Study of Adsorption and Intercalation of Orange-Type Dyes into Mg-Al Layered Double Hydroxide

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SUPPORTING INFORMATION

Keywords :
Layered double hydroxides, Methyl Orange, Orange II, Orange G, adsorption, intercalation, expansion of the layers, XRD study, calorimetry, co-adsorption, counter-ion.
**S1. Characteristics of Mg-Al-LDH-NO$_3$ solid and dye molecules**

The morphology of adsorbent was observed by scanning electron microscopy (SEM). Figure S1 (upper panel) shows the typical SEM images of the Mg-Al-LDH-NO$_3$ with well defined layered platelets. The structure of layered double hydroxide was inferred from the XRD analysis Figure S1 (lower panel). This type of material crystallizes in hexagonal lattice with $R-3m$ rhombohedral symmetry $^{1-2}$. The diffractogram exhibits the structure with a series of 00$l$ peaks, such as (003), (006) and (009) which contains information about the cell parameters. The parameters $c$ and $a$ can be estimated from the (003) ($c = 3d_{003}$) and (011) ($a = 2d_{110}$) positions, respectively $^3$. The $c$ value of 2.6 nm agrees with those previously reported in literature for Mg/Al LDH $^{3-5}$. It was used to calculate basal spacing $^6$ of the layered material, $d_{003}= 0.89$ nm. The layer thickness of brucite-like minerals is 0.48 nm $^2$ and the interlayer spacing is therefore 0.41 nm. This is in agreement with the diameter of the nitrate anion (0.4 nm) $^7$. 

![SEM Image](image-url)
S2. Repeatability and experimental uncertainties

The repeatability and experimental uncertainties of the adsorption measurements were tested in the following manner: (1) the measurements were carried out twice by adding new points to the sorption curve obtained in a previous experiment under the same experimental conditions (such points had been selected to represent low, medium, and high concentrations and they were subsequently integrated into the sorption curves reported in the manuscript); (2) the sorption experiments were repeated independently by following the same measurement procedures. In the pre-plateau region, the greatest deviations between the corresponding adsorption curves were: 10%, MO; 17%, OII; 7%, OG. In the plateau region, these deviations were: 4%, MO; 23%, OII; 3%, OG.
S3. Kinetic Models

For the various models, the kinetic constants of adsorption were calculated and the linear regression correlation coefficient ($R^2$) values were compared to evaluate the best fit model.

The Lagergren-pseudo-first order model can be described by the following linear form:

$$
\log(q_l - q_t) = \log(q_l) - \frac{k_1}{2.303} t
$$

(S1)

where $q_l$ and $q_t$ are the amounts of the dye adsorbed at equilibrium and at time $t$, respectively; $k_1$ is the equilibrium rate constant in the pseudo-first order model. Values of $k_1$ and $R^2$ were found from the linear plots of $\log (q_l - q_t)$ vs. time.

The pseudo-second order kinetic model is expressed as follow:

$$
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
$$

(S2)

$$
h = k_2 q_e^2
$$

(S3)

where:

$h$ is the initial sorption rate; $q_e$ is the amount of the dye adsorbed at equilibrium and $k_2$ is the equilibrium rate constant in the pseudo-second order model. They can be calculated from the slope of the plot of $t/q_t$ as a function of time.

The Weber's interparticule diffusion model equation may written as follows:

$$
q_t = k_{id} t^{0.5} + C
$$

(S4)

where:

$k_{id}$ is the equilibrium rate constant of the interparticule diffusion model. The plots of $q_t$ as a function of $t^{0.5}$ should represent straight lines and were used to obtain the rate constants.
Figure S2. Amount of MO (a), OII (b) and OG (c) adsorbed onto Mg-Al-LDH-NO$_3$ as a function of the contact time for different initial concentrations.
**Table S1.** Kinetic parameters of Orange dyes adsorption onto Mg-Al LDHs for different initial dye concentrations.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$C_0$ (mM)</th>
<th>$q_{exp}$ (mmol/g)</th>
<th>$q_{l, cal}$ (mmol g$^{-1}$)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_{e, cal}$ (mmol g$^{-1}$)</th>
<th>$k_2$ (mmol g$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>$k_{id}$ (mmol g$^{-1}$ min$^{-1/2}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>0.4</td>
<td>1.64</td>
<td>0.66</td>
<td>0.005583</td>
<td>0.9227</td>
<td>1.61</td>
<td>0.035011</td>
<td>0.9916</td>
<td>0.05353</td>
<td>0.7918</td>
</tr>
<tr>
<td>Orange</td>
<td>0.9</td>
<td>3.25</td>
<td>1.17</td>
<td>0.015304</td>
<td>0.6689</td>
<td>3.08</td>
<td>0.020739</td>
<td>0.9935</td>
<td>0.10371</td>
<td>0.6862</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>4.47</td>
<td>2.34</td>
<td>0.008041</td>
<td>0.9204</td>
<td>4.64</td>
<td>0.008066</td>
<td>0.995</td>
<td>0.17724</td>
<td>0.8841</td>
</tr>
<tr>
<td>Orange II</td>
<td>0.1</td>
<td>0.39</td>
<td>0.15</td>
<td>0.00674</td>
<td>0.8689</td>
<td>0.38</td>
<td>0.190567</td>
<td>0.9964</td>
<td>0.01091</td>
<td>0.7877</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.55</td>
<td>0.94</td>
<td>0.00492</td>
<td>0.6274</td>
<td>1.48</td>
<td>0.457593</td>
<td>0.97</td>
<td>0.05369</td>
<td>0.9592</td>
</tr>
<tr>
<td>Orange G</td>
<td>0.17</td>
<td>0.74</td>
<td>0.32</td>
<td>0.00919</td>
<td>0.9293</td>
<td>0.71</td>
<td>0.118396</td>
<td>0.9849</td>
<td>0.0185</td>
<td>0.6359</td>
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<tr>
<td></td>
<td>0.45</td>
<td>1.42</td>
<td>0.62</td>
<td>0.00467</td>
<td>0.7353</td>
<td>1.41</td>
<td>0.02727</td>
<td>0.9891</td>
<td>0.03598</td>
<td>0.7358</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.76</td>
<td>0.34</td>
<td>0.00306</td>
<td>0.3532</td>
<td>1.70</td>
<td>0.079305</td>
<td>0.996</td>
<td>0.02745</td>
<td>0.4127</td>
</tr>
</tbody>
</table>
Figure S3. First order sorption kinetics of MO (a), OII (b) and OG (c) adsorption onto Mg-Al-NO₃ LDH for different initial concentrations.
Figure S4. Intra-particle mass transfer diffusion model for MO (a), OII (b) and OG (c) adsorption onto Mg-Al-NO$_3$ LDH for different initial dye concentrations.

2. Miyata, S., The Syntheses of Hydrotalcite-Like Compounds and Their Structures and Physico-Chemical Properties I: The Systems Mg$^{2+}$-Al$^{3+}$-No$_3^-$, Mg$^{2+}$-Al$^{3+}$-Cl$^-$, Mg$^{2+}$-Al$^{3+}$-Clo$_4^-$, Ni$^{2+}$-Al$^{3+}$-Cl and Zn$^{2+}$-Al$^{3+}$-Cl. Clays Clay Miner. 1975, 23, 369-375.


