Supporting Information

Equilibrium, Thermodynamic and DFT Modelling Studies For the Removal of Dichromate Ions From Wastewater Using Calix[4]arene Modified Silica Resin

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FT-IR Characterization

Figure S1 describes the characterization of CMS resin which shows that the spectrum **(a)** is of *p*-diethylaminomethylcalix[4]arene, which have bands at 3365, 2920, 1606, 1434 and 1251 cm^{-1} for OH, C-H, C-C, C=C, C-O and C-N stretching frequencies, respectively and the peak at 1043 cm^{-1} is OH bending vibrational frequency. The spectrum **(b)** is pure silica which have bands at 1095 cm^{-1} for Si-O-Si stretching while the 3430 and 1631 cm^{-1} are O-H stretching and O-H-bending, frequencies respectively. The spectrum **(c)** is of CMS resin, which have some new extra bands at 3370, 2935, 2678 and 1473 cm^{-1} for OH, C-H, C-C and C=C groups of compound **3** that has been attached onto silica surface.

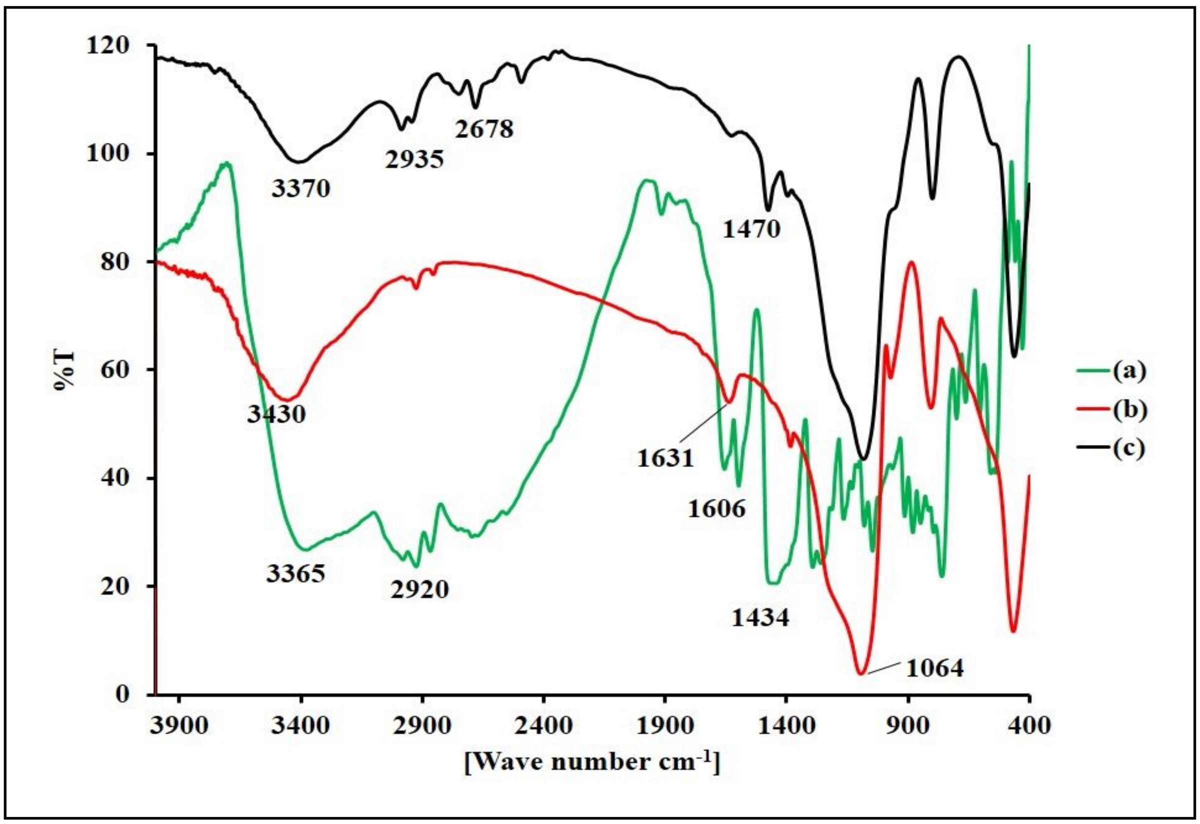

Figure S1. FT-IR characterization of **CMS** resin

SEM Characterization of **CMS** resin

The surface of CMS resin was characterized by SEM technique. Figure S2 (a) shows the pure silica, which is smooth and crystalline; while Figure S2 (b) reveals the CMS resin, which is rough and amorphous. This roughness and smaller size after attachment of compound 3 indicates that adsorbent has larger surface area for adsorption.

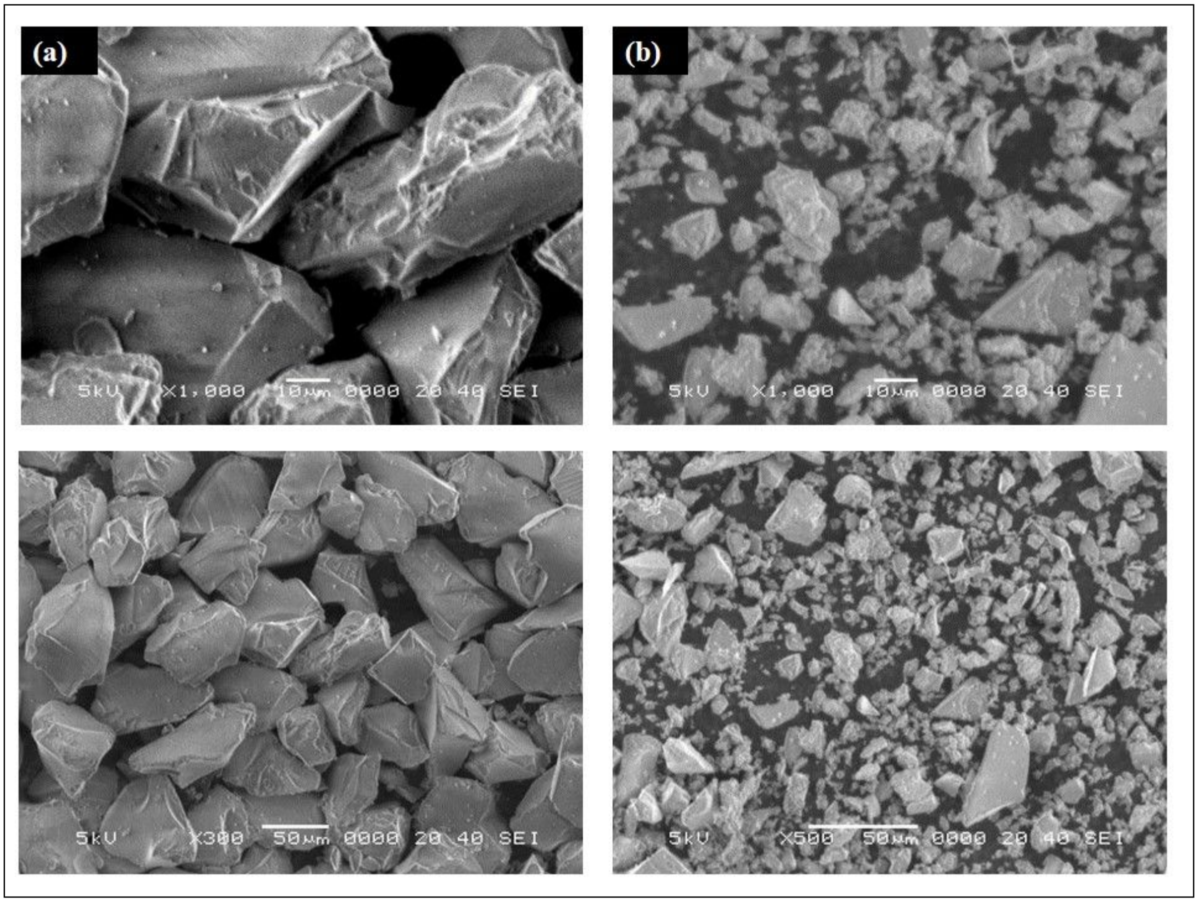

Figure S2. SEM images of (a) pure silica and (b) **CMS** resin.

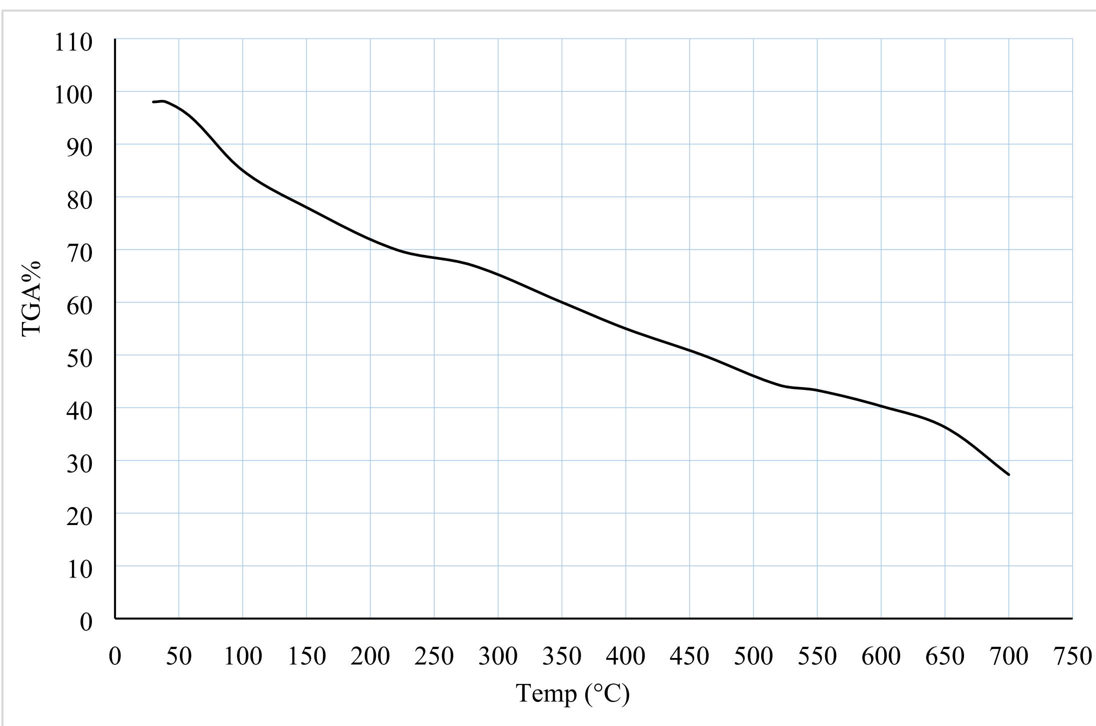

Figure S3. Thermogravimtric curve of **CMS** resin.

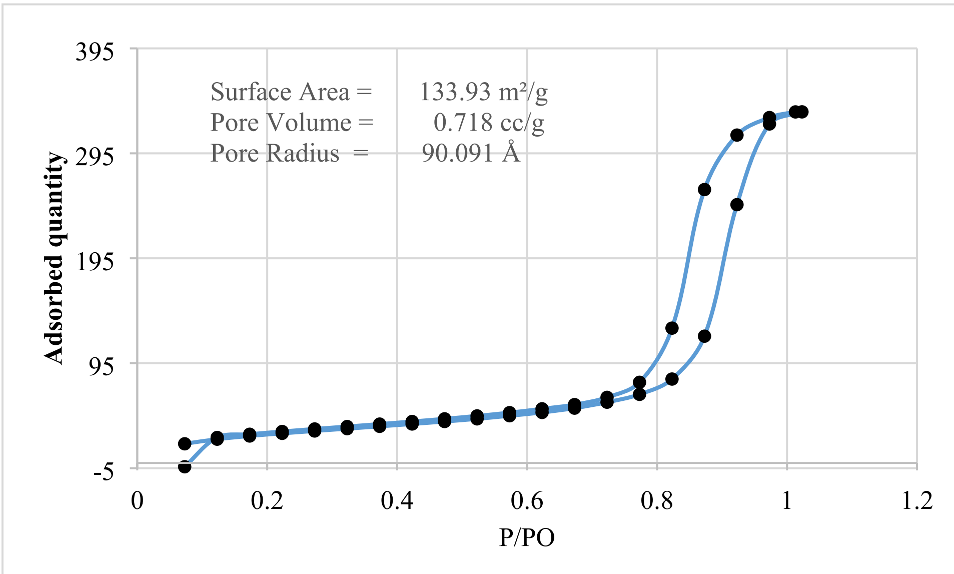

Figure S4. BET analysis of **CMS** resin.

Table S1 Effect of pH on % adsorption of dichromate ions

pH	Concentration (mol/L)	% Adsorption	pH	Concentration (mol/L)	% Adsorption
1.0	2.50×10^{-5}	92.99	3.5	2.50×10^{-5}	91.32
1.1	2.50×10^{-5}	92.87	3.6	2.50×10^{-5}	91.11
1.2	2.50×10^{-5}	92.86	3.7	2.50×10^{-5}	90.00
1.3	2.50×10^{-5}	92.85	3.8	2.50×10^{-5}	89.88
1.4	2.50×10^{-5}	92.78	3.9	2.50×10^{-5}	89.16
1.5	2.50×10^{-5}	92.76	4.0	2.50×10^{-5}	87.19
1.6	2.50×10^{-5}	92.66	4.1	2.50×10^{-5}	85.21
1.7	2.50×10^{-5}	92.65	4.2	2.50×10^{-5}	84.12
1.8	2.50×10^{-5}	92.64	4.3	2.50×10^{-5}	80.19
1.9	2.50×10^{-5}	92.61	4.4	2.50×10^{-5}	78.43
2.0	2.50×10^{-5}	92.50	4.5	2.50×10^{-5}	74.87
2.1	2.50×10^{-5}	92.41	4.6	2.50×10^{-5}	70.39
2.2	2.50×10^{-5}	92.38	4.7	2.50×10^{-5}	65.14
2.3	2.50×10^{-5}	92.37	4.8	2.50×10^{-5}	60.01
2.5	2.50×10^{-5}	92.35	4.9	2.50×10^{-5}	51.08
2.6	2.50×10^{-5}	92.31	5.0	2.50×10^{-5}	30.10
2.7	2.50×10^{-5}	92.2	5.2	2.50×10^{-5}	25.10
2.8	2.50×10^{-5}	92.10	5.5	2.50×10^{-5}	18.19
2.9	2.50×10^{-5}	92.00	5.7	2.50×10^{-5}	17.81
3.0	2.50×10^{-5}	91.89	6.0	2.50×10^{-5}	12.09
3.1	2.50×10^{-5}	91.78	6.5	2.50×10^{-5}	10.99
3.2	2.50×10^{-5}	91.67	7.0	2.50×10^{-5}	5.21
3.3	2.50×10^{-5}	91.58	7.3	2.50×10^{-5}	2.19
3.4	2.50×10^{-5}	91.48	7.4	2.50×10^{-5}	1.58

Table S2 Effect of adsorbent dosage on % adsorption of dichromate ions

Adsorbent Dosage(mg)	Concentration (mol/L)	% Adsorption
10	2.5×10^{-5}	76.176±0.65637
15	2.5×10^{-5}	88.011±0.56811
20	2.5×10^{-5}	93.101±0.53705
25	2.5×10^{-5}	99.130±0.50438
30	2.5×10^{-5}	99.140±0.50433
35	2.5×10^{-5}	99.114±0.50331
40	2.5×10^{-5}	99.144±0.50431
45	2.5×10^{-5}	99.150±0.50428
50	2.5×10^{-5}	99.154±0.50426

Table S3 Langmuir adsorption Isotherm model

C*e*/C*ads* (mmol/g)				
Temperature (K)	298	303	308	313
***Ce*(mol/L)**				
0.001	0.0180±0.280	0.0681±0.632	0.0791±0.073	0.0807±0.061
0.002	0.0318±0.123	0.0810±0.567	0.0986±0.061	0.1164±0.042
0.007	0.0415±0.121	0.0917±0.416	0.1753±0.054	0.2359± 0.021
0.015	0.0497±0.102	0.0991±0.227	0.1258±0.050	0.2436±0.020
0.031	0.0499±0.100	0.0999±0.208	0.2277±0.050	0.2508±0.019

Table S4 Freundlich adsorption Isotherm model

lnC*ads* (mmol/g)				
Temperature (K)	298	303	308	313
ln*Ce*(mol/L)				
-14.13005483	-11.6139±0.0456	-12.3456±0.040	-11.9871±0.041	-13.0982±0.038
-13.10581192	-10.9553±0.0467	-12.0921±0.041	-11.9980±0.041	-12.8197±0.041
-11.80529642	-10.3613±0.048	-11.0833±0.045	-10.889±0.045	-11.9156±0.045
-11.08754493	-9.6756±0.051	-11.0147±0.047	-10.114±0.049	-10.7651±0.055
-10.3724093	-8.9895±0.055	-10.1181±0.049	-10.017±0.049	-9.6221±0.062
-9.432071562	-8.3649±0.059	-9.9911±0.050	-9.1480±0.0547	-8.1090±0.066

Table S5 D-R adsorption Isotherm model

ε^2				
Temperature (K)	**298**	**303**	**308**	**313**
lnC*ads* (mmol/g)				
-11.61386483	1225.576169±0.040	1402.989137±0.035	1336.8117±0.037	1423.14515±0.034
-10.95521883	1054.339715±0.047	1312.87220±0.038	1161.4423±0.042	1274.3478±0.039
-10.36124379	855.4741883±0.058	1216.8790±0.041	961.5689±0.0517	1085.42311±0.046
-9.675582968	754.6134688±0.066	1126.98176±0.051	862.81567±0.057	974.6521±0.051
-8.989470019	660.4112763±0.075	879.11092±0.062	781.4771±0.064	850.5109±0.057
-8.364957496	546.1024437±0.091	634.23110±0.083	631.1571±0.076	766.14890±0.066

Table S6 The effect of temperature on % adsorption of dichromate ions onto CMS resin

% Adsorption				
Temperature (K)	**298**	**303**	**308**	**313**
Time				
5	75.10±0.064	81.73±0.061	85.82±0.058	88.82±0.056
10	78.97±0.060	82.98±0.060	88.81±0.056	91.95±0.054
15	82.24±0.060	85.23±0.058	93.76±0.053	94.19±0.053
30	83.57±0.055	88.82±0.056	97.55±0.051	98.02±0.051
45	90.38±0.053	89.17±0.056	99.50±0.050	99.50±0.050
60	92.39±0.054	90.56±0.055	99.75±0.050	99.52±0.050
90	92.40±0.051	91.94±0.054	99.05±0.050	99.03±0.053
120	92.53±0.054	92.48±0.054	99.04±0.050	99.02±0.051

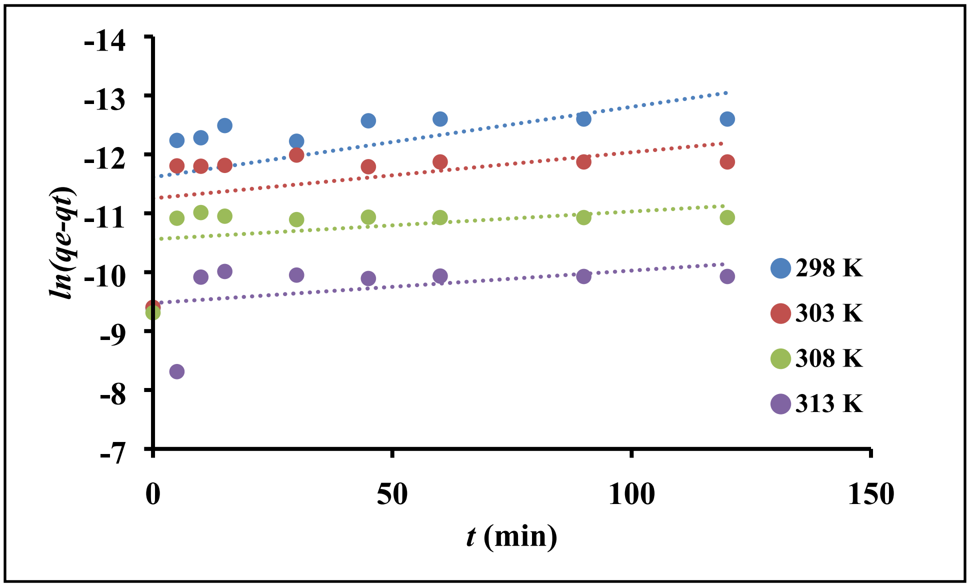

Figure S5. Pseudo first graph for the adsorption of dichromate ions from water (10 mL 2.5×10^{-5} mol/L), 25 mg of **CMS** resin per 10mL of adsorbate with 60 min shaking time at 298-313K)

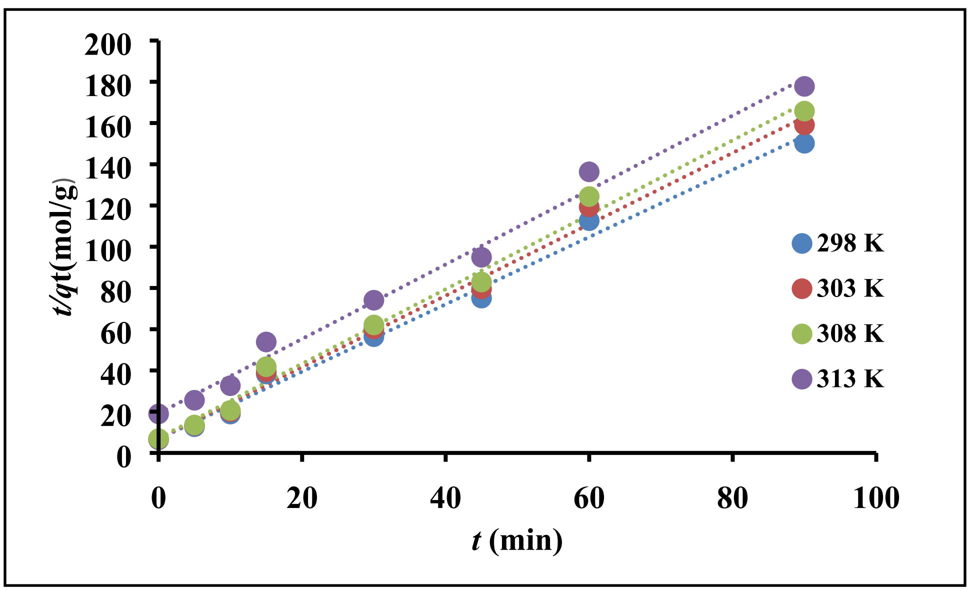

Figure S6. Pseudo second order kinetic graphs for the adsorption of dichromate ions from water (10 mL 2.5×10^{-5} mol/L), 25 mg of **CMS** resin per 10mL of adsorbate with 60 min shaking time at 298-313K).

Table S7. Kinetic study for the adsorption of dichromate ions

Kinetic Study								
T (K)	Pseudo 1[st] order				Pseudo 2[nd] order			
	298	303	308	313	298	303	308	313
T(min)	ln(*qe-qt*)	ln(*qe-qt*)	ln(*qe-qt*)	ln(*qe-qt*)	*t/qt*(mol/g)	*t/qt*(mol/g)	*t/qt*(mol/g)	*t/qt*(mol/g)
5	-9.39±0.053	-9.40±0.0532	-9.31±0.0537	-8.31±0.0602	6.37±0.0784	6.67±0.0749	6.93±0.0722	18.93±0.0264
10	-12.23±0.042	-11.80±0.0424	-10.91±0.0458	-9.91±0.0504	12.71±0.0331	13.35±0.0375	13.54±0.0369	25.54±0.0196
15	-12.28±0.042	-11.79±0.0424	-11.01±0.0454	-10.01±0.049	18.86±0.0393	20.00±0.0250	20.60±0.0243	32.60±0.0153
30	-12.48±0.043	-11.81±0.0423	-10.95±0.0457	-9.95±0.0502	38.29±0.0265	39.37±0.0127	41.81±0.0120	53.81±0.0093
45	-12.22±0.041	-11.98±0.0417	-10.89±0.0459	-9.89±0.0505	56.39±0.0131	60.13±0.0083	62.06±0.0081	74.06±0.0068
60	-12.57±0.044	-11.79±0.0424	-10.93±0.0457	-9.93±0.0503	75.09±0.0089	79.54±0.0063	82.88±0.0060	94.88±0.0053
90	-12.59±0.045	-11.87±0.0421	-10.92±0.0458	-9.92±0.0504	112.64±0.0067	119.31±0.0042	124.33±0.0040	136.33±0.0037
120	-12.61±0.041	-11.71±0.0421	-10.93±0.0458	-9.94±0.0504	150.189±0.004	159.08±0.0031	165.77±0.0030	177.77±0.0028

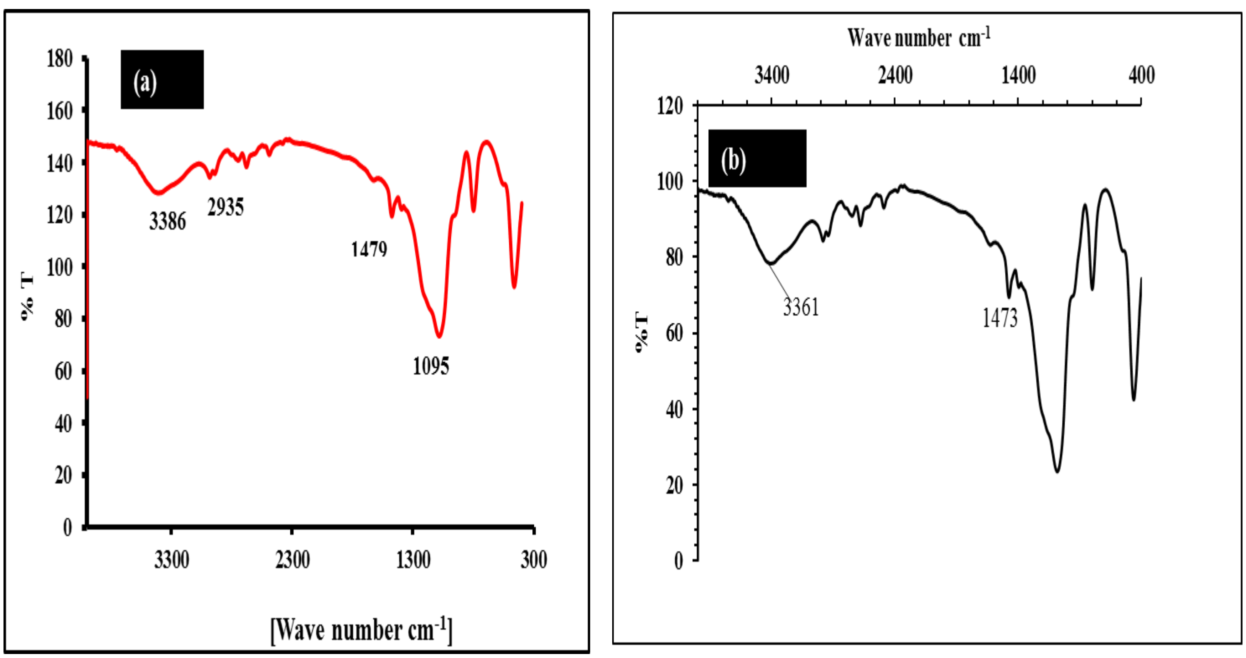

Figure S7: FT-IR spectra of **CMS** resin before use (a) and after reuse (b).