Electronic Supplementary Information (ESI)

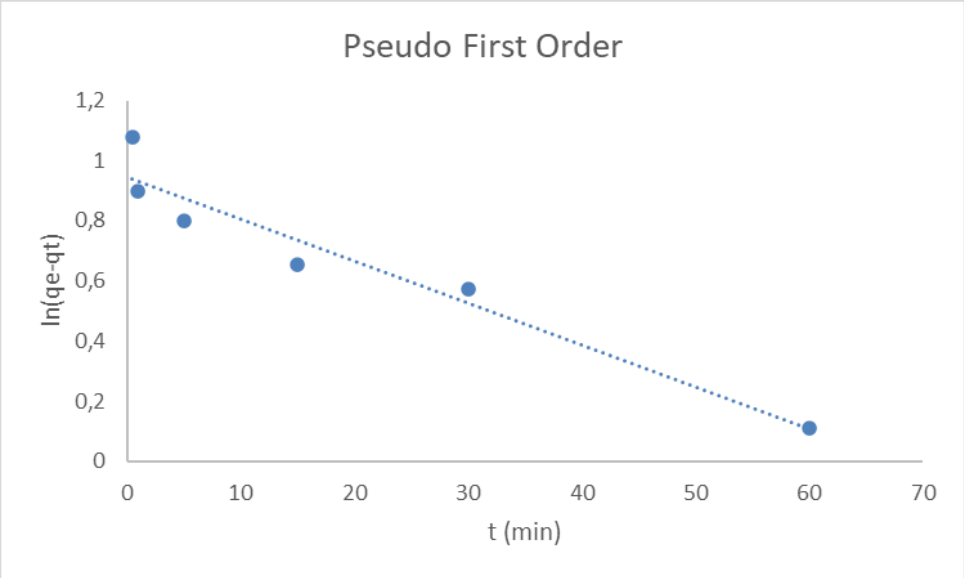
Cellulose Citrate: a Convenient and Reusable Bio-adsorbent for Effective Removal of Methylene Blue Dye from Artificially Contaminated Water

*Fabrizio Olivito,[*1] Vincenzo Algieri,[*1] Antonio Jiritano,[1] Matteo Antonio Tallarida,[1] Antonio Tursi,[2] Paola Costanzo,[1] Loredana Maiuolo[1] and Antonio De Nino[*1]*

Corresponding authors email addresses

fabrizio.olivito@unical.it, vincenzo.algieri@unical.it, denino@unical.it

Adsorption kinetics



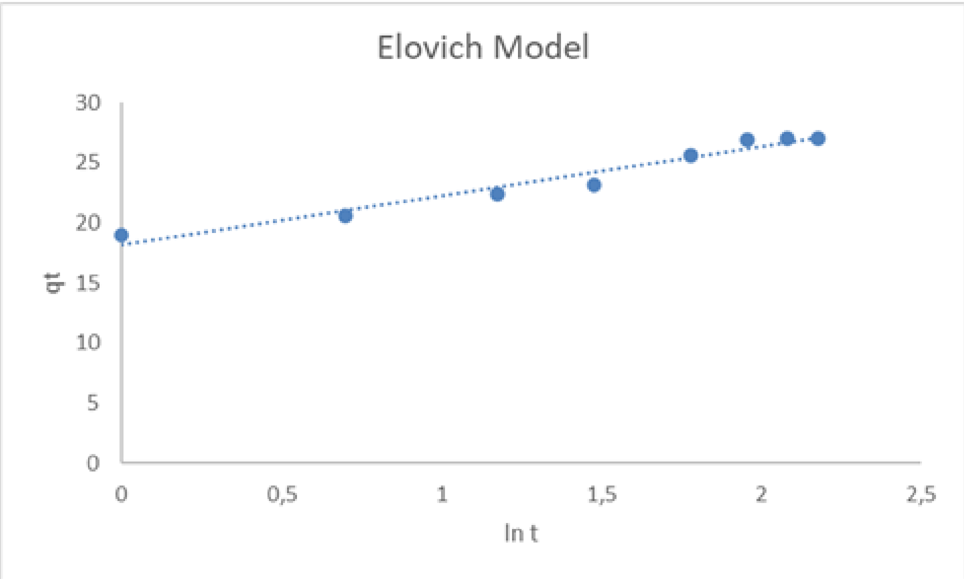
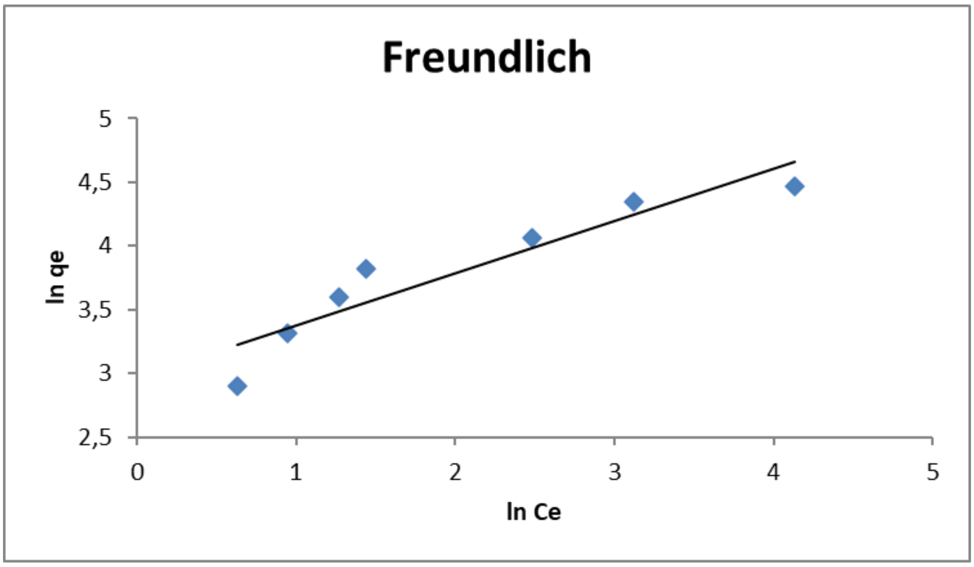


Fig. S1 Pseudo first order and Elovich model plots

Adsorption isotherms



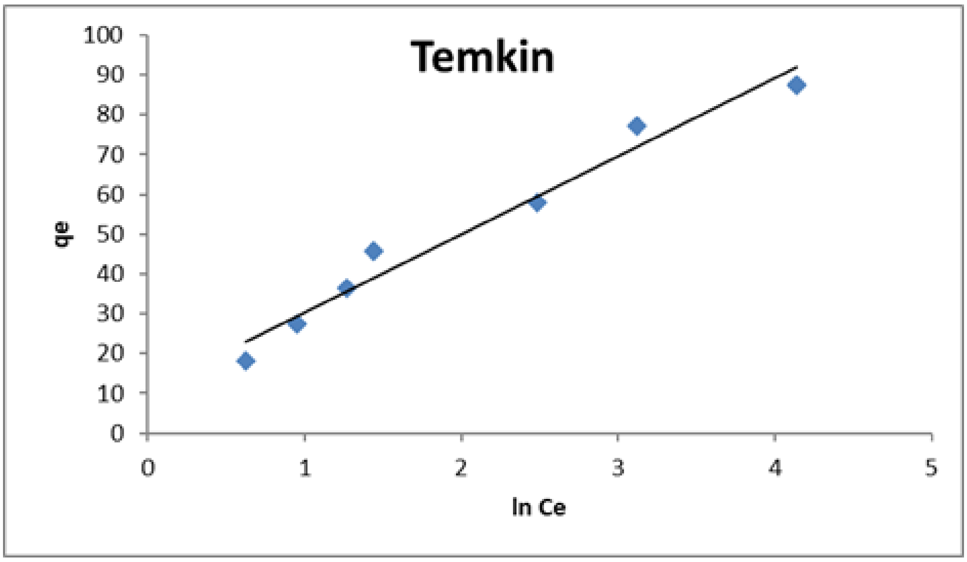


Fig. S2 Freundlich and Temkin isotherms plots

Equations

Different equations used in the study:

$$\text{Pseudo} - \text{first order equation: } ln(q_e - q_t) = lnq_e - k_1 t \quad (1)$$

$$\text{Pseudo} - \text{second order equation: } {}^{t}/_{q_t} = {}^{1}/_{k_2 q_e^2} + ({}^{1}/_{q_e})t \quad (2)$$

$$\text{Elovich equation: } q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt \quad (3)$$

Where, q_e and q_t are the amounts of dye adsorbed on cellulose-citrate (mg/g) at equilibrium and at time t. k_1 (min^{-1}) and k_2 (g/mg/min) are the pseudo-first order rate constant and the pseudo-second-order rate constant. α ($mg\ g^{-1}\ min^{-1}$) is the initial adsorption rate and β ($g\ mg^{-1}$) is the relationship between the degree of surface coverage and the activation energy involved in the chemisorption.

$$\text{van't Hoff equation: } lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (4)$$

where, ΔS^o, ΔH^o and R represent entropy change, enthalpy change and the universal gas constant (8.314 J/mol K) respectively. T (K) is the absolute temperature and K_c (L/g) is the standard thermodynamic equilibrium constant, which is expressed by

$$K_c = \frac{q_e}{C_e} \quad (5)$$

where, q_e is the amount of adsorbed MB dye per unit mass of adsorbent at equilibrium (mg/g) and C_e is the equilibrium aqueous concentration of MB.

Further, the value of the Gibbs free energy change **Δ*G*°** (J/mol) is calculated as:

$$\Delta G^o = -RTlnK_c \quad (6)$$

The negative value of **Δ*G*°** indicates the spontaneity of a chemical reaction.

$$\text{Langmuir isotherm: } \frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \quad (7)$$

$$\text{Freundlich isotherm: } lnq_e = lnk_F + \frac{1}{n} lnC_e \quad (8)$$

$$\text{Tempkin isotherm: } q_e = \beta lnk_T + \beta lnC_e \quad [\text{where, } \beta = RT/b] \quad (9)$$

where the Langmuir constants q_m and k_L represent the maximum adsorption capacity of the adsorbent and the constant energy related to the heat of adsorption, while C_e (mg/L) is the concentration of adsorbate in the liquid phase at equilibrium and q_e (mg/g) is the amount of adsorbate adsorbed on the solid phase at equilibrium. k_F (mg/g) $(L/mg)^{1/n}$ indicates the adsorption capacity, and n reflects the intensity of adsorption according to the Freundlich theory. The constant β(L/mg) is related to the heat of adsorption, k_T (mg/L) is a constant of the Tempkin isotherm, b

(J/mol) is the energy constant of the Tempkin isotherm, R (8.314 J/K mol) is the gas constant and T (K) is the absolute temperature.

One of the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant, separation factor, R_L, defined as follows:

$$R_L = \frac{1}{1 + k_L C_0} \qquad (12)$$

The value of R_L indicates the type of the isotherm; which is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). [1]

In Table S1 R_L values for each used concentration are reported:

Table S1. Values of R_L at different concentrations

C_0	**R_L**
10	0.31
20	0.18
30	0.13
40	0.10
50	0.08
70	0.06
100	0.04
120	0.04
150	0.03

References

[1] Kumari, S., Chauhan, G. S., Ahn, J.-H. *Chem. Eng.* 2016, **304**, 728.