure S11. Dynamic adsorption breakthrough curve for CHI-GA cryogel AgNPs SPR absorption peak at 420 nm and a flow rate of 0.8 mL/min: A and B) 18mg/L AgNPs stock solution; C and D) 14 mg/L AgNPs stock solution.

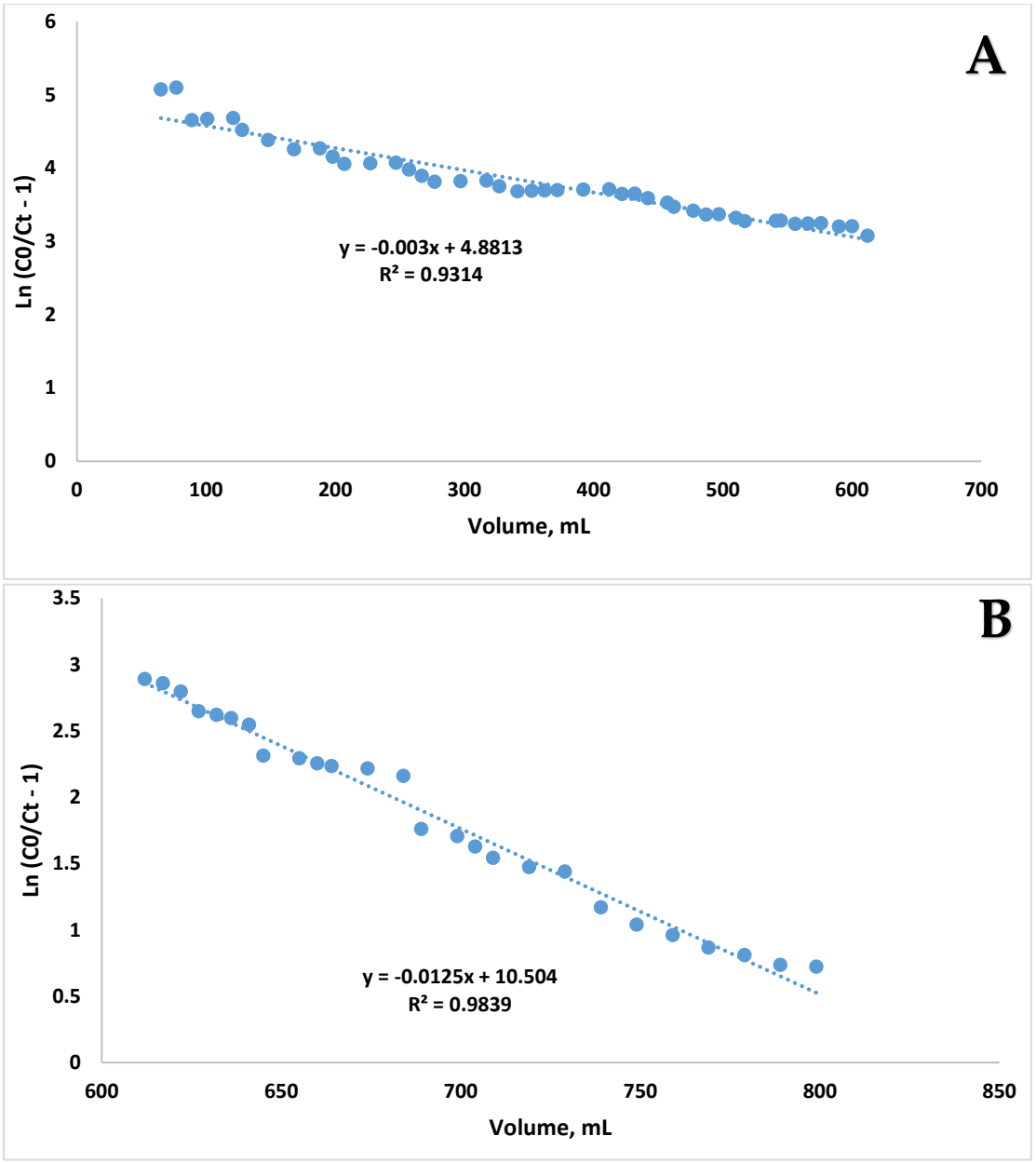


Figure S12 Thomas model fitting before and after breakthrough

Table S1. Variables in calculating the adsorption capacity

Variable	Value	Units
Inlet concentration	14	mg/L
Kth (Thomas const)	0.000378227	= Slope/Co
Slope	0.003	absolute value
Intercept	4.8813	
Thomas Equation	y = (Kth · Qo · m/Q) - (KT · Co · t)	
Q (flowrate)	0.8	mL/min

Qo (capacity)	132	mg/g

Reference:

1. Zhangabay, Z., & Berillo, D.. Antimicrobial and antioxidant activity of AgNPs stabilized with Calendula officinalis flower extract. *Results in Surfaces and Interfaces*, 2023, 100109. https://doi.org/10.1016/j.rsurfi.2023.100109