Supplementary Information

Layered Double Hydroxide/Chitosan Nanocomposite Beads as Sorbents for Selenium Oxoanions

Man Li††, Andrew Dopilka††, Andrea N. Kraetz2, Hangkun Jing1, and Candace K. Chan†*  

1. Materials Science and Engineering, 2. Chemical Engineering;  

School for Engineering of Matter, Transport and Energy;  

Nanosystems Engineering Research Center for Nanotechnology – Enabled Water Treatment  

Arizona State University, Tempe, AZ 85287, United States  

††These authors contributed equally to this work  

*Corresponding author: candace.chan@asu.edu, (480) 727-8614
1. Materials and Reagents

Chitosan flakes were obtained from Dungeness Environmental (L/N CMP02P79, Alaskan Crab Chitosan) and used as received.

Granular LDH was obtained from Sasol Germany GmbH (PURALOX MG 63 HT – Granulate) with a reported median particle diameter of 1.46 mm. The granular media were gently hand ground with a mortar and pestle to form the LDH nanopowder (Figure S1) used for the preparation of the LDH/chitosan composite beads prepared by the first approach (direct mixing of LDH). For evaluation in jar tests, the granular LDH was used as received.

For the in-situ synthesis of LDH, MgCl₂ (product no. M8266-100G, purity ≥ 98%) and AlCl₃·6H₂O (product no. 06232-50G, purity ≥ 99.0%) were obtained from Sigma-Aldrich and used as precursors.

Synthetic water samples were prepared from ultrapure de-ionized (DI) water (18.2 MΩ, pH 5.5) spiked with selenium. Stock solutions (1000 ppm) of selenate, Se(VI), and selenite, Se(IV), were prepared by dissolving Na₂SeO₄ (Sigma-Aldrich, product no. 71948-100G, purity ≥ 98.0%) or NaHSeO₃ (Sigma-Aldrich, product no. S5261-25G, purity ≥98) into DI water.

2. Materials Synthesis

2.1 Chitosan Beads

Typically, 1 g of chitosan flakes were dissolved in 60 mL 0.1 M HCl solution, then stirred for four hours to make a clear chitosan gel. A 19G needle was fitted on a syringe and 20 mL of the chitosan gel was pushed into 100 mL of 0.1 M NaOH dropwise. The chitosan gel droplets in the alkaline solution were soft, clear, and around 3 mm in diameter. The solution containing the chitosan gel droplets was stirred overnight slowly to form chitosan beads. The soft
beads were washed using DI water and dried at room temperature in the fume hood for 3 days to form solid beads that shrunk in size to around 1 mm.

2.2 Directly Mixed-LDH/Chitosan Nanocomposite Beads

The ground LDH granular powder (0.1414 g) was directly mixed into 20 mL of chitosan gel (contains 0.33 g of chitosan), which turned white and sticky after being mixed with LDH. The gel was stirred overnight to make a uniform composite gel. Composite beads were formed by pushing the gel through a syringe fitted with a 19G needle into 100 mL of 0.1 M NaOH solution. After stirring overnight in the alkaline solution, the clear beads turned white.

2.3 In-situ LDH/Chitosan Nanocomposite Beads

The in-situ LDH/chitosan nanocomposite beads were prepared by mixing MgCl₂ and AlCl₃·6H₂O (LDH precursors) into the chitosan gel, followed by stirring overnight to make the gel mixture. Different wt% (0 ≤ x ≤ 70) of the LDH precursors were added to the chitosan gel with the Mg/Al molar ratio fixed at 3:1) to prepare the IS-X’ beads, where X’ = the wt% of LDH precursors. As an example, for X’ = 30 wt%, 0.0766 g MgCl₂ (0.000807 mol) and 0.0648 g AlCl₃·6H₂O (0.000268 mol) (i.e., M = 0.1414 g) were added to the 20 mL of chitosan gel (contains 0.33 g of chitosan). The gel mixture was light yellow and clear in appearance, similar to the pure chitosan gel. Composite beads were formed by pushing the gel from a syringe fitted with a 19G needle into 100 mL of 0.1 M NaOH solution. After stirring overnight in the alkaline solution, the clear mixture gel beads turned white.

2.4 Preparation of in-situ LDH Nanopowder

For comparison, pure LDH without chitosan was also prepared by co-precipitation. Briefly, 0.33 g of MgCl₂ and AlCl₃·6H₂O precursors were added into 20 mL 0.1 M HCl solution,
then dropped into 100 mL of 0.1 M NaOH using a syringe. The suspension was stirred overnight and filtered to form LDH and dried at 50 °C. The molar Mg/Al ratio of the obtained product was determined to be 2.58, according to ICP-MS analysis of an acid digested sample.

3. Materials Characterization

X-ray diffraction (XRD) characterization was performed using monochromatic Cu$_{k\alpha}$ radiation ($\lambda=1.5405$ Å) (Panalytical X’pert Pro). The reference pattern for Mg$_{0.667}$Al$_{0.333}$(OH)$_2$(CO$_3$)$_{0.167}$(H$_2$O)$_{0.5}$ from PDF 01-089-0460 was used for comparison.

Scanning electron microscopy (SEM) was performed with a Nova 200 NanoLab (FEI) focused ion beam. The sample was coated using Au sputtering for 45 s before use.

Fourier transform infrared (FTIR) spectra of samples were collected over the wavenumber range 400-4800 cm$^{-1}$ on a Bruker IFS66V/S FTIR spectrometer in the ATR-FTIR mode using a diamond ATR sample module. FTIR characterization of chitosan flakes and beads: Characteristic chitosan bands are identified as the N-H stretching at around 3360 cm$^{-1}$, C-H stretching at 2872 cm$^{-1}$, amide and amino groups at 1653 cm$^{-1}$ and 1587 cm$^{-1}$, amide methyl group at 1375 cm$^{-1}$, bridge O (glycosidic linkage) stretching at 1151 cm$^{-1}$, and C-O stretching at 1025 cm$^{-1}$.

FTIR characterization of LDH: The broad band at 3450 cm$^{-1}$ is from the OH stretching from the hydroxyl groups in the LDH. The characteristic band corresponding to interlayer carbonate anions is at 1363 cm$^{-1}$. The lattice vibrations of the Mg,Al-oxide octahedral sheets are found at 555 cm$^{-1}$, 644 cm$^{-1}$, and 736 cm$^{-1}$. The mode found at 620 – 670 cm$^{-1}$, which is assigned to the vibration of hydroxide, is found at lower wavenumbers when some of the carbonate anions are replaced by chloride. Since the in-situ LDH precursors consisted of chloride salts, this may suggest the incorporation of some chloride anions into the interlayer space during the synthesis. The interlayer hydration deformation bands ($\delta$H$_2$O)
typically found at around 1652 cm\(^{-1}\).\(^7,^8\) were also present in the sample, confirming the presence of water molecules inside the LDH interlayer space. The broad band at 3450 cm\(^{-1}\) is from the OH stretching from the hydroxyl groups in the LDH.\(^4\)

Thermal gravimetric analysis of the samples was performed using a Setaram TG 92 by heating to 1000 °C in air using a 5 °C/min ramp rate. For the chitosan beads, the TGA curve is consistent with pyrolysis in a two-stage process beginning at around 300 °C,\(^9\) with about 94% weight loss after heating to 1000 °C. The TGA of the in-situ LDH is also similar to other reports and is consistent with a two-stage weight loss, correlating to loss of interlayer water molecules, followed by the removal of the interlayer anions in the second weight loss region from about 250 – 500 °C.\(^10,^11\) The mass remaining after heating to 1000 °C in air was around 58 wt%, which is attributed to the fully dehydroxylated/decarbonated Mg-Al oxide.\(^12,^13\)

\(\text{N}_2\) adsorption measurements were performed on the granular LDH and in-situ LDH nanopowder after heating the samples at 110 °C for 4 – 5 h. The measurements were performed at 77 K using a Micromeritics TriStart II 3020.

The composition of the in-situ LDH nanopowder was determined using acid digestion followed by analysis using inductively coupled plasma – mass spectroscopy (ICP-MS). The powder was dissolved in concentrated nitric acid. This solution was evaporated and then combined with 2% nitric acid to form a 5 mL solution and then ICP-MS was used analyze the concentrations of dissolved ions in the solution. The mass concentrations of magnesium and aluminum were converted to moles and the Mg/Al ratio was determined to be 2.58.

4. Analysis of Selenium Concentrations in Water

Spiked water samples were filtered using a 0.2 micron Isopore track etched polycarbonate membrane in a Pall syringe filter. Then, 2% nitric acid was added to the filtered
sample solution for analysis of total selenium concentrations with inductively coupled plasma -
optical emission spectroscopy (ICP-OES, ICAP-6300, Thermo Co.) or inductively coupled plasma - mass spectroscopy (ICP-MS, iCap Q quadrupole, Thermo Co.) for low levels.

5. Determination of Expected and Actual wt% of LDH in Composite Beads

Assuming the in-situ LDH composition follows the formula\(^{14}\):

\[
\text{Mg}_1\cdot\text{yAl}_2\cdot(\text{OH})_2\cdot(\text{CO}_3^{2-})_{\frac{y}{2}}\cdot(\text{H}_2\text{O})_{1-\frac{3y}{2}}
\]

and using the measured Mg/Al ratio of 2.58 (from the ICP-MS analysis of the digested sample),
the formula of the in-situ LDH was taken to be Mg\(_{0.72}\)Al\(_{0.28}\)(OH\(_2\))(CO\(_3^{2-}\))\(_{0.14}\)(H\(_2\)O\(_{0.58}\) with a
molecular weight of 77.9 g/mol.

The product yield for the co-precipitation of LDH from the precursors was calculated by
adding 0.179 g MgCl\(_2\) and 0.151 g AlCl\(_3\)·6H\(_2\)O to 20 mL of 0.1 M HCl solution, followed by
dropping into 100 mL of 0.1 M NaOH. The amount of LDH recovered after filtering and drying
at 50 °C was 0.1859 g. Using the above composition and molecular weight, the theoretical mass
of LDH expected to be produced from the reaction is:

\[
= (0.179 \text{ g MgCl}_2) \cdot \frac{(1 \text{ mol MgCl}_2)}{(95.211 \text{ g MgCl}_2)} \cdot \frac{(1 \text{ mol LDH})}{(0.72 \text{ mol Mg})} \cdot \frac{(77.9 \text{ g LDH})}{(1 \text{ mol LDH})} = 0.2034 \text{ g}
\]

Thus, the reaction resulted in a 91.3% yield.

With this information, the expected mass of LDH in the IS-X’ composite beads was
estimated from the nominal amount of precursors added to the chitosan gel. It was assumed that
the product yield of LDH within the chitosan matrix was the same as when precipitated in just
the NaOH solution. An example calculation for the IS-30 composite beads is shown below.
Nominal wt\% of precursors in chitosan = 30\% (e.g., from 0.0766 g MgCl$_2$, 0.1414 g AlCl$_3$·6H$_2$O, and 0.33 g chitosan)

Theoretical mass of LDH = \( \frac{(0.0766 \text{ g MgCl}_2)}{(95.211 \text{ g MgCl}_2)} \times \frac{(1 \text{ mol LDH})}{(0.72 \text{ mol Mg})} \times \frac{(77.9 \text{ g LDH})}{(1 \text{ mol LDH})} \)

= 0.087 g

Expected mass of LDH = (0.087 g)\times(0.913) = 0.079 g

Expected wt\% of LDH in chitosan = \( \frac{(0.079 \text{ g})}{(0.33 \text{ g} + 0.079 \text{ g})} \times 100 = 19.3\% \)

According to the TGA results in Figure 4, the mass of in-situ LDH remaining after heating at 1000 °C (i.e., the residual LDH) was 57.97% of the initial mass. It was assumed that all of the LDH domains in the IS and DM composite beads had the same weight loss behavior as the in-situ LDH, which was prepared in the absence of chitosan. The TGA results showed that the mass of chitosan beads after pyrolysis was ~6% of its initial mass. Based on the nominal amount of chitosan in the precursor gel, the mass loss due to pyrolysis was determined, assuming that the chitosan domains in the IS and DM composite beads had the same weight loss behavior as the pure chitosan beads. Using the nominal composition of chitosan in the beads, the amount of residual chitosan remaining after the pyrolysis was determined and the difference from the total remaining mass after heating to 1000 °C was assumed to be the mass of the residual LDH. From this information, the initial wt\% of the LDH in the composite bead was determined. An example calculation for the IS-30 composite beads is shown below.
Nominal wt% of chitosan = 70%

Final wt% remaining (after TGA to 1000 °C in air) = 15.54%

Wt% of residual chitosan (assuming 6.05 wt% remaining) = (0.7)*(6.05%) = 4.235 wt%

Wt% of residual LDH = (15.54) - (4.235) = 11.305 wt%

Wt% of initial LDH (assuming residual LDH is 57.97% of initial LDH) = \frac{(11.305)}{(57.97)} * 100 = 19.5%

6. Selenium Sorption Tests

6.1 Removal efficacy

Jar tests to assess the selenium removal efficacy of the sorbents were performed at room temperature using 1 ppm Se(VI) in DI water as the test solution. Sampling was performed after 48 h of contact time. Magnetic stirring was used for jar tests conducted on the bead media, while a compact digital mini rotator (Thermo Scientific, Catalog no. 88880025) shaking at 300 rpm was used for tests performed using the LDH granular media to minimize attrition.

Experiments were conducted to test the removal efficacy of the IS-50 nanocomposite beads at different pH solutions using a dosage of 2 g/L sorbent (corresponding to 1 g/L with respect to the amount of chitosan in the bead). The experiments were conducted in 50 mL centrifuge tubes with 40 mL of solution. The initial pH of a 1 ppm solution of selenate in DI water was adjusted by adding 0.1 M HCl and 0.1 M NaOH. The pH was measured before and after using a Hanna pH/mV Meter (HI9125). The solutions were left to equilibrate for 48 h on a compact digital mini
rotator shaking at 250 rpm. Experiments were duplicated twice with error bars showing the range of duplicates.

6.2 Adsorption kinetics

The adsorption kinetics of the sorbents were evaluated by preparing 1 ppm and 5 ppm selenate and selenite solutions in DI water. The experiments were conducted in 250 mL Nalgene polypropylene plastic bottles with 200 mL of solution with a dosage of 2 g/L (total sorbent mass) for IS-50 and 1 g/L for in-situ LDH and granular LDH. 2 mL aliquots were taken at intervals of 15 min, 30 min, 1, 2, 4, 6, 8, 24, and 48 hours. All kinetic experiments were conducted on a digital compact mini rotator (Thermo Scientific, Catalog no. 88880025) shaking at 250 rpm. The samples were analyzed via ICP-OES for their selenium concentration. The experiments were duplicated twice with error bars showing the range of the duplicates. The kinetic data were fit to a pseudo-second order kinetic model,\(^3\) as shown in Equation S1:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]  

(S1)

Where \(q_e\) is the amount of selenium anion sorbed at equilibrium (units of mg/g), \(k_2\) is the rate constant of sorption (units of g/mg·h), \(q_t\) is the amount of selenium anion sorbed at a particular time \(t\) (units of mg/g). The constants were determined from the plot of \(\frac{t}{q_t}\) vs. \(t\), where \(q_e\) is taken to be the inverse of the slope and \(k_2\) is calculated from the reciprocal product of the y-intercept and \(q_e^2\). The kinetic data were also fit to an intraparticle diffusion model,\(^4\) as shown in Equation S2:

\[
q_t = k_i t^{1/2} + C_i
\]  

(S2)
where $q_t$ is the amount of selenium anion sorbed at a particular time $t$ (units of mg/g), $k_i$ is the intraparticle diffusion rate constant (mg/g·h$^{1/2}$), and $C_i$ is a constant corresponding to the thickness of the boundary layer.

6.3 Adsorption isotherms

Adsorption isotherms were performed on the IS-50 nanocomposite beads in selenite and selenate solutions prepared by spiking DI water with a concentration ranging from 1 ppm to 25 ppm with a dosage of 2 g/L sorbent. The isotherms were conducted in 150 mL Nalgene polypropylene sample bottles with a volume of 100 mL of solution and an equilibration time of 48 h. All isotherms were conducted on a digital compact mini rotator (Thermo Scientific, Catalog no. 88880025) shaking at 250 rpm. The experiments were duplicated twice with error bars showing the range of the duplicates. The equilibrium adsorption data were fitted to both Langmuir and Freundlich models. The Langmuir isotherm can be expressed as shown in Equation S3, where $C_e$ (ppm) is the concentration of Se(VI) at equilibrium; $q_e$ (mg/g) is the adsorption ability of adsorbent for loading selenium at each $C_e$; $q_{\text{max}}$ (mg/g) is the maximum adsorption ability of loading selenium onto adsorbent; $K$ (L/mg) is the equilibrium constant.

$$q_e = \frac{q_{\text{max}}K C_e}{1 + KC_e}$$  \hspace{1cm} (S3)

The Langmuir equation can also be expressed as shown in Equation S4.

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}K} + \frac{C_e}{q_{\text{max}}}$$  \hspace{1cm} (S4)

Therefore, the slope of the Langmuir plot is $1/q_{\text{max}}$ and the intercept is $1/q_{\text{max}}K$.

The Freundlich model can be expressed by the empirical equation (Equation S5), where $K_f$ (L/mg) is the Freundlich isotherm constant and is an indicator of adsorption capacity; $n$ is the
adsorption intensity; $C_e$ (ppm) is the equilibrium concentration of selenium; $q_e$ (mg/g) is the adsorption ability of adsorbent for loading selenium at each $C_e$; $q_{max}$ (mg/g) is the maximum adsorption ability of loading selenium onto adsorbent.\(^5\)

$$q_e = K_f C_e^{1/n} \quad (S5)$$

By linearizing Equation S5, we can obtain Equation S6:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (S6)$$

Herein, the $1/n$ is a function of the strength of adsorption in the adsorption process. When $1/n$ is below one, it indicates good adsorption; if $1/n$ is above one, then it indicates cooperative adsorption.\(^8\) From the results in Table 3, $1/n < 1$ for both oxoanions, indicating good sorption on the nanocomposite beads.

7. Supporting Figures

Figure S1. SEM images of LDH nanopowders obtained after hand grinding the LDH granular media.
Figure S2. (A) Photograph of in-situ synthesized LDH/chitosan composite beads with 60 wt% LDH precursor. Most of the beads were misshapen. (B) Photograph of composite gel containing 70 wt% LDH precursor and chitosan after dropping into the NaOH solution. The beads were not well-formed and the solution became white. After stirring overnight, all the beads were broken and only a white precipitate remained, suggesting the LDH precipitated separately from the chitosan.

Figure S3. Kinetics of selenite, Se(IV), and selenate, Se(VI) sorption on granular LDH using a sorbent dose of 1 g/L. Each point represents an average of duplicates, with error bars showing the range.
Figure S4. Kinetics of selenite and selenate adsorption onto in-situ LDH nanopowder and data fitting to intraparticle diffusion model described by Weber and Morris.\textsuperscript{4} Initial selenium concentration of (A) 1 ppm, (B) 5 ppm. The linear fit was made during the time points between 1-4 h and the obtained slope ($m$), y-intercept ($b$), and correlation coefficient ($r^2$) from the linear fit are shown in the graphs.

8. Supporting Tables

Table S1. N\textsubscript{2} sorption results

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular LDH</td>
<td>116</td>
<td>0.415</td>
<td>109.51</td>
</tr>
<tr>
<td>In-situ LDH Nanopowder</td>
<td>144</td>
<td>0.177</td>
<td>52.32</td>
</tr>
</tbody>
</table>
Table S2. Adsorption kinetics results and pseudo second-order fitting ($C_0$: initial anion concentration, $k_2$: rate constant, $q_e$: anion removal capacity at equilibrium, $r^2$: correlation coefficient)

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>Species</th>
<th>Sorbent</th>
<th>$k_2$ (g/mg·h)</th>
<th>$q_e$ (mg/g)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Se(IV)</td>
<td>In-Situ LDH</td>
<td>9.05 ± 0.35</td>
<td>0.84 ± 0.02</td>
<td>0.9988</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granular LDH</td>
<td>6.41 ± 1.34</td>
<td>0.90 ± 0.02</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (total sorbent mass)</td>
<td>5.56 ± 0.58</td>
<td>0.41 ± 0.00</td>
<td>0.9997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (LDH mass only)</td>
<td>2.02 ± 0.21</td>
<td>1.12 ± 0.01</td>
<td>0.9998</td>
</tr>
<tr>
<td>1 ppm</td>
<td>Se(VI)</td>
<td>In-Situ LDH</td>
<td>10.04 ± 4.30</td>
<td>0.87 ± 0.00</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granular LDH</td>
<td>4.86 ± 0.63</td>
<td>0.95 ± 0.05</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (total sorbent mass)</td>
<td>4.52 ± 0.38</td>
<td>0.43 ± 0.01</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (LDH mass only)</td>
<td>1.64 ± 0.15</td>
<td>1.17 ± 0.03</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>Se(IV)</td>
<td>In-Situ LDH</td>
<td>1.73 ± 0.62</td>
<td>3.86 ± 0.15</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granular LDH</td>
<td>0.71 ± 0.00</td>
<td>4.95 ± 0.08</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (total sorbent mass)</td>
<td>1.93 ± 0.09</td>
<td>2.33 ± 0.02</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (LDH mass only)</td>
<td>0.70 ± 0.03</td>
<td>6.39 ± 0.06</td>
<td>0.9999</td>
</tr>
<tr>
<td>5 ppm</td>
<td>Se(VI)</td>
<td>In-Situ LDH</td>
<td>1.34 ± 0.74</td>
<td>3.61 ± 0.09</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granular LDH</td>
<td>0.72 ± 0.15</td>
<td>5.01 ± 0.10</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (total sorbent mass)</td>
<td>0.69 ± 0.10</td>
<td>1.23 ± 0.08</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IS-50 Beads (LDH mass only)</td>
<td>0.25 ± 0.04</td>
<td>3.39 ± 0.23</td>
<td>0.9998</td>
</tr>
</tbody>
</table>
Table S3. Comparison of maximum adsorption capacities obtained from Langmuir isotherms of nanocomposite chitosan beads with different nanocrystalline metal oxide (NMO) particles as fillers

<table>
<thead>
<tr>
<th>NMO Composition</th>
<th>Bead Composition</th>
<th>Sorbent Dosage (g/L)</th>
<th>( q_{\text{max}} ) (mg/g NMO)</th>
<th>( q_{\text{max}} ) (mg/g Sorbent)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )-Al(_2)O(_3) (&lt; 50 nm, 40 m(^2)/g)</td>
<td>8.3 wt% Al(_2)O(_3)</td>
<td>1.75</td>
<td>Se(IV): 11.08</td>
<td>Se(VI): 20.11*</td>
<td>Se(IV): 0.92 \footnote{[a]}</td>
</tr>
<tr>
<td>Anatase TiO(_2) (&lt;25 nm, 50 m(^2)/g)</td>
<td>12.4 wt% TiO(_2)</td>
<td>1.83</td>
<td>Se(IV): 5.29</td>
<td>Se(VI): 12.80*</td>
<td>Se(IV): 0.66 \footnote{[c]}</td>
</tr>
<tr>
<td>Mg-Al-CO(_3)-LDH (&lt; 50 nm, 144 m(^2)/g)</td>
<td>36.46 wt% LDH</td>
<td>2</td>
<td>Se(IV): 17.00 \footnote{[e]}</td>
<td>Se(VI): 12.29 \footnote{[f]}</td>
<td>Se(IV): 6.21</td>
</tr>
</tbody>
</table>

*The chitosan matrix used by Yamani et. al. was also able to remove Se(VI), so this number is inflated since the mass of chitosan is not accounted for.

\footnote{[a]} Calculated from reported \( q_{\text{max}} \) of 11.08 mg Se(IV)/g NMO by considering 0.145 g NMO/L dosage based on the 8.3 wt\% of NMO in the composite.

\footnote{[b]} Calculated from reported \( q_{\text{max}} \) of 20.11 mg Se(VI)/g NMO by considering 0.145 g NMO/L dosage based on the 8 wt\% of NMO in the composite.

\footnote{[c]} Calculated from reported \( q_{\text{max}} \) of 5.29 mg Se(IV)/g NMO by considering 0.227 g NMO/L dosage based on the 12.4 wt\% of NMO in the composite.

\footnote{[d]} Calculated from reported \( q_{\text{max}} \) of 12.80 mg Se(VI)/g NMO by considering 0.227 g NMO/L dosage based on the 12.4 wt\% of NMO in the composite.

\footnote{[e]} Calculated from measured \( q_{\text{max}} \) of 6.21 mg Se(IV)/g NMO (for IS-50 beads) by considering 0.7292 g NMO/L dosage based on the 36.46 wt\% of NMO in the composite.

\footnote{[f]} Calculated from measured \( q_{\text{max}} \) of 4.29 mg Se(VI)/g NMO (for IS-50 beads) by considering 0.7292 g NMO/L dosage based on the 36.46 wt\% of NMO in the composite.
9. References:


