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

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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:

\[
\text{Pseudo – first order equation: } ln(q_e - q_t) = lnq_e - k_1t 
\]  
(1)

\[
\text{Pseudo – second order equation: } \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \left(\frac{1}{q_e}\right)t
\]  
(2)

\[
\text{Elovich equation: } q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t 
\]  
(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. \(\alpha\) (mg g\(^{-1}\) min\(^{-1}\)) is the initial adsorption rate and \(\beta\) (g mg\(^{-1}\)) is the relationship between the degree of surface coverage and the activation energy involved in the chemisorption.

\[
\text{van’t Hoff equation: } lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} 
\]  
(4)

where, \(\Delta S^o\), \(\Delta H^o\) 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

\[
K_c = \frac{q_e}{C_e} 
\]  
(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 \(\Delta G^o\) (J/mol) is calculated as:

\[
\Delta G^o = -RT\ln K_c 
\]  
(6)

The negative value of \(\Delta G^o\) indicates the spontaneity of a chemical reaction.

\[
\text{Langmuir isotherm: } \frac{C_e}{q_e} = \frac{1}{k_Lq_m} + \frac{1}{q_mC_e} 
\]  
(7)

\[
\text{Freundlich isotherm: } lnq_e = lnk_f + \frac{1}{n}lnC_e
\]  
(8)

\[
\text{Tempkin isotherm: } q_e = \beta lnk_f + \beta lnC_e \quad \text{[where, } \beta = RT/b\]  
(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 \(\beta\) (L/mg) is related to the heat of adsorption, \(k_f\) (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:

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

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 ($R_L = 0$).

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

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.31</td>
</tr>
<tr>
<td>20</td>
<td>0.18</td>
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<tr>
<td>30</td>
<td>0.13</td>
</tr>
<tr>
<td>40</td>
<td>0.10</td>
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<tr>
<td>50</td>
<td>0.08</td>
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<tr>
<td>70</td>
<td>0.06</td>
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<tr>
<td>100</td>
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</tr>
<tr>
<td>120</td>
<td>0.04</td>
</tr>
<tr>
<td>150</td>
<td>0.03</td>
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</tbody>
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References