Electronic Supplementary Information

Synthesis of green magnetic biopolymer derived from *Oak fruit* hull tannin for efficient simultaneous adsorption of a mixture of Malachite Green and Sunset Yellow dyes from aqueous solutions

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Figures

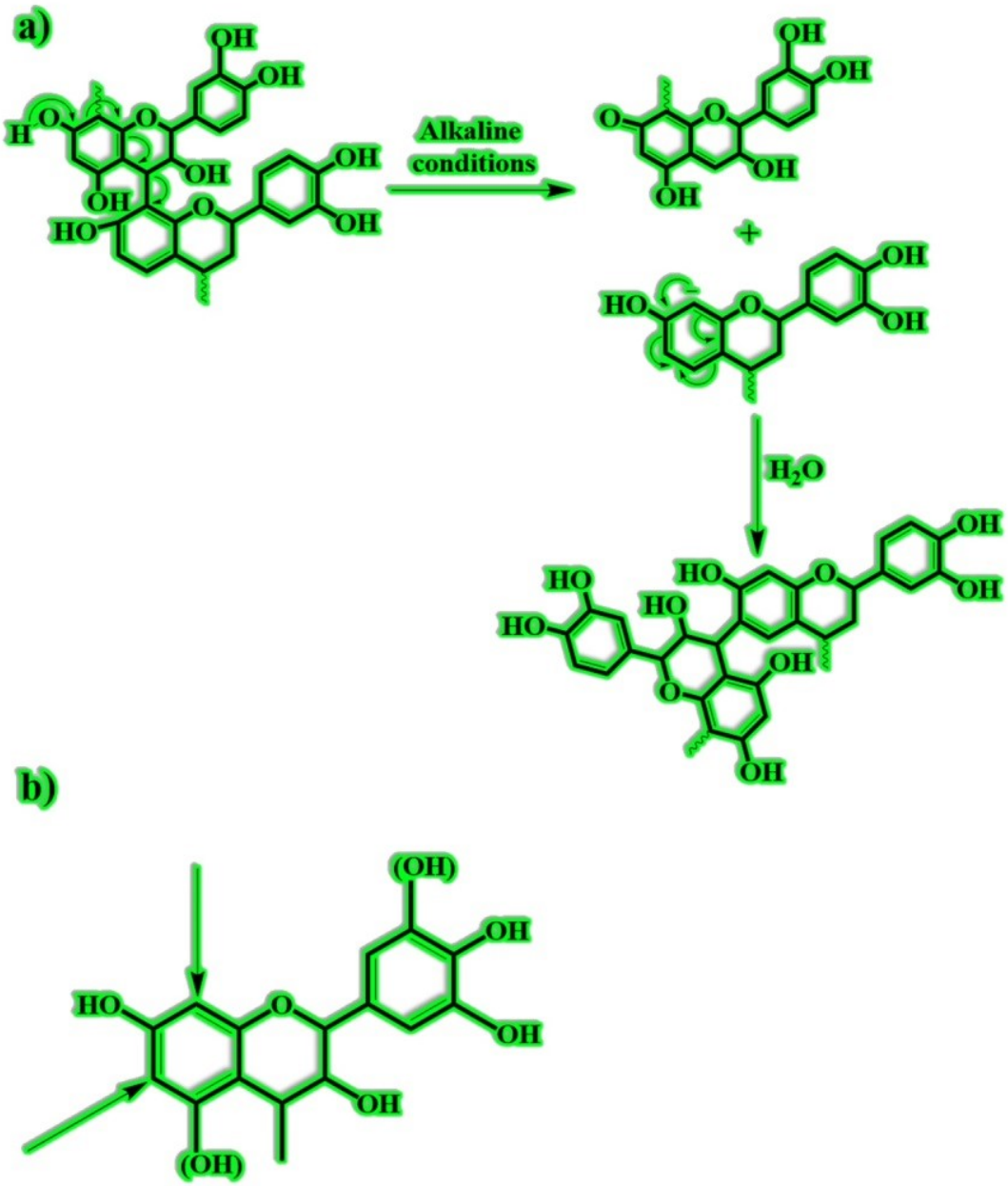

Fig. S1. Alkaline auto condensation (a) [1] and probable flavonoid unit in a condensed tannin (b). [2]

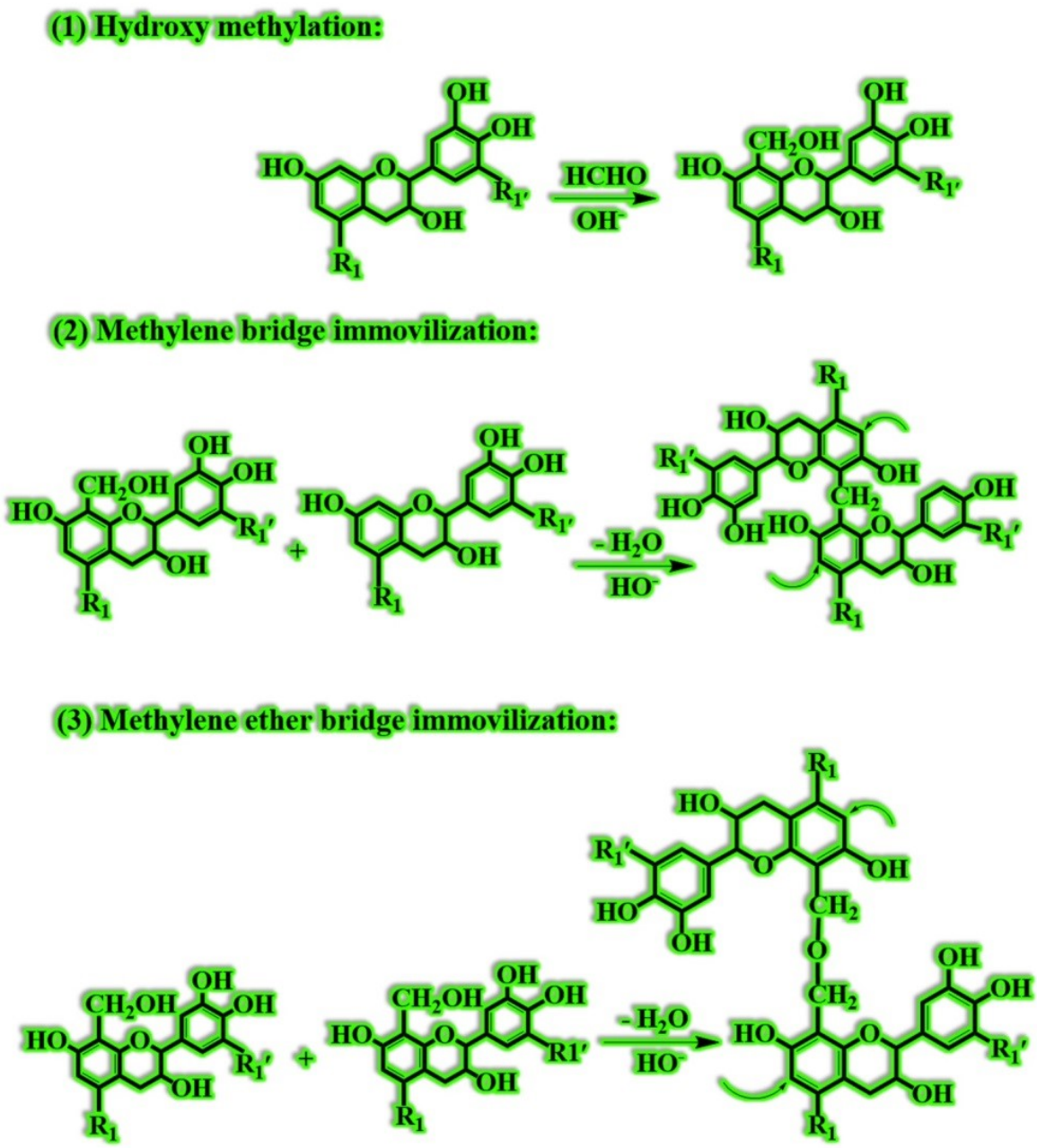

Fig. S2. Probable generic gelification mechanism between condensed tannin and formaldehyde. [2, 3]

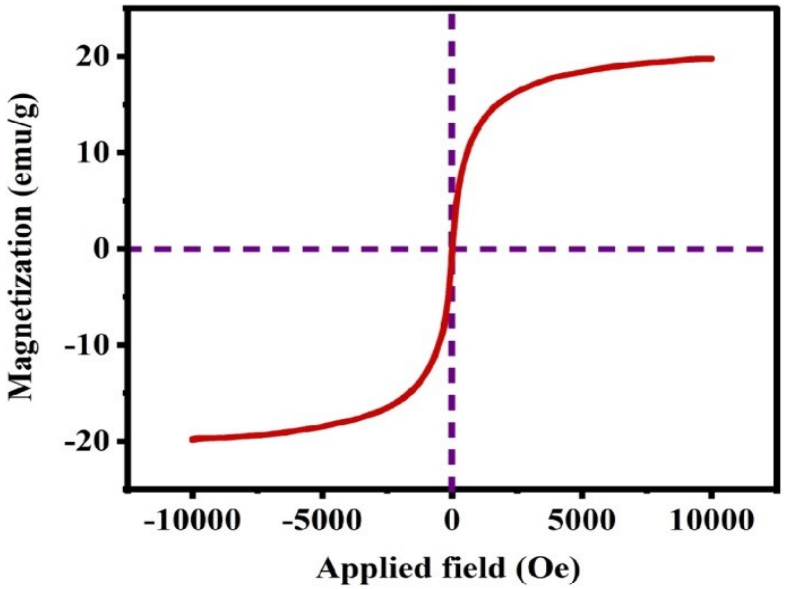

Fig. S3. Vibration sample magnetometry (VSM) data of Fe_3O_4-OT recorded at room temperature.

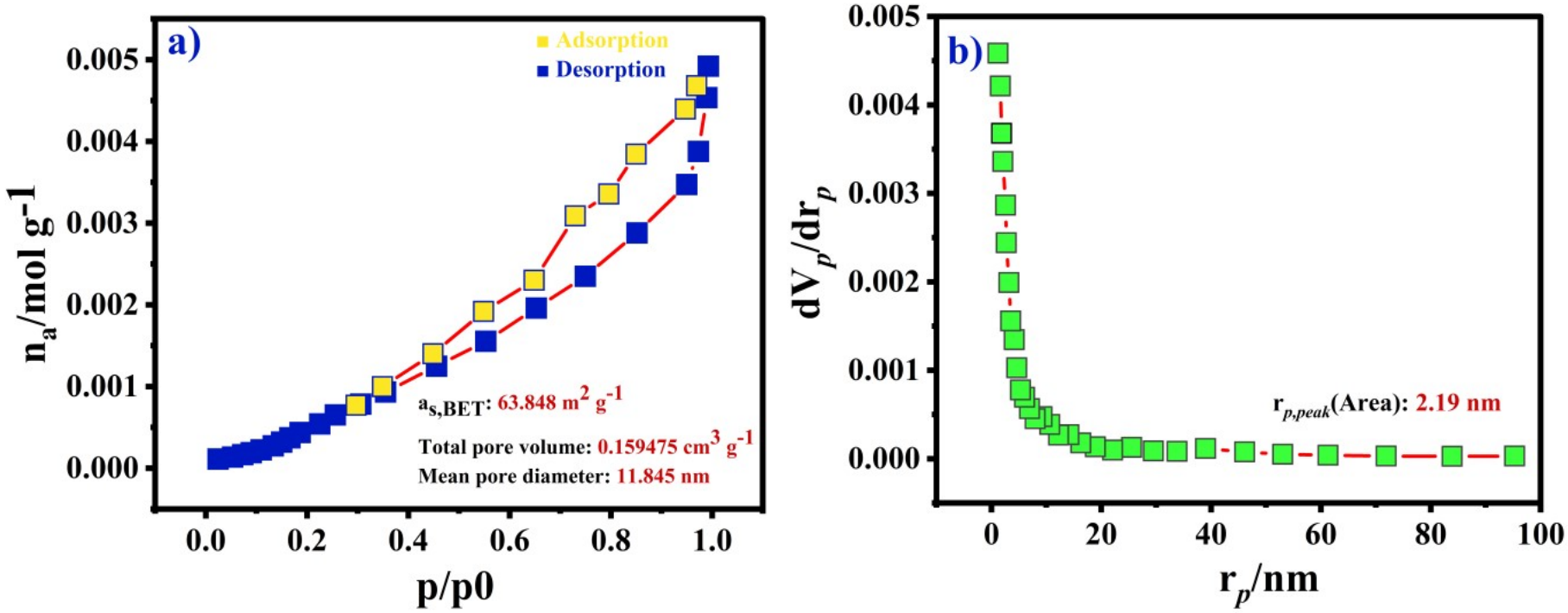

Fig. S4. Nitrogen adsorption and desorption diagram (a) and BJH diagram (b) for Fe_3O_4-OT adsorbent.

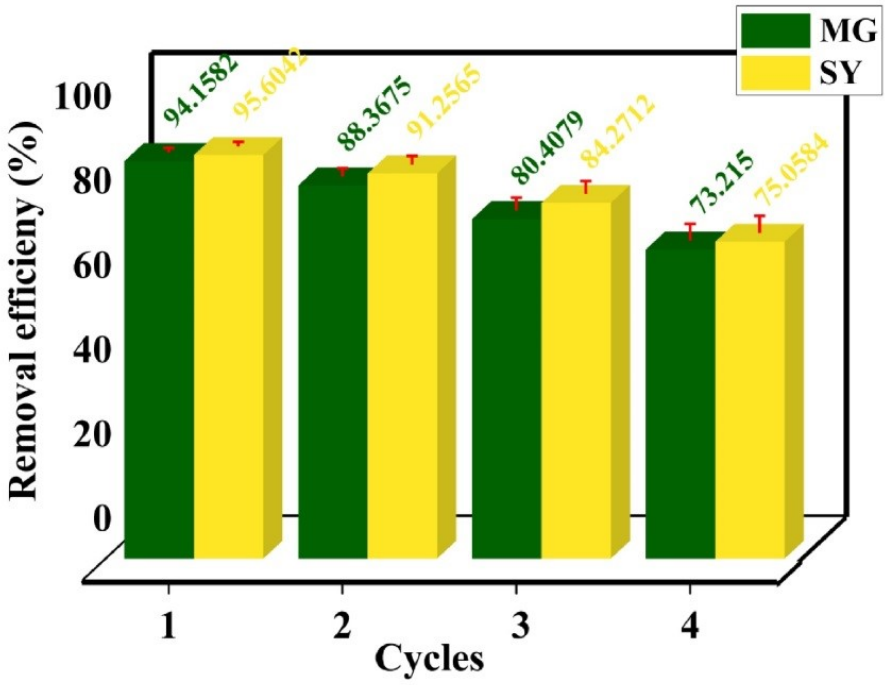

Fig. S5. The removal efficiency of MG and SY at 16 mg L^{-1} initial concentration on Fe_3O_4-OT in different cycles**.**

Tables

Table S1. Physical properties and molecular structure of MG and SY.

Name of the commercial dye	Malachite Green (MG)	Sunset Yellow (SY)
Colour Index Name	Aniline green	Orange-yellow
λmax (nm)	617	480
Molecular Weight (g mol^{-1})	364.911	452.400
Charge	(+)	(-)
Chemical Formula	$C_{23}H_{25}N_2$	$C_{16}H_{10}N_2Na_2O_7S_2$

Table S2. Assignment of groups in the FTIR spectrum of the Fe_3O_4-OT.

Band (cm^{-1})	Functional group
3400	–OH stretching
2900	C–H stretching vibrations in methylene (-CH_2-)
2800	C–H stretching vibrations in methyl and methylene groups
1720	–C=O stretching vibrations
1627	C=C stretching in the aromatic ring
1450, 1500 and 1616	C–C skeletal vibrations
1100 and 1380	C–O stretching vibrations
1205	C–O–C symmetric stretch
1035	C–O ethers stretching
620 to 823	C–H deformation vibrations in the aromatic ring
455 and 764	=C–H bending vibrations
524	CCO and CCC ring deformation
578	Fe-O stretching vibrations of Fe^{2+} and Fe^{3+}

Table S3. Variance analysis for response surface quadratic model for adsorption efficiency (%) of MG and SY onto Fe_3O_4-OT.

Source of variation	DF	R% MG					DF	R% SY			
		Sum of squares	Mean of squares	F-value	P-value			Sum of squares	Mean of squares	F-value	P-value
Model	20	370.3	18.52	23.22	< 0.0001		20	3321.8	221.5	41.79	< 0.0001
X_1	1	0.442	0.442	0.554	0.4723		1	953.0	953	179.9	< 0.0001
X_2	1	128.4	128.4	161.11	< 0.0001		1	91.31	91.31	17.23	0.0022
X_3	1	16.21	16.21	20.33	0.0009		1	142.5	142.5	26.88	0.0004
X_4	1	30.46	30.46	38.21	< 0.0001		1	235.4	235.4	44.42	< 0.0001
X_5	1	4.00	4.00	5.02	0.0467		1	243.4	243.4	45.92	< 0.0001
X_1X_2	1	15.79	15.79	19.81	0.0010		1	41.89	41.9	7.91	0.0211
X_1X_3	1	3.73	3.73	4.68	0.0535		1	190.9	190.9	36.02	< 0.0001
X_1X_4	1	20.18	20.18	25.31	0.0004		1	20.14	20.14	3.80	0.0893
X_1X_5	1	7.50	7.50	9.41	0.0107		1	307.8	307.8	58.09	< 0.0001
X_2X_3	1	0.505	0.505	0.633	0.4431		1	16.38	16.38	3.09	0.01211
X_2X_4	1	0.105	0.105	0.132	0.7231		1	275.8	275.8	52.04	< 0.0001
X_2X_5	1	15.37	15.37	19.28	0.0011		1	119.5	119.5	22.56	0.0008
X_3X_4	1	0.393	0.393	0.493	0.4972		1	181.3	181.3	34.22	0.0002
X_3X_5	1	2.25	2.25	2.82	0.1214		1	381.0	381.0	71.90	< 0.0001
X_4X_5	1	17.57	17.57	22.03	0.0007		1	121.6	121.6	22.95	0.0008
X_1^2	1	1.67	1.67	2.09	0.1758		1	12.98	12.98	2.24	0.1629
X_2^2	1	81.8	81.8	102.6	< 0.0001		1	7.08	7.08	1.22	0.2928
X_3^2	1	24.4	24.4	30.58	0.0002		1	0.245	0.245	0.042	0.8410
X_4^2	1	4.34	4.34	5.44	0.0397		1	0.205	0.205	0.035	0.8545
X_5^2	1	3.68	3.68	4.62	0.0547		1	1.34	1.34	0.231	0.6403
Residual	11	8.77	0.797				11	63.81	5.80		
Lack of Fit	6	5.91	0.985	1.72	0.284		6	26.63	4.44	0.597	0.727
Pure Error	5	2.86	0.573				5	37.17	7.43		
Corr. Total	31	379.1					31	3406.6			

Table S4. Adsorption parameter of isotherm for the adsorption of MG and SY onto Fe_3O_4-OT (volume, 50 mL; adsorbent dose, 20 mg; contact time, 20 min; temperature, 25 ºC; pH, 6.5).

Isotherm	Plot	Parameters	MG	SY
Langmuir $\frac{C_e}{q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m}$	C_e/q_e *vs.* C_e	Q_m (mg g^{-1})	49.00	53.96
		K_L (L mg^{-1})	3.496	1.903
		R^2	0.997	0.993
		$R_L=1/(1+(K_L \times C_0))$	0.009-0.054	0.017-0.095
Freundlich $lnq_e = lnK_F + \frac{1}{n} lnC_e$	$ln\ q_e$ *vs.* $ln\ C_e$	1/n	0.162	0.311
		K_F (L mg^{-1})	4.597	4.345
		R^2	0.967	0.929
Temkin $q_e = B_1\ ln\ K_T + B_1\ ln\ C_e$	q_e *vs.* $ln\ C_e$	B_1	4.240	8.903
		K_T (L mg^{-1})	1.00	1.00
		R^2	0.892	0.968
Dubinin-Radushkevich $ln\ q_e = lnQ_S - k\varepsilon^2$	$ln\ q_e$ *vs.* ε^2	Q_s (mg g^{-1})	38.88	44.36
		β	-4.3E^{-09}	-3.7E^{-08}
		E (kJ mol^{-1})	10.763	3.682
		R^2	0.785	0.930

Table S5. kinetic parameters for MG and SY dyes adsorption onto Fe_3O_4-OT (volume, 50 mL; initial concentration for each dye, 16 mg L^{-1}; adsorbent dose, 20 mg; temperature, 25 ºC; pH, 6.5).

Model	Plot	Parameters	MG	SY
First-order- kinetic $\ln(q_e - q_t) = \ln q_e - k_1 t$	*ln* $(q_e - q_t)$ *vs. t*	k_1 (min^{-1})	0.103	0.116
		$q_{e\ (calc)}$ (mg g^{-1})	33.64	28.89
		R^2	0.948	0.977
Pseudo-second-order-kinetic $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	t/q_t *vs. t*	k_2 (min^{-1})	0.002	0.004
		$q_{e\ (calc)}$ (mg g^{-1})	48.51	45.44
		R^2	0.991	0.996
		h (mg g^{-1} min^{-1})	6.503	9.734
Intraparticle diffusion $q_t = k_{diff} t^{1/2} + C$	q_t *vs.* $t^{1/2}$	$K_{diff,}$ (mg g^{-1} $min^{-1/2}$)	5.435	4.274
		C (mg g^{-1})	9.643	16.44
		R^2	0.943	0.933
Elovich $q_t = \frac{1}{\beta}\ln(t) + \frac{1}{\beta}\ln(\alpha\beta)$	q_t *vs. ln t*	β (g mg^{-1})	0.094	0.120
		α (mg g^{-1} min^{-1})	14.37	32.69
		R^2	0.971	0.966
Experimental data		$q_{e\ (exp)}$ (mg g^{-1})	39.21	39.53

Table S6. Thermodynamic parameters for the adsorption of MG and SY onto magnetic Fe_3O_4-OT (volume: 50 mL; initial dye concentration for each dye: 16 mg L^{-1}; adsorbent dose: 20 mg; contact time: 20 min; pH: 6.5).

	MG		SY	
T(k)	**k_C**	**ΔG°(kJ mol^{-1})**	**k_C**	**ΔG°(kJ mol^{-1})**
288	6.98	-4.65	10.53	-5.64
298	15.24	-6.75	22.91	-7.76
308	16.88	-7.24	26.54	-8.40
318	36.78	-9.53	53.32	-10.51
R^2	0.933		0.948	
ΔS°(j mol^{-1} k^{-1})	151.0		152.7	
ΔH°(kj mol^{-1})	38.72		38.19	

References

1. A. Arbenz and L. Avérous, *Green Chem.* 2015, **17**, 2626-2646.

2. J. Beltrán-Heredia, P. Palo, J. Sánchez-Martín, J. R. Domínguez and T. González, *Ind. Eng. Chem. Res.*, 2012, **51**, 50-57.

3. J. Sánchez-Martín, J. Beltrán-Heredia and C. Carmona-Murillo, *Ind. Crops Prod.*, 2011, **33**, 409-417.