HG(II) REMOVAL FROM AQUEOUS SOLUTION BY MAGNETIC POWDERED ACTIVATED CARBON: CLOSING THE MASS BALANCE

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Introduction

Activated carbon is known to remove Hg(II) from aqueous solutions[1]. MPAC (magnetic powdered activated carbon) has the potential to reduce aqueous mercury concentrations to between 1 ppb (half of the MCL for drinking water as determined by the EPA) to 0.2 ppb (the analytical detection limit using cold vapor atomic absorption (CVAA) spectroscopy) and has proven to be recoverable through magnetism. Magnetic recapture allows for simple separation of the sorbent from the waste stream and increases the ease of residuals management according to the cradle to grave responsibility of the Resource Conservation and Recovery Act (RCRA).

MPAC Hg-removal performance is verified by integral mass balance of Hg. The batch system contained a sealed Teflon mercury-carbon contact chamber with magnetic mixing and constant headspace N_2 flow through an inlet/outlet port to a $KMnO_4$ trap. The mass balance will be closed within 20% by quantifying the residual aqueous Hg, adsorbed Hg extracted from MPAC by HF digestion, and volatilized Hg captured in the $KMnO_4$ trap (Equations 1-3).

$$Hg_{initial} = Hg_{final} \qquad (1)$$
$$Hg_{initial} = Hg(II)_{aq} \qquad (2)$$
$$Hg_{final} = Hg(II)_{ads} + Hg(0)_{ads} + Hg(0)_{vol} + Hg(II)_{aq} \quad (3)$$

Experimental

MPAC Synthesis

MPAC composites were synthesized by heterogeneous nucleation, first forming an aqueous solution of Fe(II) and Fe(III) salts (ferric chloride ($FeCl_3$) and ferrous-ferric oxide (FeO, Fe_2O_3)) (Eq. 4 to 9 (1)). Rapid alkaline hydrolysis was induced by adding 5M NaOH to the solution of iron oxides until pH 10 (Eq. 10 (1)). The ferrihydrite formed precipitates onto the carbon surface (Calgon WPH PAC) but is thermodynamically unstable and transforms into magnetite (Fe_3O_4) in presence of Fe^{+2} (Eq. 11 (1)). Samples were oven-dried at 100°C overnight.
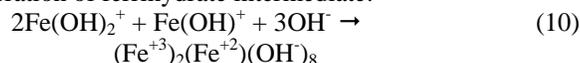
Dissociation:
$$FeCl_3 \leftrightarrows Fe^{3+} + 3Cl^- \qquad (4)$$
$$Fe_2O_3 \leftrightarrows 2Fe^{+3} + 3O^{-2} \qquad (5)$$
$$FeO \leftrightarrows Fe^{+2} + O^{-2} \qquad (6)$$
$$H_2O \leftrightarrows H^+ + OH^- \qquad (7)$$
Hydrolysis of ferrous and ferric ions:
$$Fe^{+2} + OH^- \rightarrow Fe(OH)^+ \qquad (8)$$
$$Fe^{+3} + OH^- \rightarrow Fe(OH)_2^+ \qquad (9)$$

Generation of ferrihydrate intermediate:
$$2Fe(OH)_2^+ + Fe(OH)^+ + 3OH^- \rightarrow \qquad (10)$$
$$(Fe^{+3})_2(Fe^{+2})(OH^-)_8$$
Dehydration of ferrihydrate, forming magnetite:
$$(Fe^{+3})_2(Fe^{+2})(OH^-)_8 \rightarrow Fe_3O_4 + 4H_2O \qquad (11)$$

Mass Balance

The batch reactor (Fig. 1) contained a sealed Teflon mercury-carbon contact chamber with 0.8 L/min headspace N_2 flow through an inlet/outlet port to an oxidizing $KMnO_4$ trap. The MPAC was applied at a 1g/L dose to 100ppb Hg-spiked DI ($Hg(NO_3)$) with a 180 minute contact time. Previous experimentation demonstrated a 90 minute contact time was required to reach pseudo-equilibrium. Total Hg was analyzed using cold vapor atomic adsorption spectroscopy (CVAA) and EPA method 245.1. Mass balance closure was calculated by quantifying residual aqueous mercury, adsorbed mercury, and volatilized mercury captured in the $KMnO_4$ trap. To quantify the adsorbed Hg, the MPAC was filtered from aqueous solution and subjected to three sequential HF digestions.
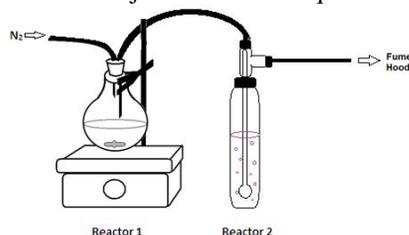

Fig. 1 Hg Mass Balance Batch Reactor

Results and Discussion

Prior to performing the Hg mass balance for adsorption onto MPAC, it was imperative to perform control runs. An air blank verified that the batch reactor was free from Hg contamination. A sorbent blank identified trace levels of Hg present in the MPAC (0.125μg Hg/ g MPAC). MPAC is synthesized using a coal-based commercially available activated carbon; coal is known to contain trace levels of Hg. A background analysis was performed by running spiked DI through the batch reactor in the absence of carbon. The analysis revealed the following: Hg volatilization occurs in the absence of carbon, quantifiable Hg residues form in test stand labware necessitating a HNO_3 rinse to fully quantify the residual Hg, and ~12% Hg is fugitive (Fig. 2). The fugitive Hg is likely due to mass and volume measurement errors amplified by the small scale of the experiment.
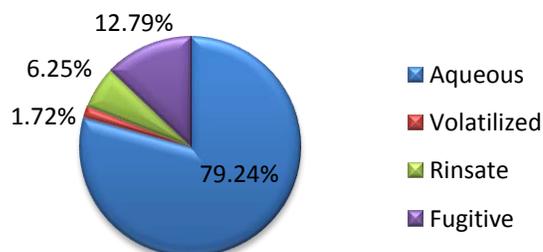

Fig. 2 Hg mass balance: Background

The Hg mass balance for Hg adsorption onto MPAC demonstrated that, at unadjusted pH (pH ~4), approximately 97% of the Hg is removed from aqueous solution with 17% volatilized and 60% adsorbed while 20% remains fugitive. The increase in volatilization relative to the background indicates that redox chemistry is involved. The higher fugitive Hg relative to the background is likely due to HF extraction inefficiency in quantifying the adsorbed Hg, mechanical loss of C resulting in lower Hg masses extracted in the HF digestion, and volumetric measurement errors amplified due to the small scale.
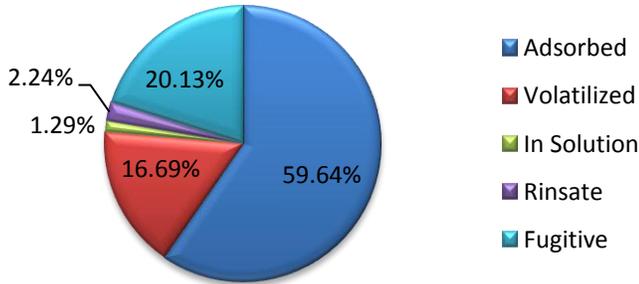

Fig. 3 Hg mass balance: 1:1 C:Fe MPAC

Conclusions

The batch reactor using N_2 flow and oxidizing volatilization trap was used to calculate the Hg mass balance for adsorption onto MPAC. The controls indicated no contamination of the test stand between runs. The sorbent blank revealed trace Hg in the MPAC. The background run demonstrated that quantifiable levels of Hg were removed from aqueous solution by volatilization, Hg residues remain in the test stand labware, and complete closure of Hg mass balance is difficult to achieve. The application of MPAC to 100 ppb spiked-DI results in 97% removal of Hg from aqueous solution with a 1g/L MPAC dose due to adsorption and volatilization. With 90% confidence, the mass balance of Hg has been closed to within ~20% by quantifying aqueous, adsorbed, and volatilized Hg. Future work will involve a pH study coupled with sequential chemical extraction to identify operational binding mechanisms

References

(1) Perez OP, Umetsu Y, Sasaki H. Precipitation and densification of magnetic iron compounds from aqueous solutions at room temperature. Hydrometallurgy 1998 NOV;50(3):223-242.