SUPRAMOLECULAR COMPOSITE MATERIALS FROM CELLULOSE, CHITOSAN AND CYCLODEXTRIN: FACILE PREPARATION AND THEIR SELECTIVE INCLUSION COMPLEX FORMATION WITH ENDOCRINE DISRUPTORS

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SUPPORTING INFORMATION

Analysis of Kinetic Data

The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to evaluate the adsorption kinetics of different polychlorophenols and BPA and to quantify the extent of uptake in the adsorption process

Pseudo-first-order kinetic model

The linear form of Lagergren's pseudo-first-order equation is given as:[1]

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad \text{[SI-1]}$$

where q_t and q_e are the amount of pollutant adsorbed at time t and at equilibrium (mg g^{-1}) respectively and k_1 (min^{-1}) is the pseudo first order rate constant calculated from the slope of the linear plot of ln ($q_e - q_t$) versus t.

Pseudo-second-order kinetic model

According to the Ho model, the rate of pseudo second order reaction may be dependent on the amount of species on the surface of the sorbent and the amount of species sorbed at equilibrium. The equilibrium sorption capacity, q_e, is dependent on factors such as temperature, initial concentration and the nature of solute-sorbent interactions. The linear expression for the Ho model can be represented as follows:[1]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad [SI-2]$$

where k_2 is the pseudo-second order rate constant of sorption (g/mg.min), q_e is the amount of analyte adsorbed at equilibrium (mg/g), q_t is the amount of analyte adsorbed at any time t (mg/g). If the initial adsorption rate h is

$$h = k_2 q_e^{2} \qquad \text{[SI-3]}$$

Then Eq SI-2 can be rearranged as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad \text{[SI-4]}$$

A linear plot can be obtained by plotting t/q_t against t. q_e and h, can obtained from the slope and intercept; k_2 can be calculated from h and q_e according to Eq SI-3.

Intra-particle diffusion model

The intra-particle diffusion equation is given as follows:[2,3]

$$q_t = k_i t^{0.5} + I \qquad \text{[SI-5]}$$

where k_i (mg g^{-1} $min^{-0.5}$) is the intra-particle diffusion rate constant and *I* (mg g^{-1}) is a constant that gives the information regarding the thickness of the boundary layer[2,3]. According to this model, if the plot of qt versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion, while, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process.

Analysis of Adsorption isotherms

Different isotherm models have been developed for describing sorption equilibrium. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were used in the present study.

Langmuir isotherm. The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules and is commonly expressed as (Langmuir, 1916):[4]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad \text{[SI-6]}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, q_m (mg g^{-1}) is the maximum adsorption capacity, and K_L (L mg^{-1}) is the adsorption equilibrium constant. The constants K_L and q_m can be determined from the slope and intercept of the plot between C_e/q_e and C_e.

Freundlich isotherm. The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as (Freundlich, 1906):[5]

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad \text{[SI-7]}$$

where q_e (mg g^{-1}) is the equilibrium concentration on adsorbent, C_e (mg L^{-1}) is the equilibrium concentration in solution, K_F (mg g^{-1}) (L $g^{-1})^{1/n}$ is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_F and 1/n are calculated from the intercept and slope of the straight line of the plot log q_e versus log C_e. n value is known to be a measure of the favorability of the sorption process.[6] A value between 1 and 10 is known to represent a favorable sorption.

Dubinin–Radushkevich (D–R) isotherm. The Dubinin–Radushkevich (D–R) isotherm model envisages about the heterogeneity of the surface energies and has the following formulation:[7]

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad \text{[SI-8]}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad \text{[SI-9]}$$

where q_m (mg g^{-1}) is the maximum adsorption capacity, β ($mmol^2$ J^{-2}) is a coefficient related to the mean free energy of adsorption, ε (J $mmol^{-1}$) is the Polanyi potential, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and C_e (mg L^{-1}) is the equilibrium concentration. The D–R constants q_m and β can be determined from the intercept and slope of the plot between ln q_e and ε^2.

The constant β in the D-R isotherm model is known to relate to the mean free energy E (KJ mol^{-1}) of the sorption process per mole of the analyte which in turn can give information about the sorption mechanism. E can be calculated using the equation 1 below.[8]

$$E = \frac{1}{\sqrt{2\beta}} \qquad \text{[SI-10]}$$

According to this theory, the adsorption process is supposed to proceed via chemisorb if E is between 8 and 16 $KJmol^{-1}$whereas for values less than 8 $KJmol^{-1}$, the sorption process is often governed by physical nature[8].

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Table SI-1. Kinetic parameters for adsorption of Chlorophenols and BPA onto 100% CS film

		Pseudo first-order kinetic model				Pseudo second-order kinetic model			
Analyte	**qe, expt (M/g)**	**qe(M/g)**	**K_1 (min^{-1})**	**R^2**	**MSC**	**qe(M/g)**	**K_2 (M^{-1} min^{-1})**	**R^2**	**MSC**
2-ClPh	1.30E-03	1.48E-03	0.089	0.9865	3.305	1.32E-03	385.9	0.9998	8.02
3-ClPh	1.62E-03	3.25E-03	0.050	0.9745	2.669	1.68E-03	133.5	0.9960	5.21
4-ClPh	1.64E-03	6.49E-04	0.051	0.9849	2.861	1.66E-03	214.6	0.9996	7.52
3,4 Di-ClPh	2.23E-03	7.23E-04	0.048	0.8769	0.761	2.27E-03	169.8	0.9999	8.72
2,4,5 Tri-ClPh	1.05E-02	9.90E-03	0.016	0.9843	3.917	1.20E-02	2.1	0.9991	6.60
BPA	1.74E-03	5.88E-04	0.040	0.8947	1.680	1.80E-03	168.3	0.9995	7.24

Table SI-2. Kinetic parameters for adsorption of Chlorophenols and BPA onto 100% CEL film

		Pseudo first-order kinetic model				**Pseudo second-order kinetic model**			
Analyte	**qe, expt (M/g)**	**qe(M/g)**	**K_1 (min^{-1})**	**R^2**	**MSC**	**qe(M/g)**	**K_2 (M^{-1} min^{-1})**	**R^2**	**MSC**
2-ClPh	4.11E-04	1.45E-04	0.029	0.6469	0.041	3.93E-04	702.3	0.9871	3.95
3-ClPh	3.19E-04	4.95E-04	0.044	0.9747	2.678	3.20E-04	293.8	0.9822	3.72
4-ClPh	5.79E-04	1.69E-04	0.055	0.9559	1.788	5.81E-04	2054.2	0.9999	9.13
3,4 Di-ClPh	7.98E-04	9.44E-04	0.142	0.9665	2.397	8.19E-04	315.6	0.9996	7.47
2,4,5 Tri-ClPh	1.87E-03	1.01E-03	0.011	0.9714	3.287	1.95E-03	25.4	0.9967	5.32
BPA	7.27E-04	4.62E-04	0.014	0.9715	3.156	8.05E-04	78.9	0.9911	4.39

Table SI-3. Kinetic Parameters for Adsorption of Chlorophenols and BPA onto 50:50 CS:β-TCD Composite Material

		Pseudo first-order kinetic model				***Pseudo second-order kinetic model***			
Analyte	**q_e, expt (M/g)**	**q_e(M/g)**	**K_1 (min^{-1})**	**R^2**	**MSC**	**q_e(M/g)**	**K_2 (M^{-1} min^{-1})**	**R^2**	**MSC**
2-ClPh	7.30E-04	7.76E-04	0.058	0.9981	5.249	7.58E-04	268.4	0.9967	5.32
3-ClPh	1.22E-03	1.96E-03	0.041	0.9936	4.046	1.25E-03	118.6	0.9934	4.71
4-ClPh	9.64E-04	4.79E-03	0.119	0.9567	1.806	8.99E-04	313.1	0.9957	5.11
3,4 Di-ClPh	1.87E-03	1.45E-03	0.055	0.9636	2.647	1.99E-03	57.1	0.9978	5.77
2,4,5 Tri-ClPh	7.45E-03	7.92E-03	0.015	0.9548	2.861	8.84E-03	2.1	0.9996	7.41
BPA	1.42E-03	1.12E-03	0.028	0.9782	3.381	1.59E-03	37.6	0.9994	7.11

Table SI-4. Kinetic parameters for adsorption of Chlorophenols and BPA onto 50:50 CEL:β-TCD Composite Material

		Pseudo first-order kinetic model				**Pseudo second-order kinetic model**			
Analyte	**q_e, expt (M/g)**	**q_e(M/g)**	**K_1 (min^{-1})**	**R^2**	**MSC**	**q_e(M/g)**	**K_2 (M^{-1} min^{-1})**	**R^2**	**MSC**
2-ClPh	1.24E-03	8.70E-04	0.041	0.8960	1.597	1.30E-03	100.2	0.9975	5.57
3-ClPh	9.26E-04	5.55E-04	0.020	0.9410	2.259	9.87E-04	77.9	0.9964	5.33
4-ClPh	1.33E-03	1.04E-03	0.028	0.8161	1.122	1.41E-03	58.0	0.9993	6.93
3,4 Di-ClPh	8.71E-04	5.28E-04	0.047	0.9422	2.185	9.12E-04	160.6	0.9992	6.84
2,4,5 Tri-ClPh	1.92E-03	1.31E-03	0.021	0.9867	3.957	2.00E-03	33.2	0.9995	7.26
BPA	1.28E-03	7.93E-04	0.030	0.9291	2.147	1.34E-03	65.5	0.9987	6.28

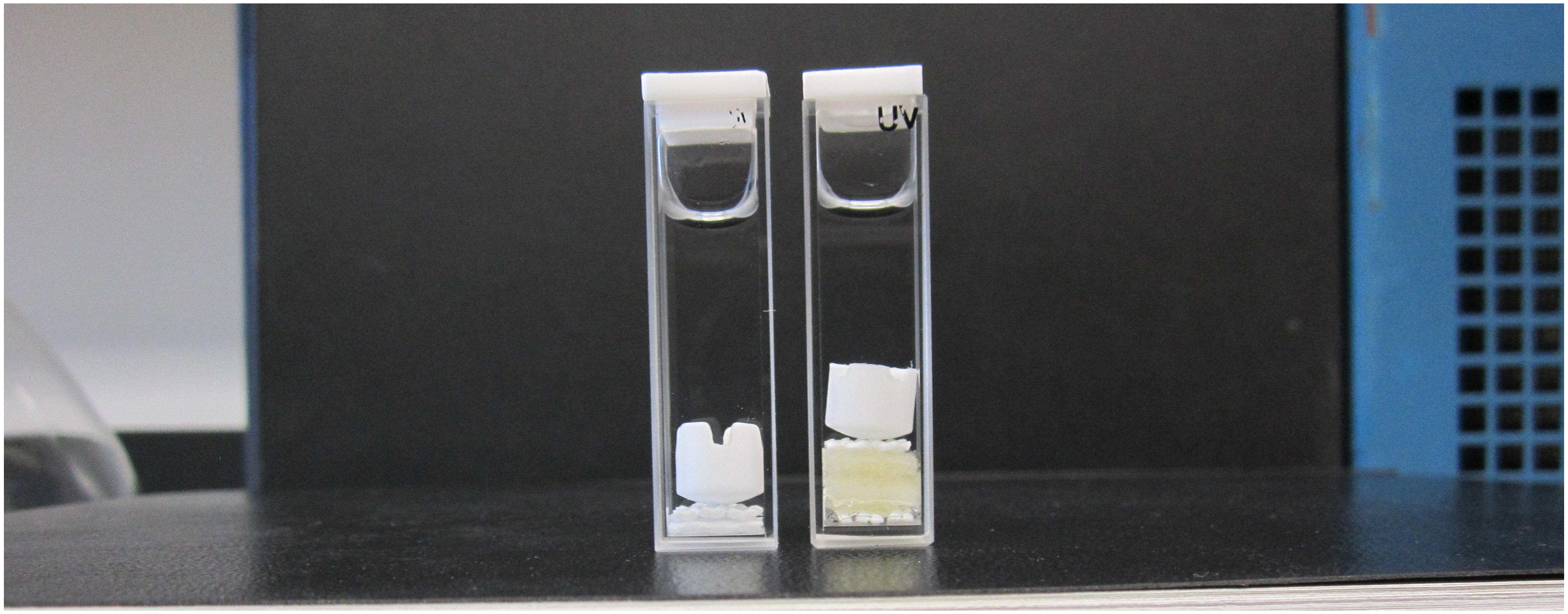


Figure SI-1. Photograph of two cells (sample cell (right) and blank (left) used to measure adsorption kinetics of the pollutants by the composite materials. See text for detail description.

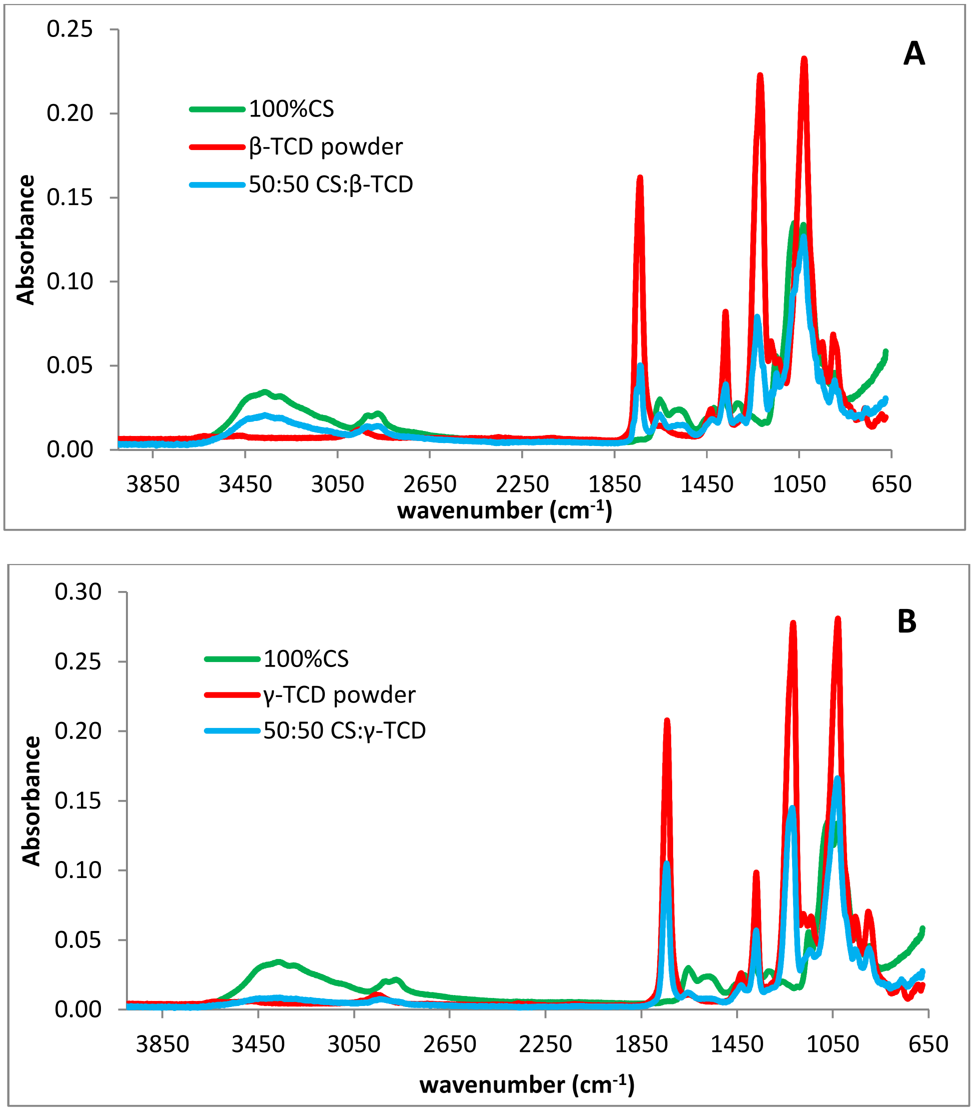


Figure SI-2. FTIR spectra of (A) 100%CS, β-TCD powder and 50:50 CS:β-TCD and (B) 100%CS, γ-TCD and 50:50 CS:γ-TCD

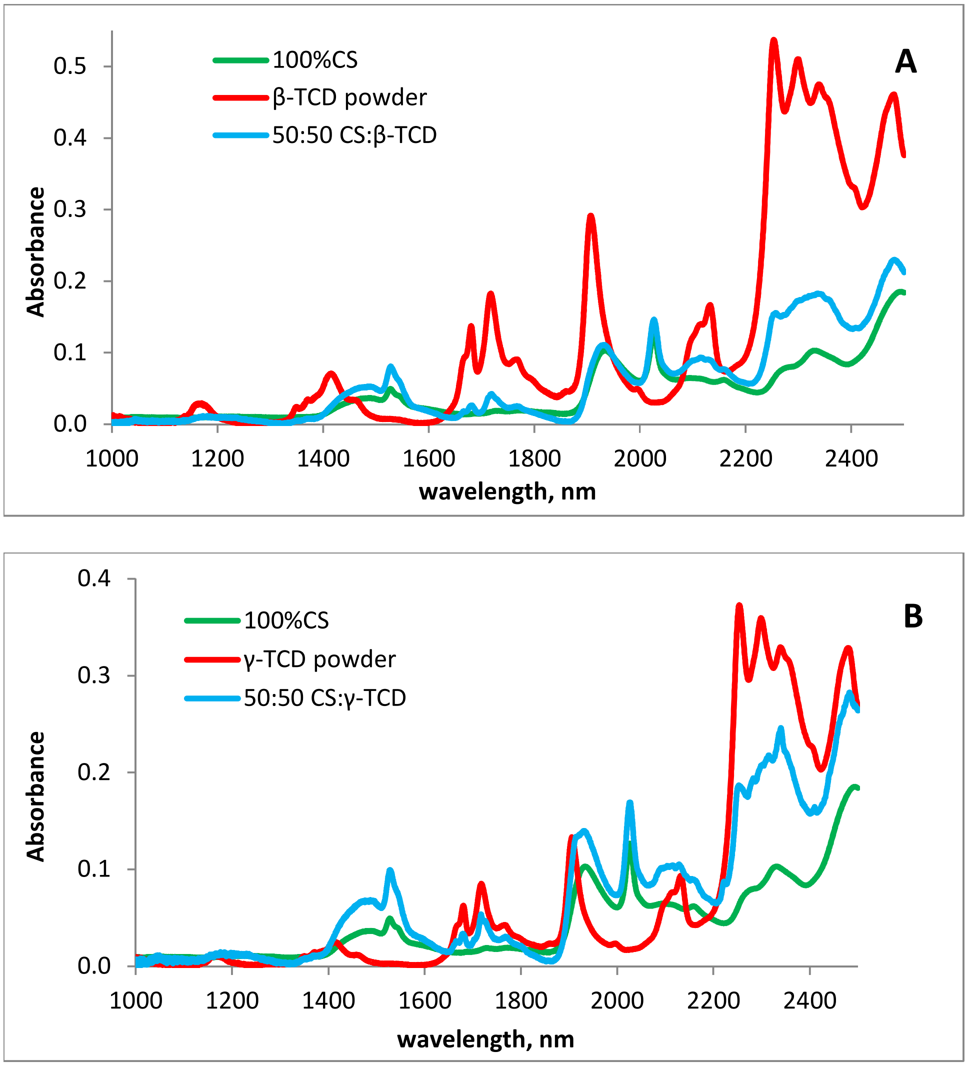


Figure SI-3. NIR spectra of (A) 100%CS, β-TCD powder and 50:50 CS:β-TCD and (B) 100%CS, γ-TCD and 50:50 CS:γ-TCD.

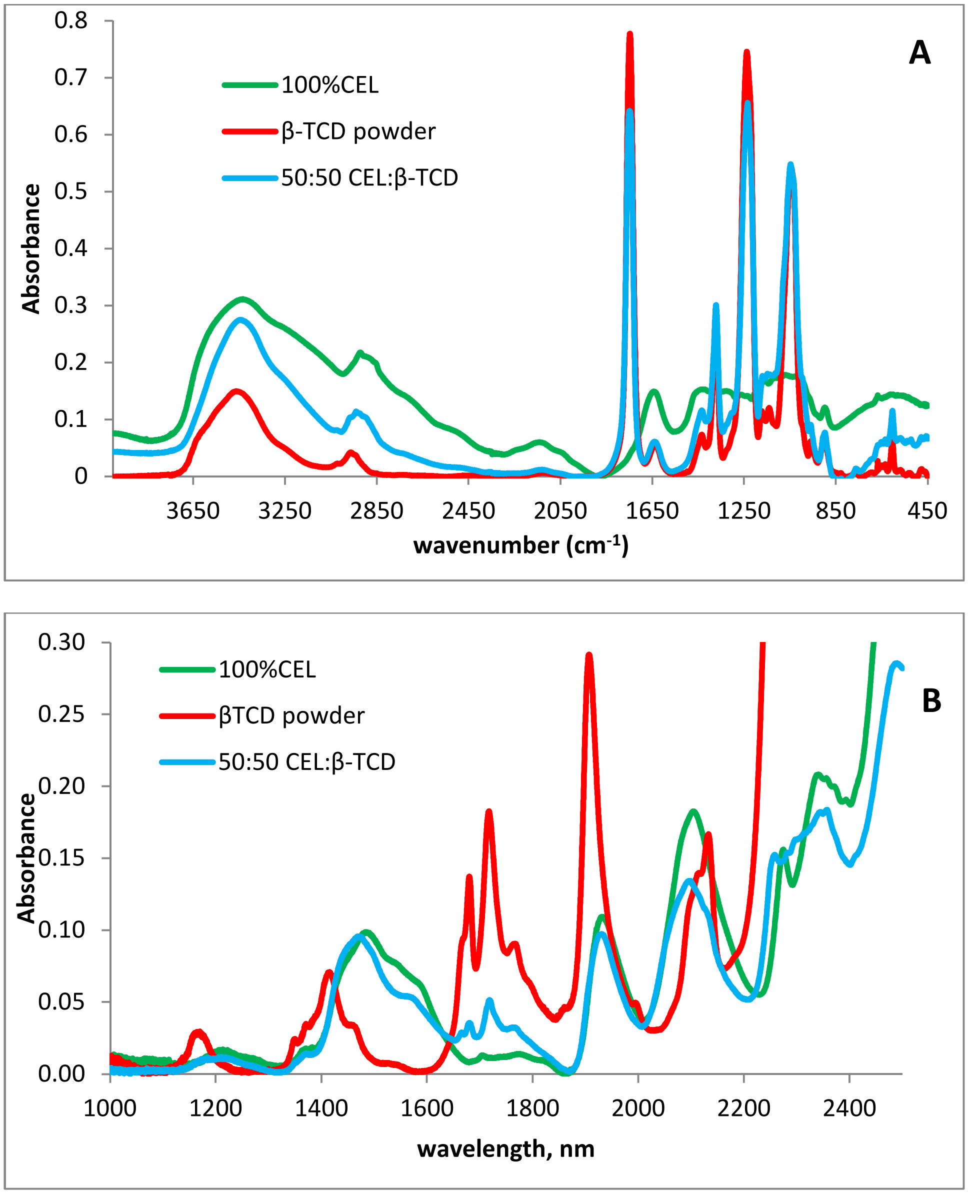
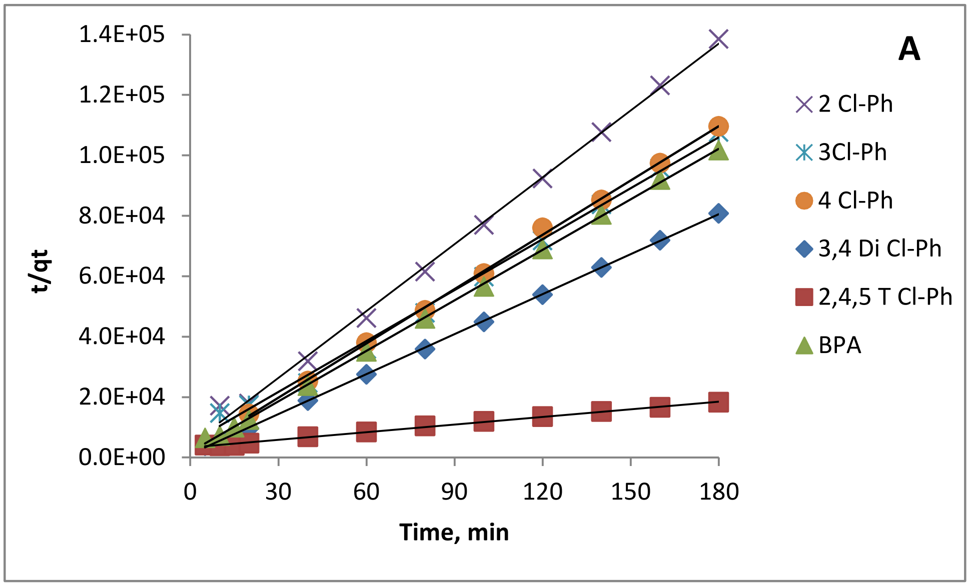


Figure SI-4. A) FT-IR and B) NIR spectra of CEL/TCD composite materials.



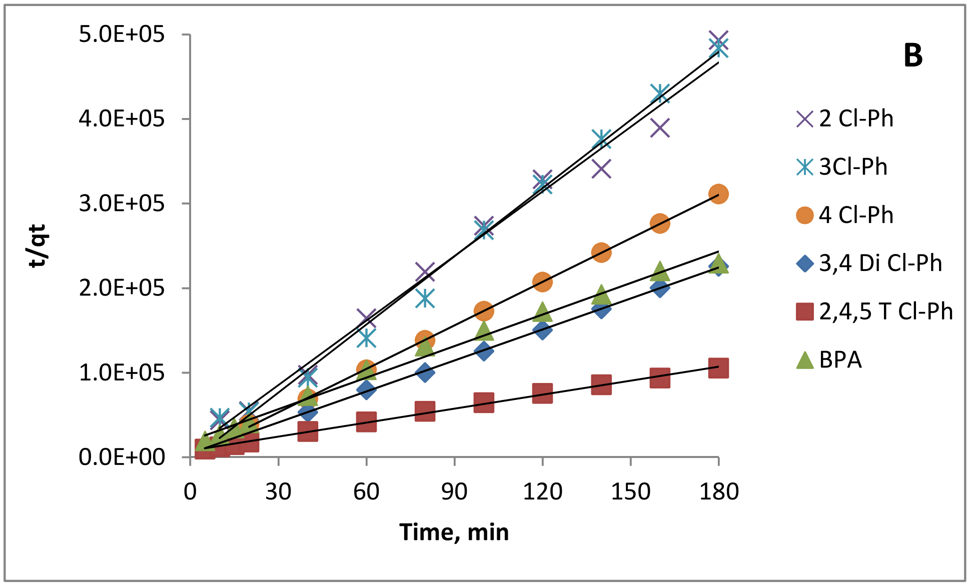


Figure SI-5: Pseudo second order linear plots for A) 100%CS and B) 100%CEL composite materials

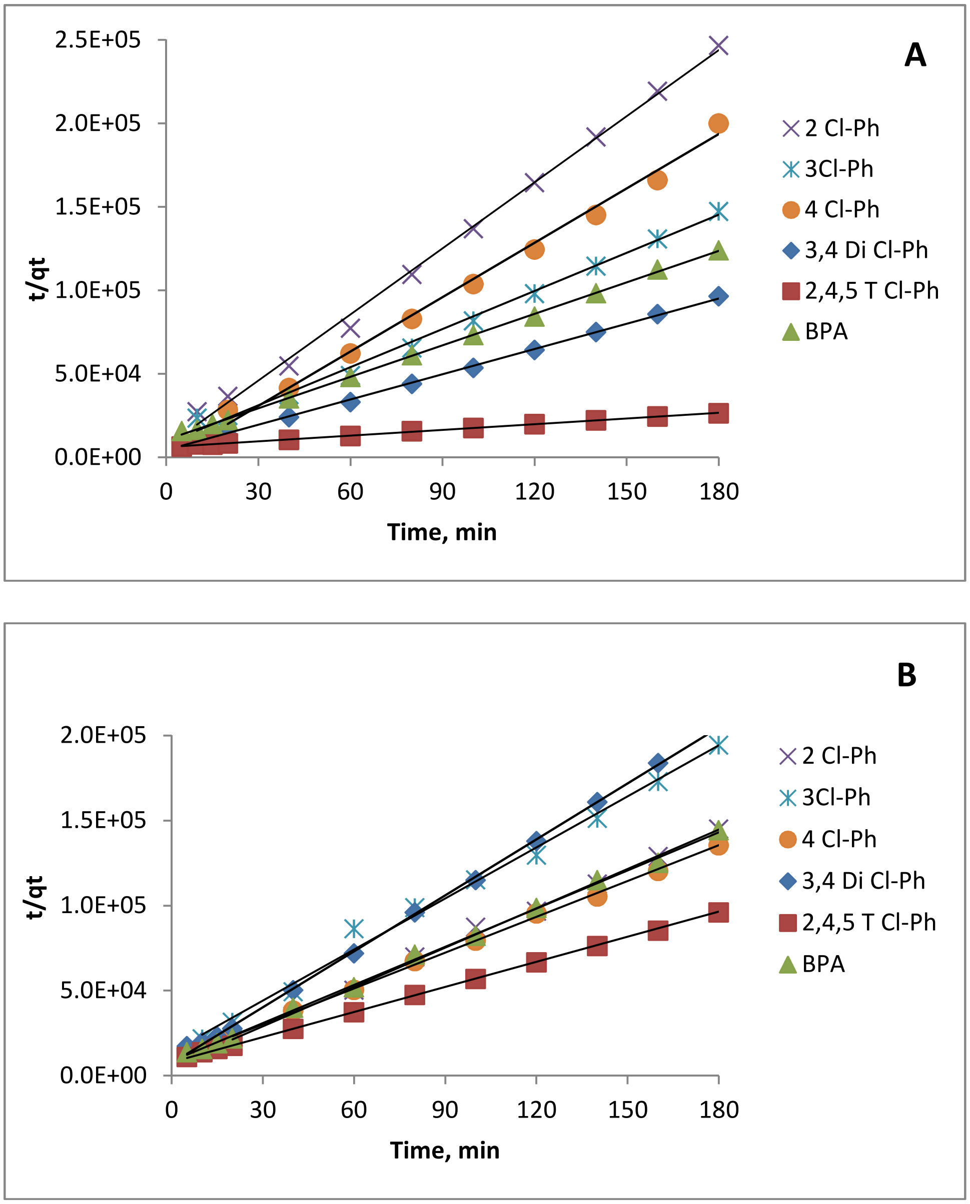


Figure SI-6: Pseudo second order linear plots for A) 50:50 CS:β-TCD and B) 50:50 CEL:β-TCD composite materials