Supporting material

Aqueous Carbofuran Removal Using Slow Pyrolysis Sugarcane Bagasse Biochar-Equilibrium and Fixed-bed Studies

Vineet Vimal, Manvendra Patel and Dinesh Mohan*

School of Environmental Sciences
Jawaharlal Nehru University
New Delhi 110067, India
Email: dm_1967@hotmail.com
Phone: 0091-11-26704616
FAX: 0091-11-26704616
1. **Kinetic models:**

Pseudo-first order\(^1\) (eqn. SM1) and Pseudo-second order\(^2\) (eqn. SM2) kinetic equations applied on the sorption data to assess the effect of both initial concentration and adsorbent dose. The equations were present below:

\[
q_t = q_e \left(1 - e^{-k_1 t}\right) \tag{SM1}
\]

Where \(k_1 (\text{min}^{-1})\) is the first order adsorption rate constant, \(q_e\) and \(q_t\) are the amounts of carbofuran adsorbed at equilibrium and at time “t”, respectively.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{SM2}
\]

Where, \(k_2\) is rate constant of pseudo second order adsorption (g mg\(^{-1}\) min\(^{-1}\)). \(k_2\) and \(q_e\) values were determined from the plots at different temperatures and concentrations. \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) can be determined experimentally from the slope and intercept of plot \(t/q_t\) versus \(t\).

2. **Isotherm models:**

Sorption data was fitted using Freundlich\(^3\), Langmuir\(^4\), and Temkin\(^5\) isotherm models. The non-linear form of Freundlich model is shown in eqn. SM3

\[
q_e = K_F C_e^{1/n} \tag{SM3}
\]

Where \(q_e\) is the amount of carbofuran adsorbed per unit biochar weight (mg/g), \(C_e\) is the equilibrium carbofuran concentration (mg/L), constant \(K_F\) indicates the biochar’s relative adsorption capacity (mg/g) and \(1/n\) is the adsorption intensity.

The linear form of Langmuir isotherm however is given in eqn. SM4.
\[ q_e = \frac{Q^0 b C_e}{1 + b C_e} \]  

(SM4)

Where \( q_e \) is the amount of carbofuran adsorbed per unit weight of adsorbent (mg/g), \( C_e \) is the carbofuran equilibrium concentration in solution in mg/L, \( Q^0 \) is the monolayer adsorption capacity (mg/g) and \( b \) is constant related to the net enthalpy. Non-linear form of Temkin\(^5\) isotherm model is given in eqn. SM5.

\[ q_e = \frac{RT}{b_T} \ln \left( a_T C_e \right) \]  

(SM5)

Where, \( q_e \) is amount of carbofuran adsorbed per unit weight of adsorbent (mg/g). \( a_T \) and \( b_T \) are the Temkin constants related to heat of sorption (KJ/mol). \( C_e \) is the equilibrium carbofuran concentration in mg/L. \( R \) is universal gas constant and \( T \) is absolute temperature.
Figure SM1. Effect of different adsorbent dosages on carbofuran adsorption [pH 6.0; Carbofuran concentration= 10 mg/L; particle size=30-50 B.S.S mesh, at 25°C]

Figure SM2. Effect of different carbofuran concentration on adsorption [pH 6.0; adsorbent (SB500) dose= 2 g/L; particle size=30-50 B.S.S mesh, at 25°C]
Figure SM3. Pseudo-second order kinetic plots for effect of different adsorbent (SB500) dosages on carbofuran adsorption [pH 6.0; Carbofuran concentration= 10 mg/L; particle size=30-50 B.S.S mesh, at 25°C]

Figure SM4. Pseudo-second order kinetic plot for effect of different carbofuran concentration on adsorption by SB500 [pH 6.0; adsorbent (SB500) dose= 2 g/L; particle size=30-50 B.S.S mesh, at 25°C]
Figure SM5: Adsorption isotherms of carbofuran by SB500 at different temperatures [pH 6.0; adsorbent (SB500) dose=2g/L; carbofuran concentration=1-100 mg/L; particle size=30-50 B.S.S mesh].
Figure SM6: Freundlich adsorption isotherms of carbofuran by SB500 at different temperatures [pH 6.0; adsorbent (SB500) dose = 2g/L; carbofuran concentration= 1-100 mg/L; particle size of 30-50 B.S.S mesh]. Colored solid lines represent the data fitted by the Freundlich isotherm model.
Figure SM7: Temkin adsorption isotherms of carbofuran by SB500 at different temperatures [pH 6.0; adsorbent (SB500) dose = 2g/L; carbofuran concentration= 1-100 mg/L; particle size of 30-50 B.S.S mesh]. Colored solid lines represent the data fitted by the Temkin isotherm model.
Table SM1. Pseudo first-order and pseudo-second order rate constants and comparative evaluation of $q_e$ as calculated experimentally and by using pseudo first and pseudo second order rate equations at different SB500 dose.

<table>
<thead>
<tr>
<th>Dose (g/L)</th>
<th>First order rate constant, $k_1$ (h$^{-1}$)</th>
<th>$R^2$</th>
<th>Second order rate constant, $k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_e$ experimental (mg/g)</th>
<th>$q_e$, calculated using first-order kinetic model (mg/g)</th>
<th>$q_e$, calculated using second-order kinetic model (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.362</td>
<td>0.558</td>
<td>0.333</td>
<td>0.986</td>
<td>1.638</td>
<td>1.396</td>
<td>1.786</td>
</tr>
<tr>
<td>2</td>
<td>0.099</td>
<td>0.683</td>
<td>0.064</td>
<td>0.978</td>
<td>6.373</td>
<td>3.349</td>
<td>6.666</td>
</tr>
<tr>
<td>4</td>
<td>0.195</td>
<td>0.663</td>
<td>0.584</td>
<td>0.994</td>
<td>18.455</td>
<td>8.109</td>
<td>19.120</td>
</tr>
</tbody>
</table>

Table SM2. Pseudo-first order and pseudo-second order rate constants and comparative evaluation of $q_e$ as calculated experimentally and by using pseudo first and pseudo second-order rate equations at different carbofuran concentrations.

<table>
<thead>
<tr>
<th>Conc. (mg/L)</th>
<th>First order rate constant, $k_1$ (h$^{-1}$)</th>
<th>$R^2$</th>
<th>Second order rate constant, $k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_e$ experimental (mg/g)</th>
<th>$q_e$, calculated using first-order kinetic model (mg/g)</th>
<th>$q_e$, calculated using second-order kinetic model (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.1027</td>
<td>0.9381</td>
<td>0.0781</td>
<td>0.979</td>
<td>6.121</td>
<td>6.449</td>
<td>6.410</td>
</tr>
<tr>
<td>10</td>
<td>0.0958</td>
<td>0.727</td>
<td>0.0756</td>
<td>0.977</td>
<td>6.373</td>
<td>3.408</td>
<td>6.518</td>
</tr>
<tr>
<td>20</td>
<td>0.1443</td>
<td>0.740</td>
<td>0.0251</td>
<td>0.953</td>
<td>8.285</td>
<td>3.677</td>
<td>9.165</td>
</tr>
</tbody>
</table>