Supporting Information

1,3- Dialkylimidazolium modified clay sorbent for perchlorate removal from water

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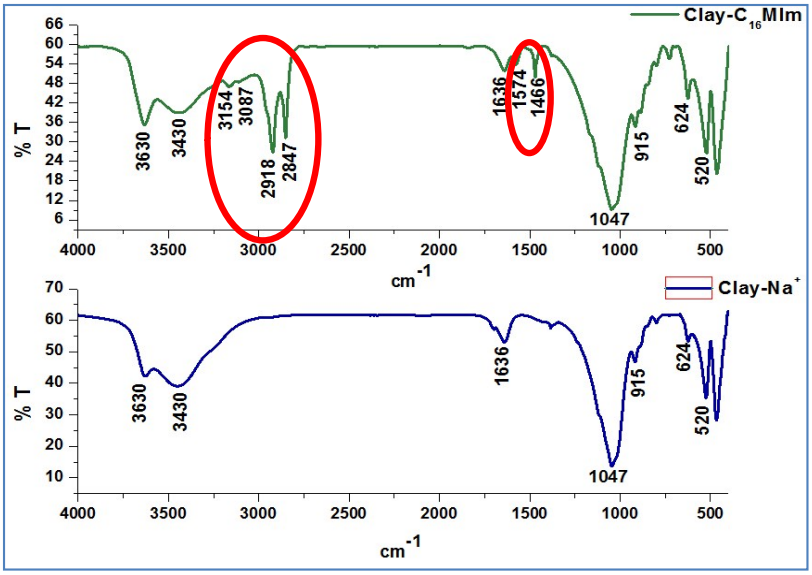
Captions

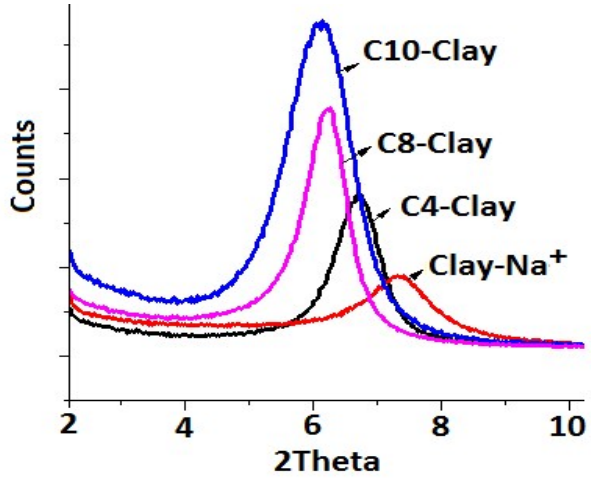
Part-I : Characterisation of modified clays

- **FT-IR spectra of Clay-Na^+ and C16-Clay**



- Characteristic C-H str. Peaks in the region between 2800-3000 cm^{-1} shows functionalization of clay.
- Peak at 3154 cm^{-1} due to C4-H and C5-H str. vibrations of imidazolium ring.
- Peak at 3087 cm^{-1} attributed to the aromatic C2-H str. in imidazolium ring.
- Peak at 1574 cm^{-1} and 1466 cm^{-1} due to C=C and C=N vibrations.

XRD spectra of Clay-Na^+ and modified clays



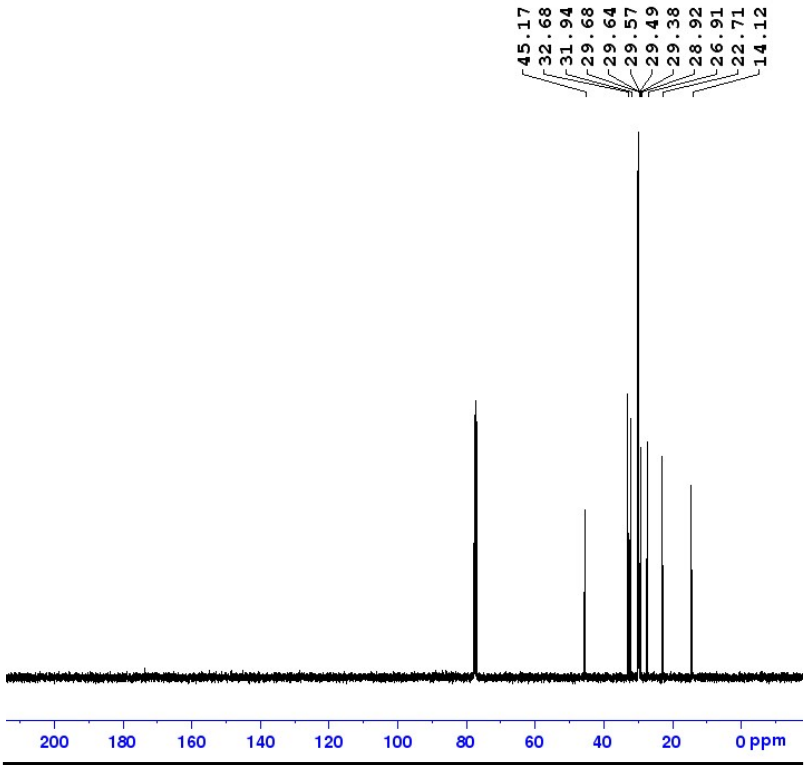
XRD analysis was performed to observe the basal spacing change between layers after exchanging sodium ions with the imidazolium cation. X-ray diffraction pattern of clay exhibits 001 peak centred at $2\theta = 7.306^o$ corresponding to a basal d-spacing of 12.09 Å. For the modified clay, the characteristic peak of the clay was shifted to lower 2θ value leading to an increase of the interlayer spacing. This shift is a clear signature of the intercalation of the imidazolium cation between the layers of MMT.

CHN analysis of Clay-Na^+ and modified clays

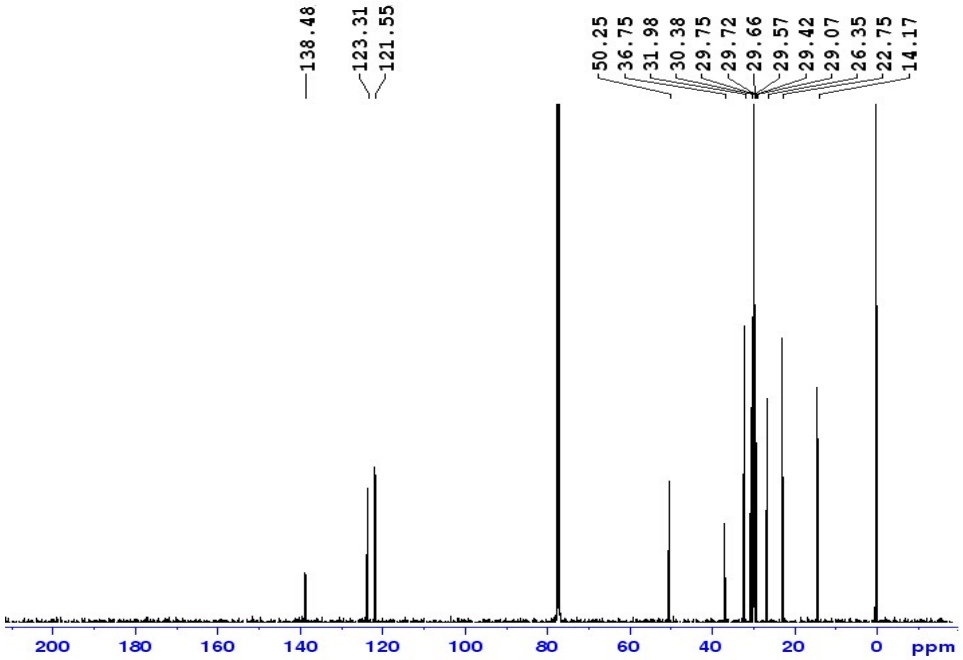
Clay	% C	% H	% N	Total (%)
Clay-Na^+	0.3	0.2	0	0.5
C4-Clay	7.9	1.4	2.2	11.5
C6-Clay	9.3	1.9	2.0	13.2
C8-Clay	12.3	1.8	2.3	16.4
C10-Clay	14.0	2.4	2.2	18.6
C16-Clay	20.1	3.4	2.1	25.6

Part-II : ^{13}C NMR spectra

i) 1-hexadecyl chloride



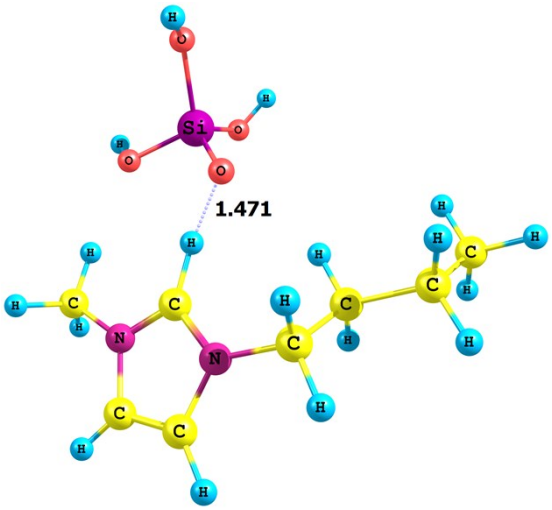
ii) 1-hexadecyl-3-methylimidazolium chloride (C16MImCl)



The CH_2-Cl peak in 1-chlorohexadecane at 45.17 ppm disappeared on completion of the reaction and a new quaternary N-CH_2 group appeared at 50.25 ppm.

Part-III: Coordinates

[1] $C4MIm^{+}$ $Si(OH)_3O^{-}$

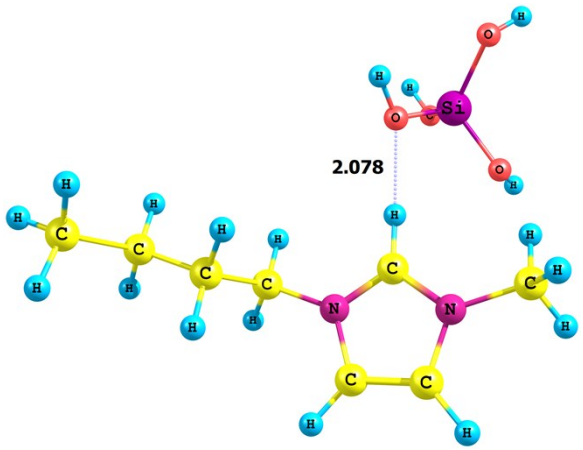


E(RB3LYP) = -1016.00605327

7	2.090268000	-0.968766000	0.327792000
6	0.784118000	-1.263715000	0.218312000
6	2.847933000	-2.085440000	0.019589000
6	1.974235000	-3.081757000	-0.284188000
7	0.701609000	-2.549396000	-0.155624000
1	-0.090910000	-0.496703000	0.375286000
1	2.146075000	-4.102877000	-0.578073000
1	3.924048000	-2.076555000	0.041121000
6	2.601888000	0.360014000	0.720161000
1	2.261899000	0.559042000	1.739118000
1	3.691257000	0.280213000	0.739353000
6	-0.558811000	-3.265874000	-0.382718000
1	-0.543252000	-3.714365000	-1.377060000
1	-0.675635000	-4.047743000	0.369783000
1	-1.386700000	-2.557013000	-0.315522000
14	-2.584056000	0.536511000	0.088695000
6	2.136903000	1.470738000	-0.222606000
1	1.041851000	1.484138000	-0.230949000
1	2.477669000	1.244097000	-1.240048000
6	2.669210000	2.840576000	0.213741000
1	2.326891000	3.049217000	1.234097000
1	3.766230000	2.821983000	0.252120000
6	2.209146000	3.968687000	-0.714051000
1	1.117943000	4.027775000	-0.744355000
1	2.589966000	4.936957000	-0.378397000
1	2.562212000	3.808322000	-1.737488000
8	-2.973065000	-1.062801000	-0.301769000
1	-3.837239000	-1.172855000	-0.707731000
8	-3.076574000	1.367959000	-1.279776000

1	-3.369572000	2.267885000	-1.120555000
8	-3.646768000	1.103912000	1.261945000
1	-3.273184000	1.102625000	2.146253000
8	-1.064046000	0.596237000	0.529188000

[2] C4MIm-Si(OH)$_4$

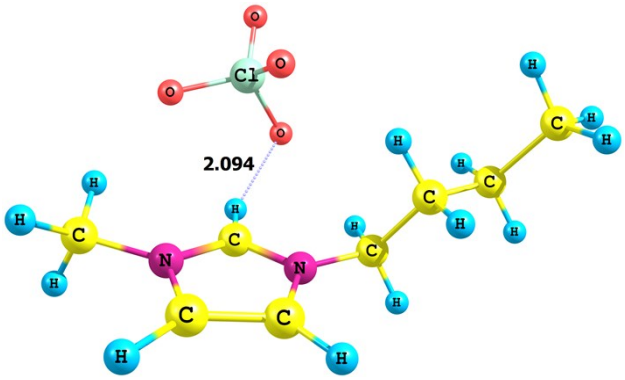


E(RB3LYP) = -1016.43802869

7	-1.688342000	1.002103000	0.469473000
6	-0.442308000	1.134656000	0.001340000
6	-2.281592000	2.250181000	0.505865000
6	-1.361963000	3.143087000	0.050132000
7	-0.219986000	2.428165000	-0.258135000
1	0.265585000	0.327184000	-0.144786000
1	-1.419545000	4.211264000	-0.071275000
1	-3.288317000	2.398227000	0.856874000
6	-2.329284000	-0.275588000	0.852598000
1	-1.525824000	-1.003111000	0.976879000
1	-2.791211000	-0.122420000	1.830218000
6	1.026298000	2.985774000	-0.806039000
1	0.907306000	3.172727000	-1.873686000
1	1.247405000	3.919936000	-0.291512000
1	1.832917000	2.276036000	-0.629565000
14	3.121311000	-0.972562000	0.032624000
6	-3.354112000	-0.752058000	-0.178652000
1	-2.857863000	-0.877830000	-1.147374000
1	-4.122207000	0.017273000	-0.315492000
6	-4.016543000	-2.069815000	0.245064000
1	-3.244653000	-2.834864000	0.388503000
1	-4.501155000	-1.935279000	1.218890000
6	-5.045621000	-2.565020000	-0.774621000
1	-4.584976000	-2.745157000	-1.750160000
1	-5.499985000	-3.501458000	-0.444795000
1	-5.850026000	-1.837100000	-0.913304000
8	3.115830000	0.633158000	0.413210000

1	3.638383000	0.904302000	1.174089000
8	4.046749000	-1.399708000	-1.249559000
1	5.006674000	-1.381134000	-1.237330000
8	3.526386000	-1.728028000	1.428718000
1	3.713671000	-2.668636000	1.476483000
8	1.571360000	-1.252196000	-0.489101000
1	1.481919000	-1.849080000	-1.239027000

[3] C4MIm-ClO_4



E(RB3LYP) = -1184.34884303

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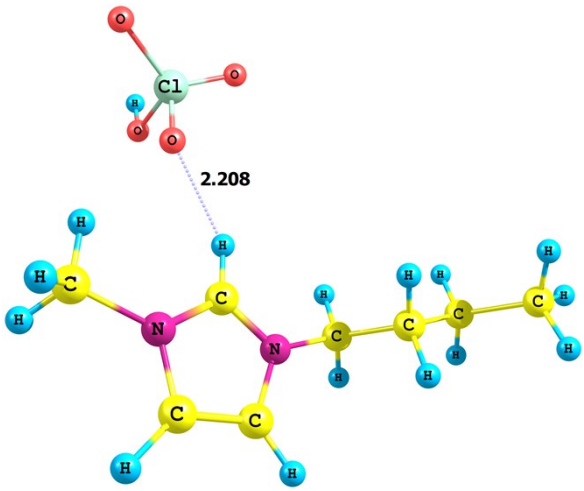
8	-2.439109000	-1.450743000	-0.083201000
8	-0.439539000	-1.655563000	1.294662000
8	-1.057371000	-3.474253000	-0.240908000
8	-0.228341000	-1.333933000	-1.114943000
6	-0.898047000	1.233902000	0.629836000
7	-1.777057000	1.975710000	-0.048893000
6	-1.096121000	3.012534000	-0.660054000
6	0.217949000	2.873459000	-0.335186000
7	0.319475000	1.756983000	0.473891000
6	-3.211308000	1.677403000	-0.157227000
6	1.563894000	1.133802000	0.976672000
6	2.438552000	0.598667000	-0.158221000
6	3.675829000	-0.126421000	0.384970000
6	4.570901000	-0.671191000	-0.731508000
1	-1.106833000	0.326182000	1.178862000
1	-1.596438000	3.743715000	-1.270783000
1	1.074885000	3.460248000	-0.615361000
1	-3.546524000	1.945762000	-1.157942000
1	-3.339503000	0.605190000	-0.012262000
1	-3.769965000	2.245710000	0.587638000
1	1.249309000	0.315125000	1.624600000
1	2.087658000	1.880678000	1.579189000
1	2.752909000	1.424421000	-0.808384000
1	1.836069000	-0.087811000	-0.759540000
1	3.350010000	-0.952728000	1.025912000

1	4.255993000	0.553524000	1.021871000
1	5.440766000	-1.189233000	-0.319923000
1	4.937178000	0.133867000	-1.376484000
1	4.025214000	-1.381041000	-1.358898000

[4] C4MIm-$HClO_4$



E(RB3LYP) = -1184.71609758

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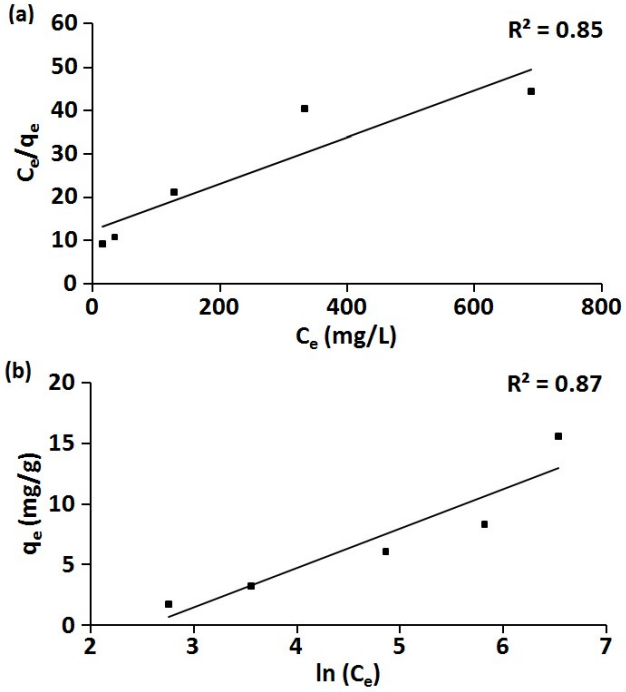
8	-2.983660000	-2.295497000	-0.052044000
8	-3.828752000	-0.443690000	1.460401000
8	-2.189693000	0.010556000	-0.276039000
8	-4.459271000	-0.578742000	-0.990987000
6	0.711100000	1.235228000	0.155454000
7	0.581324000	2.512814000	-0.218394000
6	1.815940000	3.125854000	-0.118764000
6	2.694250000	2.185002000	0.323048000
7	1.984968000	1.010747000	0.491172000
6	-0.668534000	3.155894000	-0.651988000
6	2.548064000	-0.291018000	0.919322000
6	3.338048000	-0.985865000	-0.191494000
6	3.907781000	-2.331975000	0.276763000
6	4.703650000	-3.045026000	-0.819661000
1	-0.089142000	0.512905000	0.181591000
1	1.961924000	4.164399000	-0.362801000
1	3.747763000	2.253953000	0.533449000
1	-0.540007000	3.551839000	-1.658910000
1	-1.462159000	2.412054000	-0.650628000
1	-0.919621000	3.962080000	0.036869000
1	1.707563000	-0.904015000	1.248863000
1	3.174356000	-0.095323000	1.791976000
1	4.155243000	-0.335312000	-0.522271000
1	2.684651000	-1.138700000	-1.057574000
1	3.086903000	-2.976418000	0.611934000

1	4.549806000	-2.170541000	1.150250000
1	5.094372000	-3.998091000	-0.457754000
1	5.554163000	-2.442052000	-1.149998000
1	4.079483000	-3.252544000	-1.693411000
1	-4.625490000	-0.973541000	1.658092000

Part-IV : Adsorption isotherm plot (a)Langmuir and (b) Tempkin adsorption for C16-Clay



The characteristics of Langmuir isotherm is expressed by a dimensionless parameter called equilibrium parameter R_L determined as,

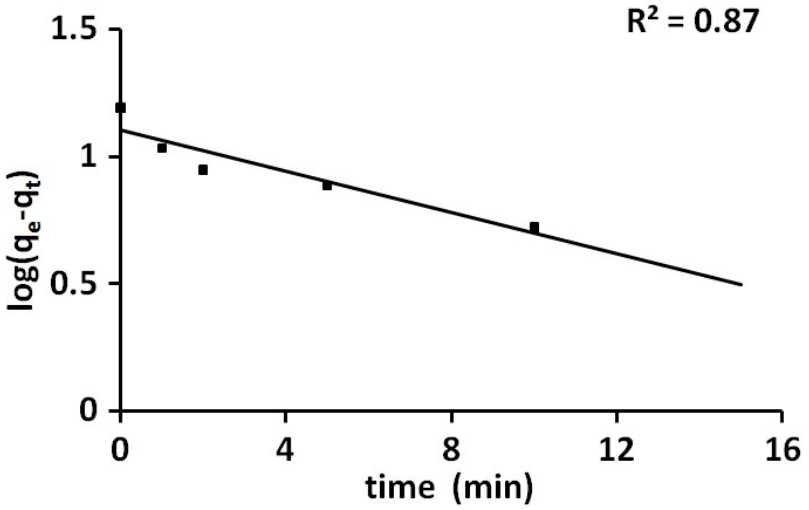
$$\mathbf{R_L = 1/(1 + bC_i)}$$

where b is the Langmuir constant and C_i is the initial concentration. R_L>1 indicates unfavourable adsorption, R_L = 0 indicate irreversible and 0 < R_L < 1 indicate favourable reaction.

Langmuir plot	
Initial perchlorate Conc.(mg/L)	**R_L**
50	0.82
100	0.70
250	0.48
500	0.31
1000	0.19

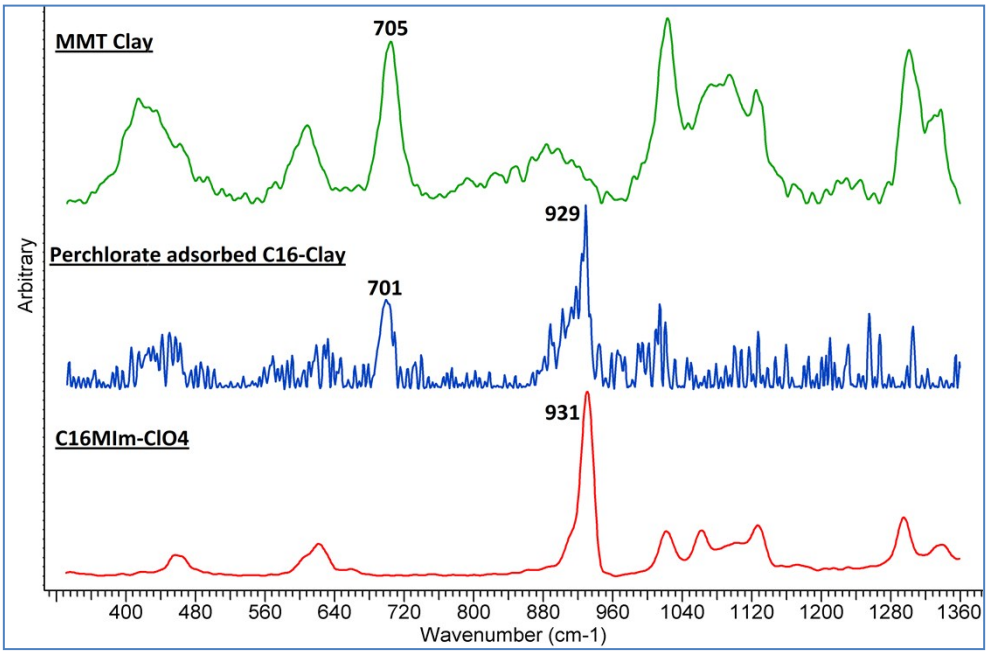
Perchlorate uptake shows R_L in the range of 0.82 to 0.19 for initial concentrations ranging from 50 mg/L to 1000 mg/L, indicating that the adsorption process is favourable. Saturated perchlorate uptake Q_o from the plot was 18.9 mg/g and experimental value was 15.6 mg/g for C16-clay.

Part-V : pseudo first order kinetic plot for C16-Clay

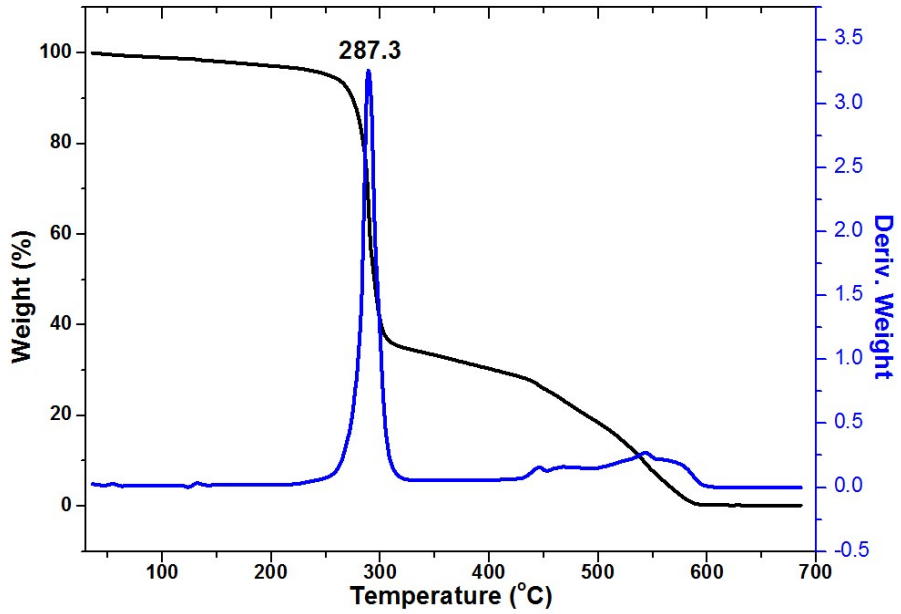


Part-VI : Evidence of C16MIm-ClO_4 formation in the clay layer

Clay shows a characteristic vibration of Si-O_b-Si at 705 cm^{-1} (O_b- bridging oxygen atoms that connects the SiO_4 tetrahedra which makes up the layers in clay). The characteristic peak of perchlorate anion at 931 cm^{-1} is seen in C16MImClO_4, the predicted product on adsorption in the clay gallery. Raman spectra of perchlorate adsorbed C16-Clay, shows the presence of characteristic peaks due to Si-O_b-Si and ClO_4^- with a peak shift. i.e. the peak due to Si-O_b-Si at 705 cm^{-1} shifted to 701 cm^{-1} indicating the change in inter gallery spacing and the peak due to ClO_4^- at 931 cm^{-1} is downshifted to 929 cm^{-1}.



Part-VII : TG/DTG of C16MIm-ClO_4



Part-VIII : Activation Energy by Kissinger Method

KAS is a multiple heating rate method and we have selected heating rate of 5, 10 and 15 ^{o}C/min. KAS method is based on the following eqn.

$$ln\frac{\beta}{T_\alpha^{\,2}} = ln[\frac{AR}{g(\alpha)E_a})] - \frac{E_a}{RT_\alpha}$$

Where β is the heating rate, T_α is the temperature in Kelvin corresponding to a fixed degree of conversion α, A is the pre-exponential factor, R is the gas constant, E_a is the activation energy at a given degree of conversion and g(α) is the integral form of kinetic model function. E_a for a given degree of conversion is obtained from the slope of the linear fit of the plot $ln\frac{\beta}{T_\alpha^{\,2}}$ versus $1/T_\alpha$.

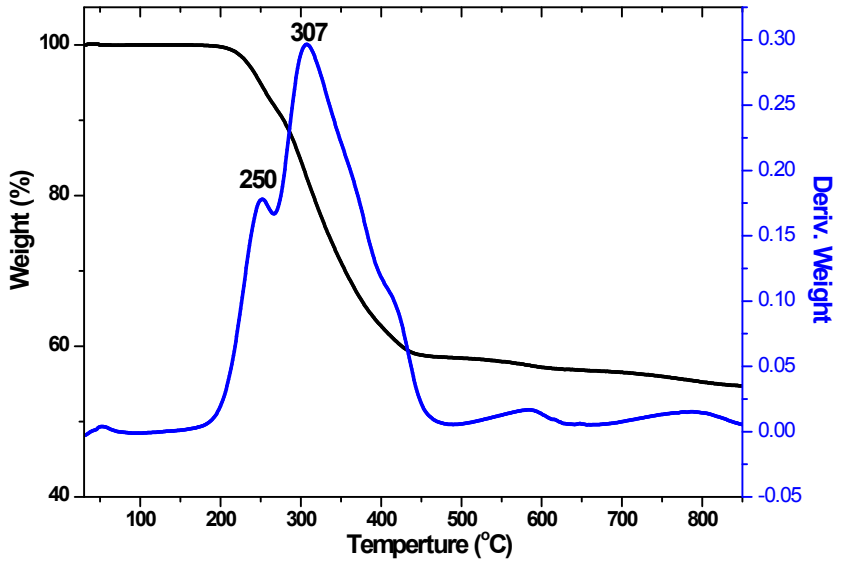
T_α (^{o}C)	T_α (K)	β	T_α^2	$\beta/T_\alpha 2$	$1/T_\alpha$	$\ln(\beta/T_\alpha 2)$
278.3	551.3	5	303931.7	1.65E-05	0.001814	-11.0151
287.3	560.3	10	313936.1	3.19E-05	0.001785	-10.3544
289.1	562.1	15	315956.4	4.75E-05	0.001779	-9.95531

E_a = 27.893* 8.314

= <u>231.9 kJ/mol</u>

Part-IX : TG/DTG of Commercial Clays

(a) Benzyldimethyldodecylammonium modified Montmorillonite Clay



(b) Dimethyldioctadecylammonium (125 meq/100 g of clay)modified Montmorillonite Clay