Supporting Information for the manuscript

**Microsized particles of Aza222 polymer as a regenerable ultrahigh affinity sorbent for the removal of mercury from aqueous solutions**

Accepted for publication in *Separation and Purification Technology* on June 7, 2013.

Published article DOI: 10.1016/j.seppur.2013.06.005

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Fractal dimension study

To determine whether the porous particles were fractals, a manufacturer-provided software module of the light scattering apparatus was used to record the dependence of the intensity $I$ of scattered light on the scattering vector $Q$: $Q = \frac{4\pi n}{\lambda} \sin\left(\frac{\phi}{2}\right)$, where $n$ is the refractive index of solvent, $\phi$ is the scattering angle, and $\lambda$ is the incident wavelength. The fractal dimension $D_f$ of aggregates was determined from the double logarithmic plot of the dependence $I(Q) \propto Q^{-D_f}$, which is valid when the aggregate is at least one order of magnitude larger than the primary particles that form the aggregate.

The observed non linear dependence of $\log(I)$ on $\log(Q)$ illustrated a non-fractal nature of the sorbent particles. Data shown below,

Figure S11: Intensity vs. scattering vector dependence plot for an aqueous suspension of processed Aza222 powder.
Theoretical estimation of Aza222 adsorption capacity

The molecular weight of the Aza222 polymer unit shown on Figure 2 is 677 g/mol. For the complexation reaction (1) the mercury concentration in the obtained complex is 200.6/948.5 = 21.1% ~ 20%. Exclusion of inner layers of the polymer will decrease this number and incorporation of complex anions such as HgCl$_3^-$, HgCl$_4^{2-}$, HgI$_3^-$ and HgI$_4^{2-}$ will increase the measured value, but those effects were not taken into account.

\[
\begin{align*}
677 & \quad 271.5 & \quad 945 \text{ g/mol} \\
\text{Aza222 + HgCl}_2 & \rightarrow [\text{Hg@Aza222}]^{2+} 2\text{Cl}^- \quad (1)
\end{align*}
\]

\[\text{Figure S12: Polymer unit and its transformation into a mercury complex.}\]

Based on Elemental Analysis (CHN/O):
Molecular Formula for repeating Aza222 unit: $\text{C}_{48}\text{H}_{66}\text{N}_8\text{Cl}_{2.5} \cdot \text{H}_2\text{O}$

\[
\text{C}_{48}\text{H}_{66}\text{N}_8\text{Cl}_{2.5} \cdot \text{H}_2\text{O (Aza222) + HgCl}_2 \rightarrow [\text{Hg@Aza222}]^{2+} 2\text{Cl}^-
\]

Theoretical estimation of Aza222 adsorption capacity becomes:

\[
\frac{200.6 \text{ g/mol}}{1142.22 \text{ g/mol}} = 0.176 \times 100\% = 17.6\% \quad (2)
\]
Dimensionless transformations for adsorption kinetics modeling

The system of equations presented in section “Adsorption kinetics modeling” can be further simplified by the transition to the dimensionless form with dimensionless variables:

\[ R = \frac{r}{R}, \quad \tau = \frac{D}{R^2} t, \quad \overline{C}(\tau) = \frac{C(t) - C_e}{C_0 - C_e} \quad (\text{with } \overline{C}(\tau = 0) = 1), \quad \text{and } \overline{q}(r, \tau) = \frac{q(r, t)}{q_e}. \]

Here, \( C_0 \) is the initial value of \( C(t) \), \( C_e \) is the liquid phase concentration at equilibrium, \( q_e = KC_0^{1/n} \) is the solid phase concentration in equilibrium with the initial liquid phase concentration. Two additional dimensionless numbers are introduced: the solute distribution parameter (\( D_g \)) and the Biot number (\( Bi \)):

\[
D_g = \frac{Mq_e}{C_0 V_e} = \frac{D_a q_e (1 - \varepsilon)}{C_0 \varepsilon} \quad \text{(S11a)}
\]

\[
Bi = \frac{k_f R (1 - \varepsilon)}{D_g D_s \varepsilon \phi \left(1 - \frac{C_e}{C_0}\right)} \quad \text{(S11b)}
\]
Determination of particle porosity

The porosity of the sorbent particles was calculated using both the N₂ adsorption results and Stokes’ law, assuming that both the aggregates (of radius $R$) and the primary particles (of radius $r$) are spherical and that the primary particles are monodisperse. As follows, the analytical and experimental procedures conducted for such determination are explained.

The obtained BET surface area ($B$) can be expressed, for one aggregate particle, as:

$$B = \frac{n_{\text{prim}} 4\pi r^2}{n_{\text{prim}} m_{\text{prim}}} = \frac{4\pi r^2}{\rho_{\text{prim}} \frac{4}{3}\pi r^3} = \frac{3}{\rho_{\text{prim}} r}$$

(S12)

where $n_{\text{prim}}$ is the number of primary particles in one aggregate, while $m_{\text{prim}}$ and $\rho_{\text{prim}}$ indicate the mass and the density of one primary particle. Rearranging:

$$\rho_{\text{prim}} = \frac{3}{Br}$$

(S13)

The porosity ($\varepsilon$) of the aggregate can be expressed as the ratio of the pore volume to the total aggregate volume ($V_{agg}$), as:

$$\varepsilon = \frac{V_{agg} - n_{\text{prim}} V_{\text{prim}}}{V_{agg}} = 1 - n_{\text{prim}} \frac{V_{\text{prim}}}{V_{agg}} = 1 - n_{\text{prim}} \left( \frac{r}{R} \right)^3$$

(S14)

Finally, the total aggregate mass can be expressed in terms of the total mass of primary particles as:

$$\rho_{\text{agg}} V_{agg} = n_{\text{prim}} \rho_{\text{prim}} V_{\text{prim}}$$

(S15)
Expressing the volumes with the respective radii and rearranging,

$$n_{\text{prim}} = \frac{\rho_{\text{agg}}}{\rho_{\text{prim}}} \left( \frac{R}{r} \right)^3$$  \hspace{1cm} (SI6)

Combining eqs. (4) and (6) yields:

$$\varepsilon = 1 - \frac{\rho_{\text{agg}}}{\rho_{\text{prim}}}$$  \hspace{1cm} (SI7)

The value of $\rho_{\text{prim}}$ was obtained using eq. 2, the obtained data on BET surface area (3.6552 m$^2$/g) and the radius of the primary particles estimated to be 1 µm. The value of $\rho_{\text{agg}}$ was obtained by conducting settling experiments with concentrated sonicated aqueous suspensions of the sorbent powders, by using the Stokes’ law equation and fitting $\rho_{\text{agg}}$ to match the observed settling distances and times.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>(m$^2$/g)</td>
<td>3.66 ± 0.13</td>
</tr>
<tr>
<td>Micropore area</td>
<td>(m$^2$/g)</td>
<td>0.32 ± 0.40</td>
</tr>
<tr>
<td>External surface area</td>
<td></td>
<td>3.34</td>
</tr>
<tr>
<td>Micropore volume</td>
<td></td>
<td>6.50·10$^{-5}$</td>
</tr>
<tr>
<td>Volume of pores (17 to 3000) Å in diameter</td>
<td>(cm$^3$/g)</td>
<td>1.21·10$^{-3}$</td>
</tr>
<tr>
<td>Total pore volume</td>
<td></td>
<td>4.5</td>
</tr>
</tbody>
</table>

**Table SI1.** Aza 222 polymer characterization by N$_2$ adsorption at 78 K.
Determination of surface area

Shown below are the calculations of the external surface area based on the following assumptions: i) the (0.5 to 2) μm diameter of primary particles (spherules), ii) (40 to 60)%, fraction of spherules exposed to the solution, and iii) sorbent particle density of 1 g/ml.

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Fraction available</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.4</td>
<td>4.8</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6</td>
<td>7.2</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>2.4</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table SI2: Calculated surface areas for different primary particle sizes and available liquid phase contact fractions.
Particle charge measurement

To measure the zeta potential of Aza222 particles, the prepared Aza222 powder was resuspended in water and sonicated for ca. 1 min. The pH of the suspension was adjusted using concentrated HCl and NaOH solutions. First, the electrophoretic mobility of Aza222 particles was measured by phase analysis light scattering (Zeta-Plus module, ZetaPALS, Brookhaven Instrument Corp., Holtsville, NY). The measured values of the electrophoretic mobility were converted into the values of zeta potential using the Smoluchowski equation. The amount of particles and solution volume was adjusted in each case to achieve the optimal count range. Measurements were conducted in 5 runs of 5 cycles each, at a constant temperature of 25 °C, which was maintained internally by the ZetaPALS instrument. Similar measurements were conducted for two control samples - cross-linked polyethyleneimine and cross-linked polyethyleneimine saturated with carbon dioxide subject to the same preparation procedure as that employed to obtain the Aza222 powder.

A marked effect of solution pH on the zeta potential of Aza222 particles was observed (Fig. SD3). At pH values below 7, the particles had a positive zeta potential value in the (10 to 20) mV range, decreasing as neutral pH was approached, and reaching an isoelectric point at a pH value of approximately 7.2. Beyond the isoelectric point, the zeta potential value remained stable at ca. (-20 to -24) mV. To verify whether the negative charge of the polymer under alkaline conditions was due to the formation of carbamate anions as a result for the polymer’s reaction with CO₂, zeta potential was measured for cross-linked polyethyleneimine as a control. Before the experiment the polymer was
treated with CO₂ for 1 hr to ensure its transformation into a carbamate. However, measurements conducted with the control polymer showed no charge reversal at alkaline pH values.

**Figure S14:** Zeta potential as a function of solution pH for aqueous suspensions of the: a) microsized Aza222 particles (full line, diamond markers), b) Control PEI polymer (dashed line, square markers) and c) Control cross-linked PEI polymer saturated with CO₂ (dotted line, round markers).

The abrupt change in zeta potential to negative values at above-neutral pH values could be exploited to further facilitate the aggregation, precipitation, and removal of the particles upon mercury binding and charge neutralization. It must be noted however, that experimental determinations of zeta potential of mercury loaded polymer particles could not be conducted due to mercury reduction upon application of the electric field applied...
by the zeta potential instrument. This observation points to the additional possibility of electrolytically reducing the Aza222-bound mercury within the polymer, as a polymer regeneration alternative.
Adsorption isotherm modeling

The obtained isotherm data (excluding the physiosorption portion) was fitted using the Langmuir and Freundlich equations. The fitting procedure was performed by rearranging the Langmuir and Freundlich equations, to allow for a linear regression analysis.

Langmuir equation:

\[ q = \frac{QbC_e}{1 + bC_e} \]  

(1)

Where \( q \) is mass of adsorbate per mass of adsorbent at equilibrium (mg Hg/g Aza222); \( Q \) is the maximum equilibrium loading capacity of the sorbent (mg Hg/g Aza222), \( b \) is the relative energy of adsorption parameter (L/mg) and \( C_e \) is the concentration of adsorbate in the liquid phase at equilibrium (mg/L).

Rearranging (1),

\[ \frac{C_e}{q} = \frac{1}{Qb} + \frac{C_e}{Q} \]  

(2)

A plot of \( \frac{C_e}{q} \) vs \( C_e \) will yield a linear plot of slope \( 1/Q \) and y-intercept \( 1/(Qb) \), allowing for the calculation of these two parameters.

Freundlich equation:

\[ q = KC_e^n \]  

(3)
Where $K$ is the adsorption capacity at unit concentration and $1/n$ is an adsorption intensity parameter (between 0 and 1).

Applying logarithm to (3) yields,

$$\log(q) = \log(K) + n\log(C_e)$$

A plot of $\log(q)$ vs $\log(C_e)$ will yield a linear plot of slope $n$ and y-intercept $\log(K)$, allowing for the calculation of these two parameters.

The plots obtained for the rearranged Langmuir and Freundlich equations are shown below,

![Langmuir fit](image)

**Figure S15.** Plot of $\frac{C_e}{q}$ vs $C_e$ and linear regression fit for the isotherm adsorption data
From the performed regression analysis, the Langmuir model offers a more accurate representation of the isotherm adsorption behavior ($R^2 = 0.986$). Figure SI6 illustrates the isotherm adsorption experimental data, and the plot of the Langmuir curve using the parameters obtained from the fitting procedure.

**Figure S16.** Plot of $\log(q)$ vs $\log(C_e)$ and linear regression fit for the isotherm adsorption data.

**Figure S17.** Plot of adsorption isotherm experimental data and the curve obtained using the calculated Langmuir parameters.