

Removal of Azo Dyes Orange II and Reactive Black 5 from Aqueous Solutions by Adsorption on Chitosan Beads Modified with Choline Chloride: Urea Deep Eutectic Solvent and FeO

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Supplementary information

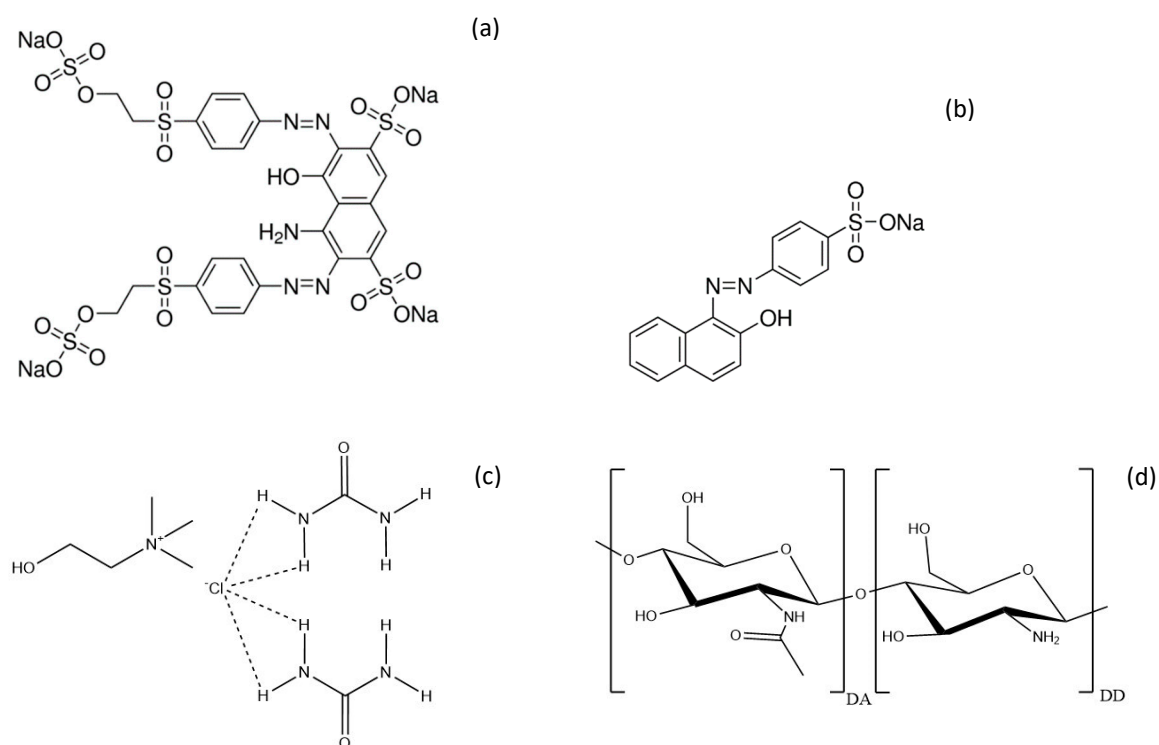


Figure S1: Structures of the dyes RB5 (a) and OII (b), the proposed structure for choline chloride:urea 1:2 eutectic mixture (Longo and Craveiro, 2018) (c), and chitosan structure (d).

Table S1: Compounds used in this study and specifications -(chemical name, supplier, purity provided by supplier and CAS number).

Chemical name	Supplier	Purity	CAS number
Chitosan	Acros Organics	-	9012-76-4
Choline chloride	Acros Organics	99%	67-48-1
Urea	Labkem	98-102%	57-13-6
Reactive Black 5	Sigma Aldrich	50%	17095-24-8
Orange II	Acros Organics	100%	633-96-5
NaOH	Fisher Scientific	≥ 97%	1310-73-2
FeCl ₃ ·6H ₂ O	Honeywell, Fluka	97%	10025-77-1

FeCl ₂ ·4H ₂ O	Honeywell, Fluka	≥ 99%	13478-10-9
EDTA	Sigma-Aldrich	≥ 97.0%	6381-92-6
DMSO	Merck	≥ 99.9%	67-68-5
Ethanol absolute	Scharlau	99.9%	64-17-5
Acetic acid glacial	Labkem	99.8%	64-19-7
Sulfuric acid	Labkem	> 95%	7664-93-9
Hydrochloric acid	VWR	37%	7647-01-0
Ammonium hydroxide	Sigma-Aldrich	25% NH ₃ basis	1336-21-6
NaCl	Merck		7647-14-5

2.5. Adsorption isotherm

Langmuir, Freundlich and Temkin isotherm models have been used to study the affinity, trend, and adsorption mechanism of the dye towards sorbent. Equations S1 – S3 represent the mentioned models, respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (S1)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (S2)$$

$$q_e = B \ln K_T + B \ln C_e \quad (S3)$$

C_e is concentration of adsorbate at equilibrium (final concentration of solute (mg/L)/liquid-phase concentrations of dye at equilibrium); q_e is the amount of dye adsorbed at equilibrium (mg/g); K_L (L/mg or L/mol) is the Langmuir constant related to adsorption capacity (mg g⁻¹), which can be correlated with the variation of the suitable area and porosity of the adsorbent, implying that large surface area and pore volume will result in higher adsorption capacity. It is calculated from the intercept of the different straight lines (linear plot of C_e/q_e vs. C_e) at different temperatures. K_F , Freundlich constant (L/g), is related to the adsorption capacity, and $1/n$ is a function of the strength of adsorption, indicating the affinity between the adsorbent and adsorbate. A value of $1/n$ below unity would imply a chemical process, and above unity, a physical process; it also indicates the heterogeneity of the surface: the more heterogeneous the surface, the more the $1/n$ value approaches zero (Vinay 2014). K_T is Temkin isotherm constant (L g⁻¹). T (K) is the absolute temperature. R represents the universal gas constant (8.314 J mol⁻¹K⁻¹). $B = RT/b$ is a constant which is related to the heat of adsorption (J mol⁻¹); q_m is the maximum amount of dye adsorbed (mg/g) / maximum monolayer adsorption capacity (calculated from the slope of the different straight lines at different temperatures).

The value of the dimensionless constant called the separation factor R_L , based on the following equation (S4) could be used to predict the degree of favourability of the Langmuir isotherm for equilibrium data:

$$R_L = \frac{1}{1 + K_L C_{max}} \quad (S4)$$

K_L is Langmuir's constant and C_{max} is the highest initial dye concentration. R_L values indicate the adsorption to be unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$, and irreversible when $R_L = 0$.

2.6 Adsorption kinetics models:

The adsorption kinetic models used were pseudo-first and pseudo-second order models (Eq. S5 and S6, respectively), Elovich kinetic model (Eq. S7) and intraparticle diffusion (Eq. S8)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (S5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (S6)$$

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (S7)$$

$$q_t = k_3 t^{\frac{1}{2}} + I \quad (S8)$$

Where: q_e and q_t are the adsorbed dye at equilibrium and time t ; K_1 (min^{-1}) denotes the pseudo-first-order rate constant, K_2 ($\text{g mg}^{-1}\text{min}^{-1}$) denotes the pseudo-second-order rate constant; K_3 symbolizes the intraparticle propagation rate constant; I is a constant and is associated with the boundary layer thickness (Soliman et al. 2021); α implies the adsorption rate at time = 0 min; β represents the coverage extent.

Adsorption experiments

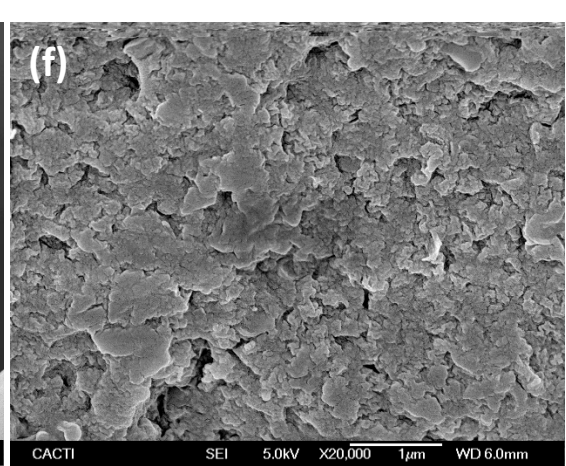
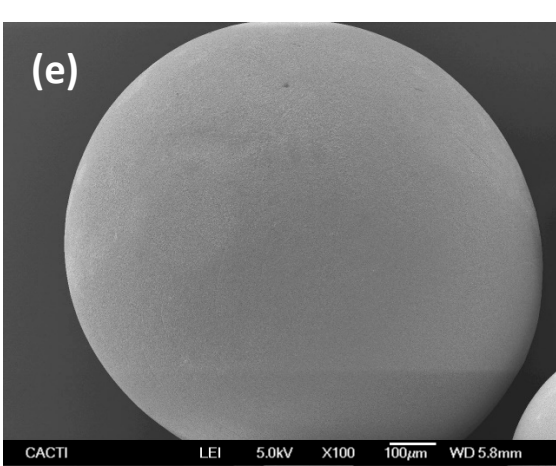
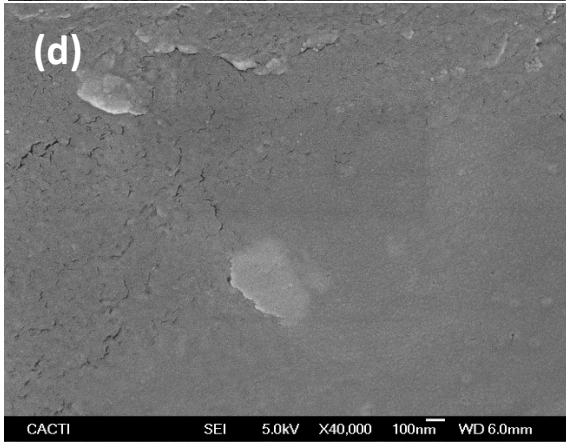
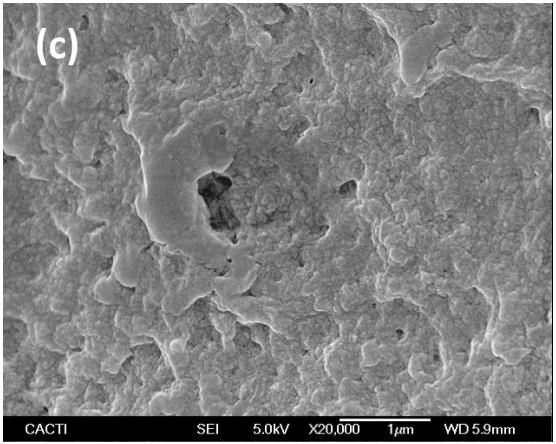
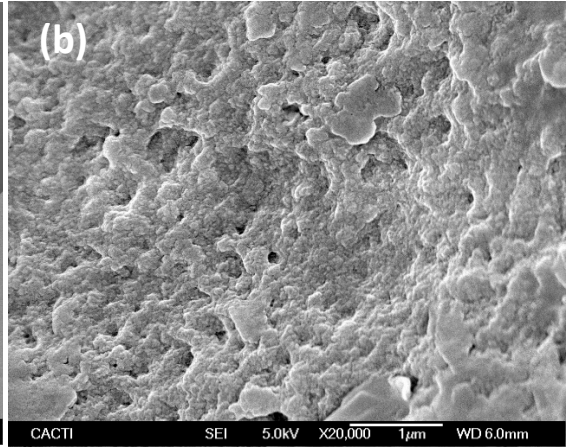
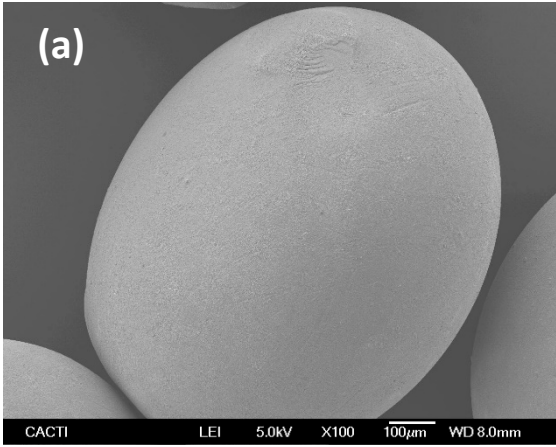
The data were presented as mean values \pm standard error of the mean calculated as follows (eq S9):

$$\text{Standard error of the mean} = \frac{\text{standard deviation}}{\sqrt{n}} \quad (S9)$$

Where n is the sample size (number of individual observations) and standard deviation is calculated as follows (eq S10):

$$\text{Standard deviation} = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \quad (S10)$$

Where \bar{x} is the mean value of the n individual observations (x).



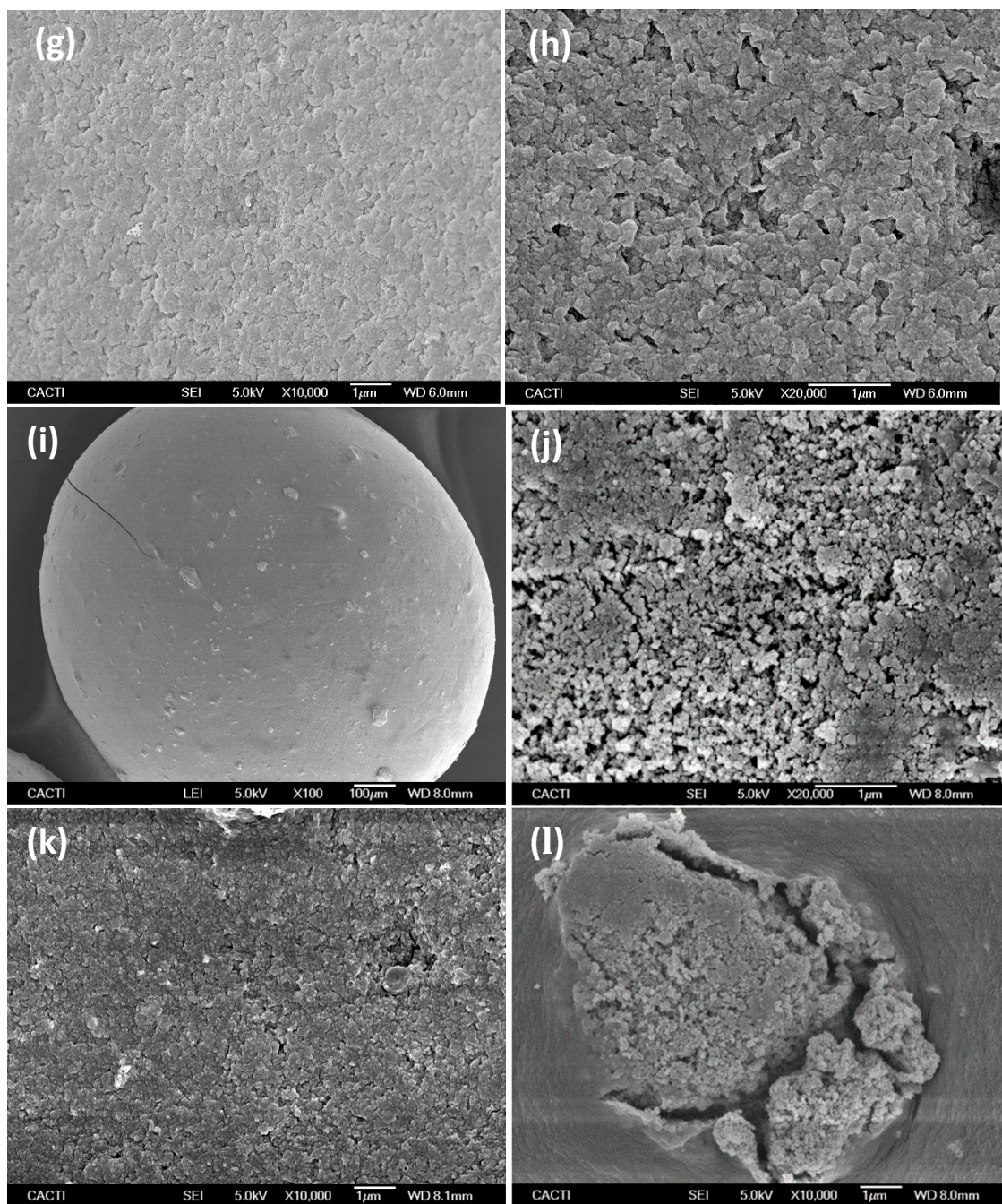


Figure S2: Images of the surface of the adsorbents obtained by scanning electron microscopy (SEM): (a-d) unmodified chitosan beads (un-Ch), (e-h) chitosan-DES beads (Ch-DES) and (i-l) chitosan-FeO-DES beads (Ch-FeO-DES).

Table S2: the main functional groups observed in the individual components of un-Ch and Ch-DES beads by FTIR analysis.

Compound	Region (cm ⁻¹)	Functional groups	Comments
Chitosan			
	3294-3352	N-H and O-H	N-H and O-H Stretching vibration
	2875-2920	C-H	CH, CH ₂ and CH ₃

	1025, 1059	C-O-C and C-OH	Stretching vibrations
	1592, 1645	N-H, C=O	N-H bending, C=O stretching vibration Amide I (CONH ₂) and II (N-H) Ionic cross-linking (acetic acid)
Choline chloride			
	3006-3026 3219	N-H	Stretching vibration
	1413-1481	C-H	bending of aliphatic C-H groups
	1480-1390	N-H	N-H vibrations in quaternary ammonium groups
	1200-880	C-N	asymmetric C-N stretching vibration
	2854-2951	C-H	Stretching vibrations of C-H in CH ₂ and CH ₃
Urea			
	3425-3326	N-H	asymmetric N-H stretching vibration of NH ₂ groups
	3228-3254	N-H	symmetric N-H stretching vibration of NH ₂ groups
	1674	C=O	stretching vibration of C=O in amide group (CONH ₂) (amide I band)
	1587	N-H	bending of N-H bond in NH ₂ groups (amide II band)
	1459, 1147	N-C-N	asymmetric and symmetric stretching vibration of N-C-N bonds
DES ChCl:Urea (1:2)			
	3500-3000		Broadening of the bands due to hydrogen bonds between acceptor and donor
	3388 and 3314	N-H and O-H	stretching vibration of N-H and O-H bonds
	3256 and 3187	N-H	stretching vibration of N-H
	1660	C=O	Shift to lower frequencies (C=O stretching vibration band of amide group CONH)

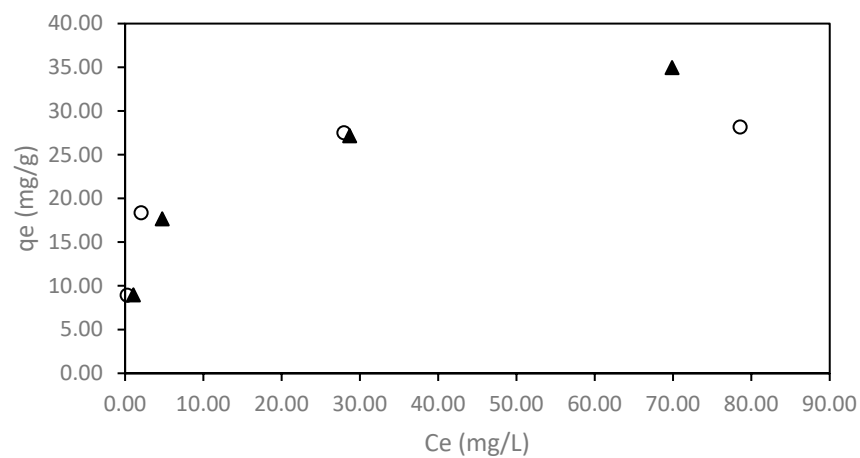


Figure S3. Adsorption isotherms for the adsorption of OII (○) and RB5 (▲) by 15 mg of Ch-DES beads at 298K.

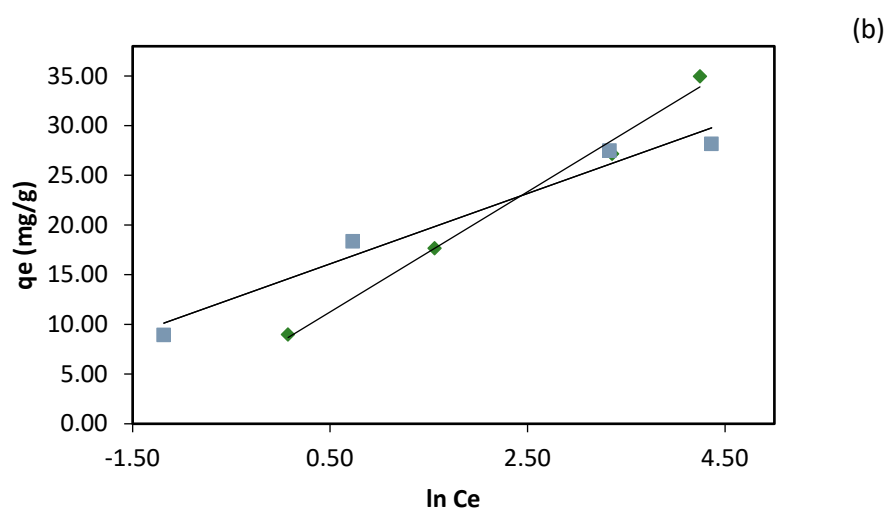
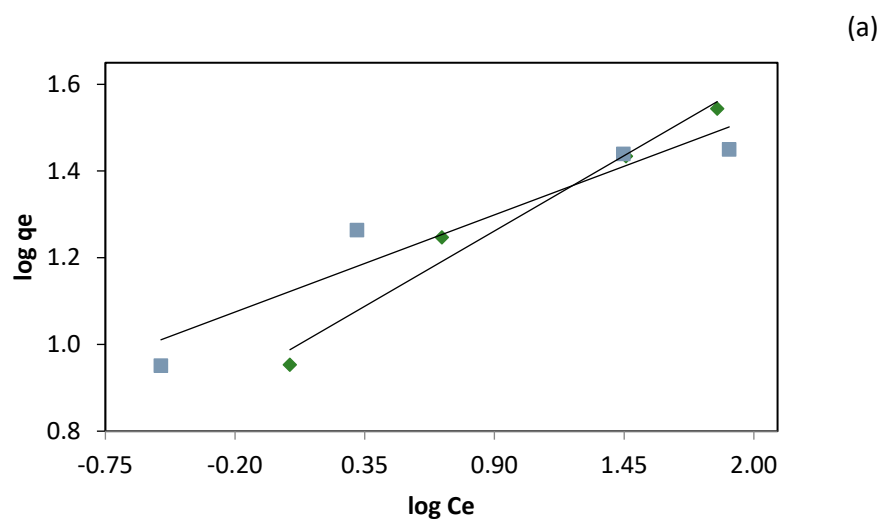


Figure S4: Freundlich (a) and Temkin (b) isotherms for the adsorption of OII (◆) and RB5 (■) by 15 mg of Ch-DES beads at 298 K.

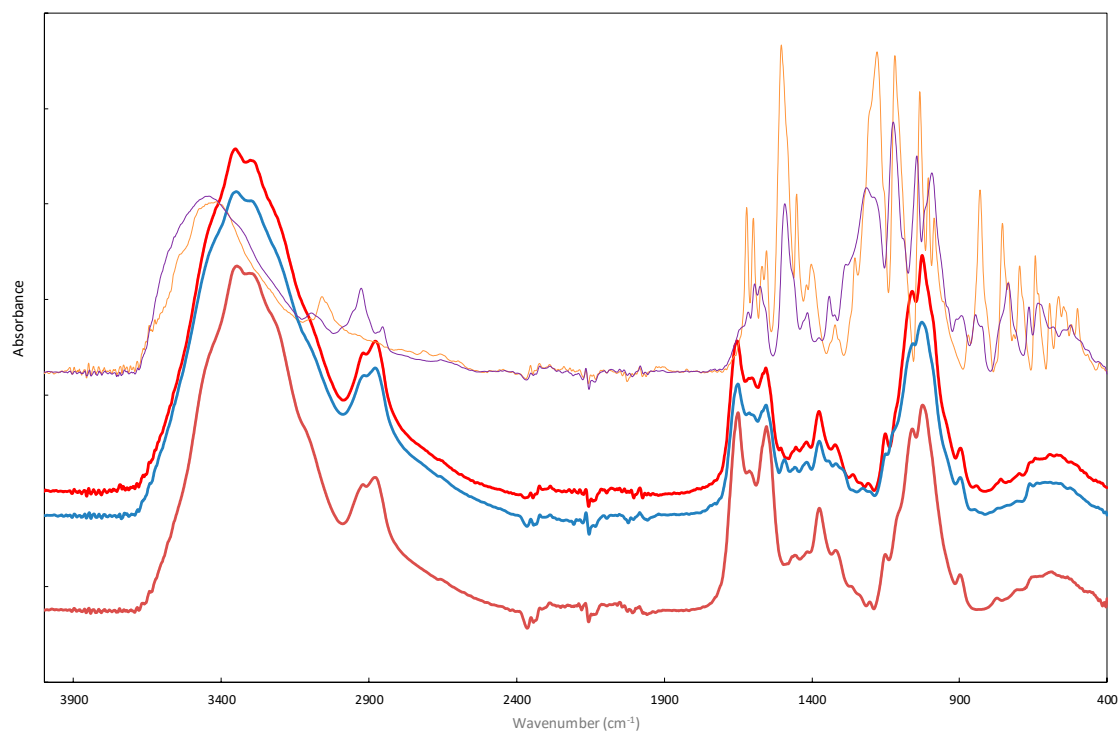


Figure S5: Fourier transform infrared (FTIR) spectra obtained after the adsorption of the dye OII onto DES-modified chitosan (— Ch-DES-OII) beads and the dye RB5 onto DES-modified chitosan (— Ch-DES-RB5) beads compared to the spectra of the adsorbent before adsorption (— Ch-DES beads), and the spectra of the dyes OII (—) and RB5 (—).