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Amino-containing polymer-coated magnetite nanoparticles as nano-adsorbents for bisphenol A: Synthesis, kinetic and thermodynamic study

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Abstract

Magnetite nanoparticles coated with poly(dimethyl aminoethyl methacrylate) (PDMAEMA@MNPs) and their quarternized form (PQDMAEMA@MNPs) were successfully synthesized and used as nano-adsorbents for bisphenol A (BPA). The particles were spherical with the average particle size between 10 nm and 20 nm in diameter with a moderate degree of nanoclustering (*ca.*150 to 200 particles/cluster). In terms of adsorption properties, the PDMAEMA@MNPs exhibited a higher BPA adsorption capacity (1.05 $mg\cdot g^{-1}$ MNP at pH 9) than the quaternized form (0.50 $mg\cdot g^{-1}$ MNP at pH 9). Equilibrium isotherm, kinetic, and thermodynamic characteristics of BPA adsorption on the PDMAEMA@MNPs were investigated. It was found that the BPA adsorption on the MNPs reached an equilibrium within 5 min and the maximum adsorption capacity (q_e) was 9.88 $mg\cdot g^{-1}$. The adsorption isotherm study results indicated that the BPA adsorption process on PDMAEMA@MNPs exhibited the best fit with the Freundlich model, and the adsorption kinetics followed the pseudo-second order model with the R^2 value of 1.00. The thermodynamic data exhibited a negative enthalpy change (ΔH° = -2585.571 $J\cdot mol^{-1}$), indicating exothermic BPA adsorption, and a negative Gibbs free energy (ΔG°), implying a spontaneous BPA adsorption process.

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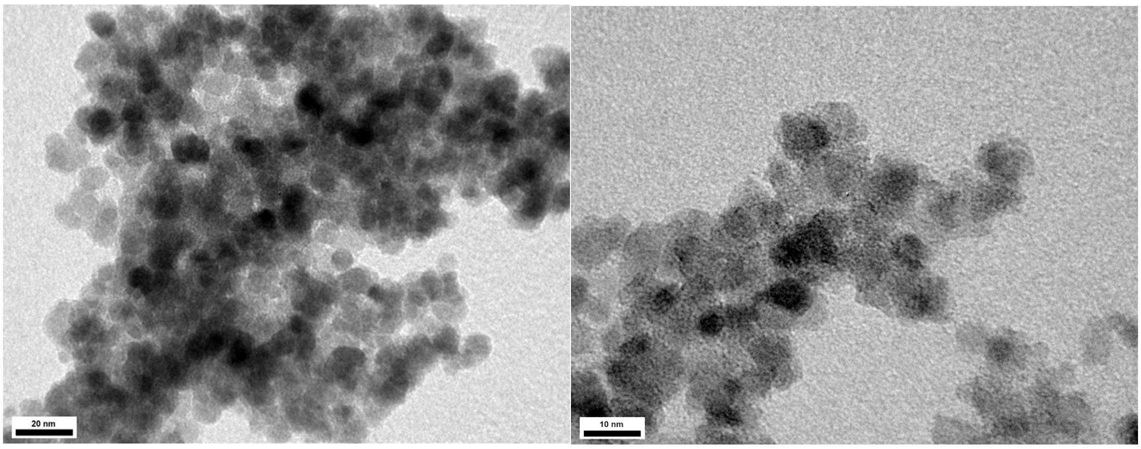

Figure S1. TEM images of PDMAEMA@MNPs (top) and PQDMAEMA@MNPs (bottom).

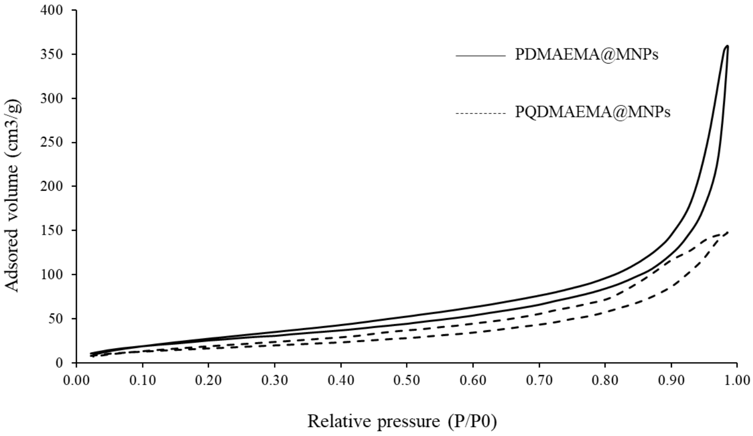

Figure S2. N_2 adsorption-desorption isotherm graph of PDMAEMA@MNPs and PQDMAEMA@MNPs.

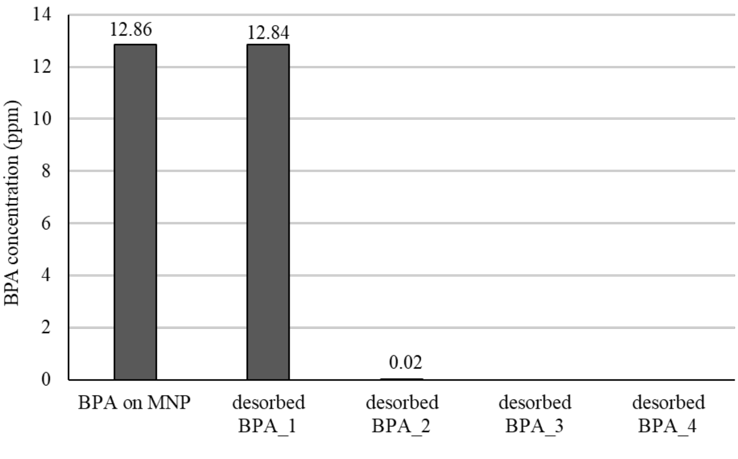

Figure S3. The concentrations of the adsorbed BPA on the MNPs and the desorbed BPA in the washing solutions after washing with methanol for four times.

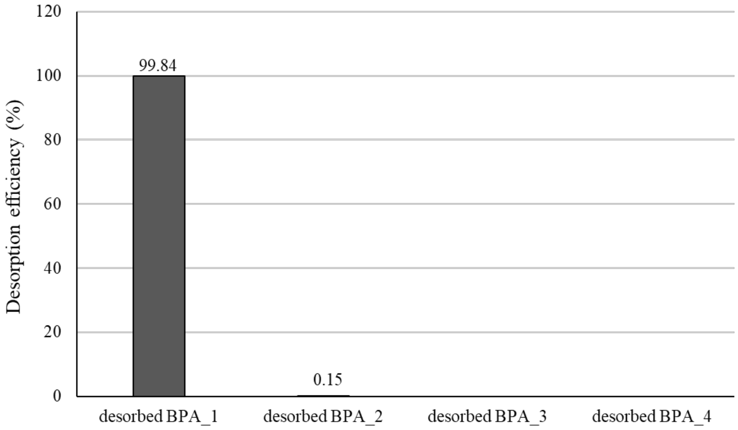

Figure S4. Desorption efficiency (%) of BPA on the MNPs by washing with methanol.

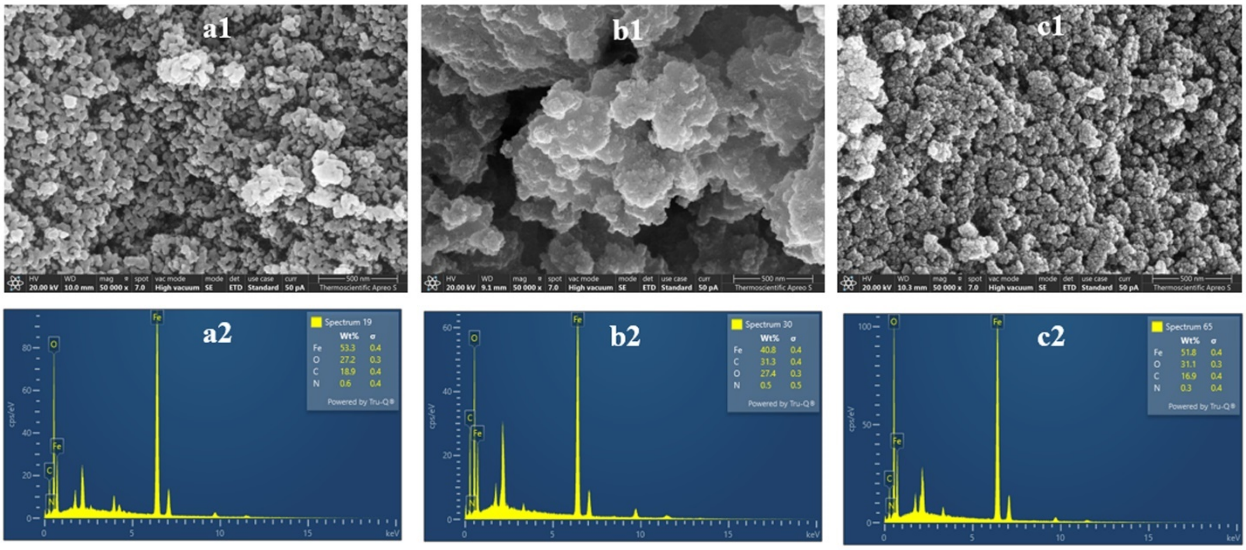

Figure S5. FE-SEM images and EDX spectra of (a1, a2) PDMAEMA@MNPs, (b1, b2) PDMAEMA@MNPs adsorbed with BPA, and (c1, c2) PDMAEMA@MNPs after desorbing BPA.

Table S1. The percentage of element composition of PDMAEMA@MNP.

Adsorbents	**Fe (%)**	**C (%)**	**N (%)**	**O (%)**	**C/Fe**
PDMAEMA@MNPs	53.3 ± 0.4	18.9 ± 0.4	0.6 ± 0.4	27.2 ± 0.3	0.35 ± 0.01
PDMAEMA@MNPs adsorbed with BPA	40.8 ± 0.4	31.3 ± 0.4	0.5 ± 0.5	27.4 ± 0.5	0.77 ± 0.02
PDMAEMA@MNPs after desorbing BPA	52.6 ± 0.4	16.5 ± 0.4	0.7 ± 0.4	30.2 ± 0.3	0.31 ± 0.01

Investigation of the adsorption kinetics using the non-linear method

The OriginPro software was used for calculating the pseudo-first-order and pseudo-second-order kinetic parameters *via* the non-linear method. Figure S6 shows the predicted pseudo first order and pseudo second-order kinetics and the calculated parameters are listed in Table S2.

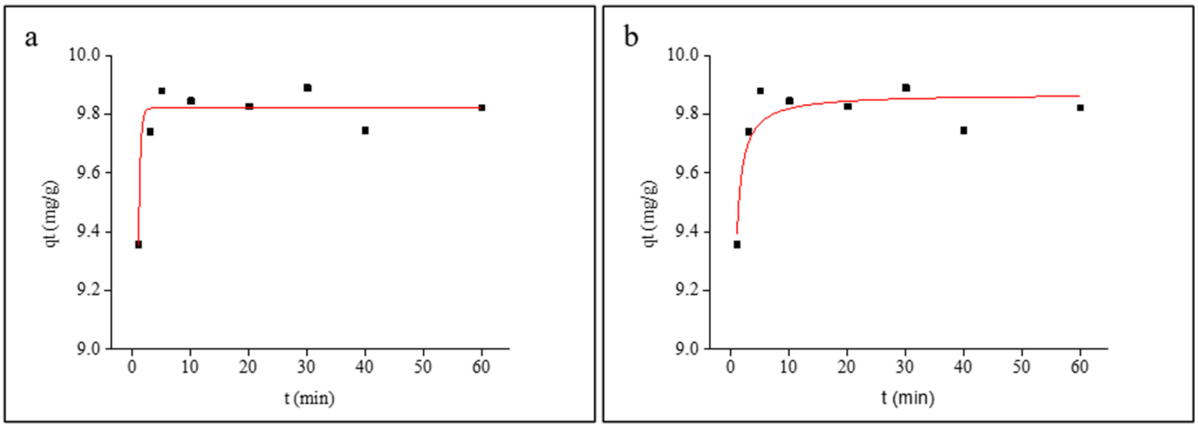

Figure S6. (a) Pseudo first-order kinetics calculated *via* the non-linear method (b) pseudo second-order kinetics calculated *via* the non-linear method.

Table S2. Kinetic parameters obtained from the non-linear methods.

Kinetic model	**$q_{e\,(exp)}$ (mg·g^{-1})**	**$q_{e\,(cal)}$ (mg·g^{-1})**	**k_1 (min^{-1})**	**k_2 (min^{-1})**	**R^2**
Pseudo first-order kinetics	9.88	9.82	3.053	-	0.8274
Pseudo second-order kinetics	9.88	9.87	-	1.996	0.8820

To compare the results obtained from the non-linear methods with those from the linear method, there was two cases for consideration;

1) Pseudo-first-order kinetics and 2) pseudo-second-order kinetics.

2) The non-linear pseudo-first-order equation showed higher R^2 value (R^2= 0.8274) than those obtained from the linear method (R^2= 0.1240). In addition, $q_{e(cal)}$ value (9.82 mg·g^{-1}) of the non-linear pseudo-first-order method was significantly different from those obtained the $q_{e(cal)}$ value obtained from the linear method (0.046 mg·g^{-1}). Therefore, the non-linear pseudo-first-order kinetic model was better fit than the linear pseudo-first order model.

3) In the case of pseudo-second-order kinetic model, the R^2 value (R^2=0.8820) of the non-linear method was significantly lower than those obtained from the linear method (R^2=1.0000). In addition, the q_e calculated from the linear (9.89 mg·g^{-1}) and the non-linear (9.87 mg·g^{-1}) methods were slightly different and these were very close to $q_{e(exp.)}$ value (9.88 mg·g^{-1}). These results implied that the linear pseudo-second-order kinetic model was better fit than the non-linear model. However, the values of the other parameters calculated from the linear method when compared to the non-linear method suggested the use of the linear method for the prediction of the adsorption kinetics in the current work.

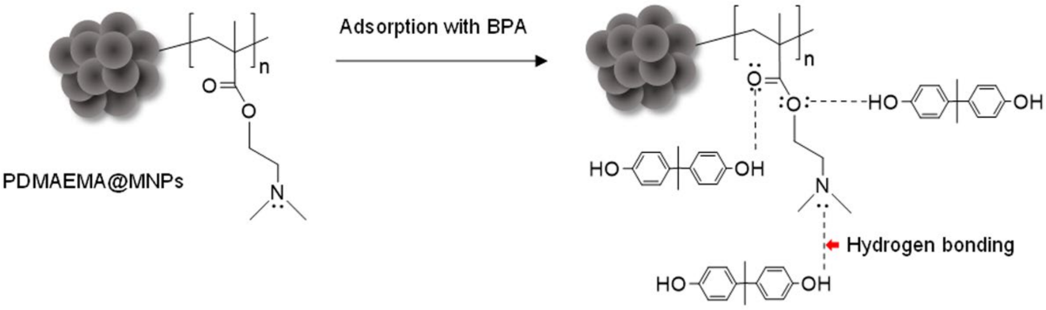

Figure S7. The proposed adsorption mechanism of BPA on PDMAEMA@MNPs through hydrogen bonding.

A calibration curve of BPA

Table S3. Peak Area of BPA at various concentrations.

Conc of BPA (ppm)	Area			Average	SD
	1	2	3		
1	41.96	44.75	44.35	43.69	1.51
3	128.25	128.84	128.63	128.57	0.30
5	215.08	214.90	220.73	216.90	3.31
10	436.61	441.55	428.88	435.68	6.39

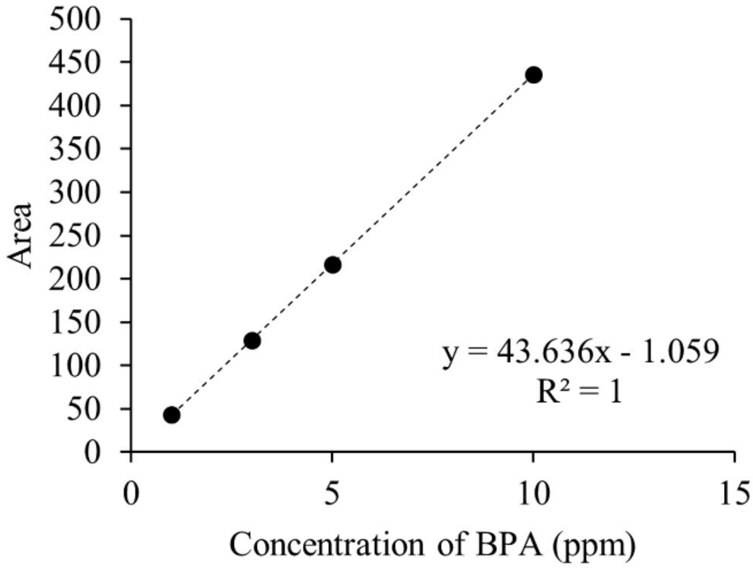

Figure S8. The calibration curve of BPA having 1 ppm to 10 ppm concentration range.

An example for the calculation of BPA concentrations in the supernatant

The equation from the standard calibration curve of BPA $y = 43.636x - 1.059$
Average peak area of loaded BPA (5.00 ppm) at pH 6185.00

$$\begin{aligned} y &= 43.636x - 1.059 \\ 185.0 &= 43.636x - 1.059 \\ x &= 4.26 \text{ ppm} \end{aligned}$$

Table S4. BPA concentration on supernatant.

Particle	pH	Area								
		1	**2**	**3**	**4**	**5**	**Average**	**SD**	**Cal**	**Cal SD**
PDMAEMA@MNPs	6	187.097	187.883	184.096	188.686	177.25	185.00	4.67	4.26	0.13
	7	169.354	166.949	166.275	161.753	167.274	166.32	2.80	3.84	0.09
	8	136.736	133.83	139.109	137.483	132.071	135.85	2.85	3.14	0.09
	9	124.73	123.632	127.031	127.038	123.193	125.12	1.83	2.89	0.07
	10	137.355	137.281	140.115	140.227	140.14	139.02	1.56	3.21	0.06
	11	235.23	232.17	207.476	229.871	233.299	227.61	11.42	5.00	0.29
QPDMAEMA@MNPs	6	183.651	184.59	189.887	194.373	185.536	187.61	4.47	4.32	0.13
	7	186.128	186.525	185.273	196.154	190.839	188.98	4.55	4.36	0.13
	8	183.002	183.726	189.749	173.545	178.496	181.70	6.07	4.19	0.16
	9	179.507	169.9	179.06	173.549	174.629	175.33	4.02	4.04	0.12
	10	174.04	180.628	176.957	174.485	177.4	176.70	2.64	4.07	0.08
	11	208.676	205.019	217.795	207.2	208.318	209.40	4.90	4.82	0.14

An example for the calculation of adsorption capability (q_e)

Weight of MNPs	1.00 mg
Loaded BPA	5.00 ppm
Observed BPA in the supernatant	4.26 ppm

$$\begin{aligned} \text{Adsorption capability (qe)} &= \left(\frac{C_0 - C_e}{m}\right)V \\ &= \frac{(5.00 - 4.26)(500 \times 10^{-6})}{1 \times 10^{-3}} \\ &= 0.37 \text{ mg}\cdot\text{g}^{-1} \end{aligned}$$

Table S5. Calculated adsorption capability (q_e).

Particle	pH	q_e ($\text{mg}\cdot\text{g}^{-1}$)	q_e ($\text{mg}\cdot\text{g}^{-1}$) SD
PDMAEMA@MNPs	6	0.37	0.07
	7	0.58	0.04
	8	0.93	0.04
	9	1.05	0.03
	10	0.89	0.03
QPDMAEMA@MNPs	6	0.34	0.06
	7	0.32	0.06
	8	0.41	0.08
	9	0.48	0.06
	10	0.46	0.04

An example for the calculation of the percentage of BPA on the MNPs

Weight of MNPs	2.00 mg
Total volume	500.00 uL
Loaded BPA	1.00 ppm
Observed BPA	0.39 ppm

$$\begin{aligned}\text{Percentage of BPA on MNPs} &= \left(\frac{C_e}{C_0}\right) \times 100 \\ &= \frac{0.39}{1.00} \times 100 \\ &= 39\%\end{aligned}$$

Table S6. Percentage of BPA on MNPs.

Loaded of BPA (ppm)	**BPA on MNPs**	**%BPA on MNPs**
1	0.386	38.629
10	7.458	74.582
50	39.597	79.194
100	78.061	78.061
200	145.367	72.683

Langmuir isotherm study

Table S7. Langmuir Isotherm parameter.

C_0	**C_p**	**C_e**	**m (g)**	**V (L)**	**q_e**	**C_e/q_e**
10	7.46	2.54	0.002	0.0005	1.86456	1.36
50	39.60	10.40	0.002	0.0005	9.89930	1.05
100	78.06	21.94	0.002	0.0005	19.51530	1.12
200	145.37	54.63	0.002	0.0005	36.34168	1.50

An example for the calculation of the Langmuir isotherm parameters (q_m and K_L)

From the equation

$$\begin{aligned}q_m &= \frac{1}{\text{Slope}} \\ &= \frac{1}{0.0053} \\ &= 188.679\end{aligned}$$

From the equation

$$\begin{aligned}K_L &= \frac{1}{q_m * \mathit{Intercept}} \\ &= \frac{1}{(188.678)(1.1417)} \\ &= 0.006051\end{aligned}$$

Freundlich isotherm study

Table S8. Freundlich isotherm parameter.

C_0	C_p	C_e	M (g)	V (L)	q_e	lnC_e	lnq_e
10	7.46	2.54	0.002	0.0005	1.86	0.93	0.62
50	39.60	10.40	0.002	0.0005	9.90	2.34	2.29
100	78.06	21.94	0.002	0.0005	19.52	3.09	2.97
200	145.37	54.63	0.002	0.0005	36.34	4.00	3.59

An example for the calculation of the Freundlich isotherm parameters (q_m and K_f)

From the equation

$$\mathrm{n} = \frac{1}{\text{slope}} = \frac{1}{0.9788} = 1.0217$$

From the equation

$$K_f = e^{\text{intercept}} = e^{-0.1662} = 0.8705$$

Pseudo-first-order kinetics study

Table S9. Pseudo-first-order kinetic values.

time (min)	q_e at 5.00 min	q_t	log(q_e-q_t)	t (min)	log(q_e-q_t)
1	9.88	9.36	-0.28	1.00	-0.28
3	9.88	9.74	-0.84	3.00	-0.84
5	9.88	9.88	-2.40	5.00	-2.40
10	9.88	9.84	-1.42	10.00	-1.42
20	9.88	9.83	-1.24	20.00	-1.24
30	9.88	9.89	0.00	30.00	0.00

An example for the calculation of the pseudo-first order parameters (k_1 and q_e)

From the equation

$$k_1 = \text{Slope} * 2.303 = 0.0269 * 2.303 = 0.0619$$

From the equation

$$q_e = 10^{\text{Intercept}} = 10^{-1.3402} = 0.0457$$

Pseudo-second-order study

Table S10. Pseudo-second-order kinetic values.

t (min)	q_t	t/q_t
1.00	9.36	0.1069
3.00	9.74	0.3080
5.00	9.88	0.5061
10.00	9.84	1.0158
20.00	9.83	2.0355
30.00	9.89	3.0335

An example for the calculation of the pseudo-second order parameters (k_2 and q_e)

From the equation

$$\begin{aligned} k_2 &= \frac{1}{\text{Intercept} * q_e^2} \\ &= \frac{1}{(0.0048)(9.89)^2} \\ &= 4.9061 \times 10^{-5} \end{aligned}$$

From the equation

$$\begin{aligned} q_e &= \frac{1}{\text{Slope}} \\ &= \frac{1}{0.1011} \\ &= 9.89 \end{aligned}$$

Thermodynamic study

Table S11. Thermodynamic values.

Temperature (K)	q_e (mg·g^{-1})	q_e (mg·g^{-1}) SD	1/T	K_d	lnK_d
303	9.58	0.19	0.003300	3.288133	1.19032
313	9.49	0.24	0.003195	3.159335	1.150361
323	9.40	0.25	0.003096	3.026548	1.107423
343	9.31	0.51	0.002915	2.918647	1.07112

An example for the calculation of the thermodynamic parameters (ΔH° ΔS° and ΔG°)

From the equation

$$\begin{aligned}\Delta H^{\circ} &= \text{R * Slope}\\ &= 8.314 * 310.99\\ &= -2585.57\ \text{J}\cdot\text{mol}^{-1}\end{aligned}$$

From the equation

$$\begin{aligned}\Delta S^{\circ} &= \text{R * Intercept}\\ &= 8.314 * 0.1574\\ &= 1.3095\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\end{aligned}$$

At the temperature = 303 K

$$\Delta H = -2585.57\ \text{J}\cdot\text{mol}^{-1}$$

$$\Delta S = 1.3095\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

From the equation

$$\begin{aligned}\Delta G^{\circ} &= \Delta H^{\circ} - T\Delta S^{\circ}\\ &= -2585.57 - (303)(1.3095)\\ &= -2982.34\ \text{J}\cdot\text{mol}^{-1}\end{aligned}$$