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## Influence of Activated Carbon Surface Oxygen Functionality on Elemental Mercury Adsorption from Aqueous Solution

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Abstract: Mercury (Hg), a naturally occurring element, is toxic and can lead to negative health impacts for humans and ecosystems. Activated carbon adsorption is effective in treating Hg-laden effluent for safe discharge. Wet chemical oxidation of activated carbon was performed to enhanced surface oxygen functionality, with the goal of enhancing aqueous ionic (Hg(II)) and elemental (Hg(0)) mercury adsorption. The modified carbons were characterized by nitrogen adsorption-desorption, point of zero charge, elemental analysis, and total acidity titration. The resulting characteristics of the surface oxygen modified carbons varied based on the nature of the modifying reagent and its concentration. The modified carbons were applied to trace level Hg solutions (50 µg/L). Hg(II) adsorption was strongly correlated with oxygen content of the C(O)-modified activated carbons, with the highest oxygen content associated with the highest Hg(II) removal. This correlation was not seen in Hg(0) adsorption. Rather, this data best fit a four variable model that identified surface area, pore volume, pH<sub>pzc</sub>, and oxygen content, with the pH<sub>pzc</sub> being the primary variable influencing results. At the experimental loading rate, no carbons leached Hg at levels requiring disposal as a hazardous waste. Kinetic models indicated both physisorption and chemisorption adsorption mechanisms.

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Lead author of review article (cited in my paper) on the topic of activated carbon surface modification

RE: Influence of activated carbon surface oxygen functionality on elemental mercury adsorption from aqueous solution

By: Emily K. Faulconer\*<sup>a,b</sup>, David W. Mazyck<sup>a</sup>

<sup>a</sup> Department of Environmental Engineering Sciences, University of Florida

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Dear Editor,

Please consider the manuscript "Influence of activated carbon surface oxygen functionality on elemental mercury adsorption from aqueous solution" (4,050 words, 3 tables, 4 figures) for possible publication as a Research Article in an upcoming issue of *Journal of Environmental Chemical Engineering*.

Your esteemed journal seems the ideal forum for a manuscript addressing surface chemistry modification and interface phenomena regarding aqueous elemental mercury adsorption. The known effects of mercury in the environment and the challenges that exist in reaching low effluent concentrations in Hg-contaminated industrial wastewater demonstrate the environmental importance of research in Hg removal technologies. Although enhancement of surface oxygen functionality of activated carbon is not novel, its influence on aqueous elemental mercury has not been investigated. Additionally, this paper discusses the influence of water cluster formation on aqueous mercury adsorption, which is not previously addressed in the literature. I trust, therefore, that you will consider my manuscript to be appropriate for your readership.

This original piece has not been previously published in whole or in part by any of its authors nor has it been simultaneously submitted for publication elsewhere. Any comments and/or suggested revisions you provide are greatly appreciated. I would be honored to contribute to such an esteemed journal. I look forward to your decision.

Respectfully,  
Emily K. Faulconer, Ph.D.  
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### Conflict of Interest Declaration

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We further confirm that any aspect of the work covered in this manuscript that has not involved either experimental animals or human patients.

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**Influence of activated carbon surface oxygen functionality on elemental mercury adsorption from aqueous solution**

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1 Abstract

2  
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5 humans and ecosystems. Activated carbon adsorption is effective in treating Hg-laden effluent for safe  
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7 discharge. Wet chemical oxidation of activated carbon was performed to enhanced surface oxygen  
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11 adsorption. The modified carbons were characterized by nitrogen adsorption-desorption, point of zero  
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13 charge, elemental analysis, and total acidity titration. The resulting characteristics of the surface oxygen  
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19 correlated with oxygen content of the C(O)-modified activated carbons, with the highest oxygen content  
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21 associated with the highest Hg(II) removal. This correlation was not seen in Hg(0) adsorption. Rather,  
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23 this data best fit a four variable model that identified surface area, pore volume, pHpzc, and oxygen  
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25 content, with the pHpzc being the primary variable influencing results. At the experimental loading rate,  
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39 Keywords: Activated carbon, mercury, adsorption, surface oxygen  
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## 1. Introduction

Mercury (Hg), a volatile toxic heavy metal, can enter the aqueous environment from anthropogenic and natural sources in both its ionic and elemental form. Due to its listing as a toxic pollutant under section 307(a) of the Clean Water Act (CWA), site-specific technology-based aqueous Hg effluent limits are regulated through the National Pollutant Discharge Elimination System (NPDES) permitting system. Treatment of mercury-contaminated wastewater remains a challenge, particularly due to the very low allowable effluent concentrations required in order to remain within the Total Maximum Daily Load (TMDL) for an impaired water. The U.S. Environmental Protection Agency (EPA) has determined the water quality criteria for the protection of wildlife and for the protection of human health to be 1.3 ng/L and 1.8 ng/L, respectively [1,2].

Sulfide precipitation, capable of achieving a minimum effluent of 10-100 ppb Hg, is a common remediation method for Hg-laden wastewater from industries such as chlor-alkali facilities and coal-fired power plants utilizing flue gas desulfurization (FGD) [3]. The organosulfides react to form insoluble metal-sulfides but these compounds are difficult to collect from the wastewater, often necessitating the use of coagulants [4]. The reducing conditions of sulfide precipitation may be ineffective for insolubilizing elemental Hg. In anticipation of new and more stringent water quality based standards, adsorption can be used as a polishing technique to reach lower mercury concentrations in industrial wastewater effluent [5]. Activated carbon is known to adsorb Hg(II) from aqueous solutions [6-16] and Hg(0) from the air phase [17-21]. It is unknown how well activated carbon adsorbs aqueous elemental mercury.

Carbon-oxygen groups, C(O), on the activated carbon surface have a demonstrated influence on aqueous Hg(II) adsorption [8]. Vapor phase research implicates C(O) complexes in Hg(0) adsorption [18,22]. Li et al. [11] proposed that C(O) complexes, particularly the reducible lactone and carbonyl groups, are the possible active sites for Hg(0) adsorption, potentially involving electron transfer from the Hg(0) to the lactone or carbonyl followed by subsequent adsorption of Hg(II) through well studied



1 mechanisms. Adsorbed Hg(0) was desorbed as Hg(II), lending support to the oxidation hypothesis. In a  
2  
3 theoretical study, Liu et al. [23] concluded that lactone and carbonyl favor Hg(0) adsorption, while phenol  
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5 and carboxyl reduce Hg(0) capture. The role of C(O) complexes in aqueous Hg(0) adsorption is not  
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7 defined in literature.  
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10 It is possible to tailor the nature and concentration of C(O) groups to increase the adsorption capacity  
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12 and selectivity for certain contaminants [8,23-31]. C(O) groups can be formed through wet chemical  
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14 oxidation using reagents such as nitric acid and hydrogen peroxide, with the amount of oxygen gained  
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16 dependent upon the method and the precursor used [24-29,32,33]. While wet chemical oxidations are  
17  
18 generally thought to minimally alter other surface chemistry characteristics such as pore size distribution,  
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20 several researchers have found that concentrated nitric acid oxidation reduced the BET surface area and  
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22 total pore volume while the pore width increased due to pore collapse [28,34].  
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27 In this work, aqueous adsorption of Hg(II) and Hg(0) onto modified activated carbon was studied in a  
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29 batch system with respect to the following carbon modification variables: modifying reagent, reagent  
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31 concentration, and activated carbon. The goal of this study was to elucidate the influence of C(O) on  
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33 aqueous Hg(0) adsorption. The objectives of this study are as follows: increase acidic C(O) on activated  
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35 carbon surfaces with minimal pore degradation, and determine which experimental conditions yield the  
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37 highest removal of aqueous mercury (Hg(II) and Hg(0)) between two types of powdered activated carbon.  
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## 42 **2. Experimental**

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44 **2.1 Materials.** All solutions were prepared using ultrapure Type I water with a resistivity of 18.2 MΩ and  
45  
46 a conductivity of 0.055 μS. Two commercially available carbons were oven-dried at 100°C for a minimum  
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48 of 24 h prior to use. Calgon WPH is a steam-activated powdered activated carbon made from bituminous  
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50 coal with a surface area of 1020 m<sup>2</sup>/g. Norit CASPF is a wood-based chemically activated powdered  
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52 activated carbon with a surface area of 1200 m<sup>2</sup>/g. Carbon modifying solutions were prepared by diluting  
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54 concentrated HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and NaOH (Fisher Scientific).  
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59 Hg(II) solutions were prepared by diluting 1000 mg/L stock Hg(NO<sub>3</sub>)<sub>2</sub> (Fisher scientific) in ultrapure  
60  
61 water. Hg(0) solutions were prepared by heating metallic mercury under N<sub>2</sub>(g) flow and bubbling the Hg-  
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1 laden N<sub>2</sub>(g) through N<sub>2</sub>(g)-purged ultrapure water. Elemental mercury solubility is reported to range from  
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3 10 µg/L to 64 µg/L [35-37]. The elemental mercury was pre-rinsed with 0.1M HNO<sub>3</sub> and ample ultrapure  
4  
5 water to remove any oxidized Hg compounds from the surface [35,37].  
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8 To capture volatilized Hg, the oxidizing purge trap was prepared using 4% w/v KMnO<sub>4</sub> (Fisher  
9 Scientific) in 10% H<sub>2</sub>SO<sub>4</sub> (Fisher Scientific). According to EPA method 245.1, the heated digestion for  
10 Hg quantification was performed using concentrated HNO<sub>3</sub> (Fisher Scientific), concentrated H<sub>2</sub>SO<sub>4</sub>  
11 (Fisher Scientific), 5% w/v KMnO<sub>4</sub>, 5% w/v K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Fisher Scientific), and 12% w/v NaCl-  
12 hydroxylamine sulfate solution (Fisher Scientific).  
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20 Solutions to determine the total acidity of the carbons were prepared by diluting concentrated NaOH,  
21 HCl, and H<sub>2</sub>SO<sub>4</sub> to 0.05 N, 0.05 N, and 0.1 N, respectively.  
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25 **2.2 Carbon modification.** Commercially available carbons were modified at room temperature by  
26 exposure to 1 M, 5 M, and 10 M solutions of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and NaOH for 6 h. Samples were then rinsed  
27 with ultrapure water until constant water contact pH. As a control, a sample of the virgin WPH carbon  
28 was stripped of its surface oxygen groups at 950°C under 150 mL/min H<sub>2</sub>(g) flow for 180 min [11,38].  
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66 The modification process has the potential to form humic substances which may block adsorbent  
67 porosity, reducing Hg adsorption. A humics removal wash of 0.1 M NaOH followed by a 0.1 M HCl rinse  
68 was investigated [24].  
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1 Nomenclature for the materials is based on the activated carbon used and both the concentration and  
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3 the identity of the modifying reagent. Nitric acid, sulfuric acid, and sodium hydroxide modified carbons  
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5 are identified as NAC, SAC, and SHAC, respectively. For example, CASPF carbon that was modified  
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7 with 5 M HNO<sub>3</sub> is represented as CASPF NAC-5M. The H<sub>2</sub>(g) stripped carbon is identified as ACH.  
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10 **2.3 Carbon characterization.** The adsorbent surface area was measured by a surface area analyzer  
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12 (Quantachrome Instruments NOVA 2200e). Each sample was outgassed at 110°C for 24 h before being  
13  
14 placed in a -196°C liquid N<sub>2</sub> bath with N<sub>2</sub>(g) adsorbate. The surface area of each carbon was calculated  
15  
16 by the Brunauer-Emmett-Teller (BET) equation [40]. Using the adsorption isotherm, the pore size  
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18 distributions over the mesopore region were calculated using the Barrett-Joyner-Halenda (BJH) equation  
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20 [41].  
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24  
25 The point of zero charge was determined using the abbreviated method (10% by weight). Ultrapure  
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27 water was purged with N<sub>2</sub>(g) for 20 min before carbon addition for a 24 h contact time, after which the  
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29 solution pH was obtained in duplicate under N<sub>2</sub>(g) flow.  
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33 Carbon samples were prepared for total acidity and basicity titration by adding 0.5g carbon and 0.1 g  
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35 KCl to 25 mL of 0.05 N NaOH and 0.05 N HCl, respectively, and rotating end-over-end for 48 h [42].  
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37 Blank solutions were prepared using 25 mL 0.05 N NaOH and 0.05 N HCl each with 0.1g KCl. After the  
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39 elapsed contact time, carbon solutions were filtered using 0.45 μm mixed cellulose filters (Fisher  
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41 Scientific). Filtrate was purged with N<sub>2</sub>(g) for 10 min prior to titration. 0.05 N NaOH samples were titrated  
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43 with 0.1 N H<sub>2</sub>SO<sub>4</sub> while 0.05 N HCl solutions were titrated with 0.05 N NaOH. The pH was measured  
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45 under N<sub>2</sub>(g) flow, using pH 4.5 and 11 as endpoints, respectively. Total acidity was calculated as the  
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47 difference between the volume of titrant consumed in the sample titrations versus the volume of titrant  
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49 consumed in the appropriate blank titrations with the difference being due to neutralization of surface  
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51 functional groups.  
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56  
57 Moisture content of the carbons was determined by the mass difference before and after heating at 90°C  
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59 for 16 h. Ash content was determined by the mass difference after heating to 650°C for 16 h. Elemental  
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1 composition (C, H, N) was determined by a Carlo Erba EA 1108 elemental analyzer. Assuming negligible  
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3 presence of other elements, oxygen content was determined by mass difference.  
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5  
6 **2.4 Adsorption experiments.** The batch reactor contained a sealed Teflon mercury-carbon contact  
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8 chamber with 0.8 L/min headspace  $N_2(g)$  flow through an inlet/outlet port to an oxidizing purge trap. All  
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10 Hg(0) experiments were performed in a glove bag under  $N_2(g)$  flow. The carbons were applied as a slurry  
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12 at a 1g/L dose to 50  $\mu\text{g/L}$  Hg-spiked ultrapure water for a 30 s contact time. After the specified contact  
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14 time, the adsorbent was separated via vacuum filtration using 0.45 $\mu\text{m}$  mixed cellulose filter (Fisher  
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16 Scientific). Samples were stored by acidifying to under pH 2 using 0.5 mL  $HNO_3$  and 1mL  $H_2SO_4$ .  
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20 Mercury concentrations were measured using EPA digestion method 245.1 and cold vapor atomic  
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22 adsorption spectroscopy (Teledyne Hydra Atomic Absorption Mercury Analyzer). The operating method  
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24 detection limit was determined to be 0.4  $\mu\text{g/L}$ .  
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28 **2.5 Data Analysis.** All experiments were performed in triplicate and average values reported with all  
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30 replicate data falling within the 95% confidence interval. Error bars represent the standard error of the  
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32 mean. Visual MINTEQ 2.61, a chemical equilibrium model, was used to calculate metal speciation,  
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34 complexation reactions, and solubility equilibria. Linear regression and ANOVA analyses were  
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36 performed using the statistical software R, version 2.14.1.  
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### 39 40 **3. Results**

41  
42 **3.1 Adsorbent Characterization: Porosity.** Nitrogen adsorption-desorption isotherms were analyzed to  
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44 produce BET surface area, average pore diameter, and total pore volume data (Table 1). Consistent with  
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46 literature, the  $H_2(g)$  stripping process did not negatively influence porosity [39]. Also consistent with the  
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48 literature, nitric acid modified samples exhibited progressive porosity damage with increasing  
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50 concentration. Conversely, sulfuric acid and sodium hydroxide modifications did not result in damage to  
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52 porosity. The humics removal wash did not significantly influence the adsorbent porosity (coefficient of  
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54 variation (CV) of only 0.4%) and thus was not applied to carbon samples. The NAC, SAC, SHAC, and  
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56 ACH carbons exhibited similar BJH pore size distributions to the virgin WPH carbon (Figure 1). The  
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58 treatment of CASPF carbon impacted porosity similarly to the WPH modification.  
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Table 1: Characterization of various C(O) modified carbons

Sample	Surface area (m <sup>2</sup> /g)	Pore Size (Å)	Pore Volume (cm <sup>3</sup> /g)	% N	% O	pHpzc	Total acidity (meq/g)
WPH	1020	11.2	0.55	0.0%	6.9%	8.36	85
ACH	1044	15.0	0.90	0.0%	1.9%	10.10	11
WPH NAC-1M	991	11.2	0.58	0.0%	8.4%	6.56	94
WPH NAC-5M	978	11.0	0.55	0.6%	15.8%	5.02	139
WPH NAC-10M	878	11.0	0.54	0.5%	19.6%	3.99	231
WPH SAC-1M	975	11.1	0.49	0.4%	6.1%	3.78	112
WPH SAC-5M	989	11.1	0.55	0.3%	5.9%	3.90	112
WPH SAC-10M	975	11.2	0.50	0.3%	10.5%	3.36	118
WPH SHAC-1M	994	11.1	0.54	0.4%	3.8%	7.37	60
WPH SHAC-5M	1000	11.1	0.55	0.4%	5.1%	7.25	64
WPH SHAC-10M	1001	11.1	0.54	0.4%	6.3%	7.13	70
CASPF	1201	11.0	0.91	0.0%	19.8%	1.93	293
CASPF NAC-10M	817	11.7	0.51	2.4%	21.2%	2.83	425
CASPF SAC-10M	1269	11.8	0.93	0.1%	13.8%	2.77	278

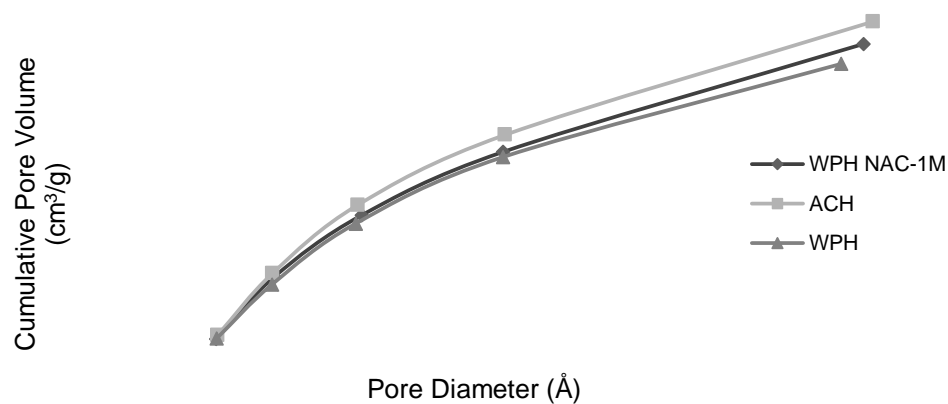


Figure 1: BJH pore size distribution of select C(O) modified carbons

1 **3.2 Adsorbent Characterization: Surface Oxygen Functionality.** With a basic  $\text{pH}_{\text{pzc}}$  and a relatively  
2  
3 low oxygen content, the total acidity of WPH carbon was expectedly low, at only 85 meq/g (Table 1). On  
4  
5 the contrary, CASPF carbon displayed an acidic  $\text{pH}_{\text{pzc}}$  and a higher oxygen content, resulting in higher  
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7 total acidity relative to WPH. The control carbon, stripped of nearly all C(O), demonstrated a very basic  
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9  $\text{pH}_{\text{pzc}}$  and a total acidity near zero.  
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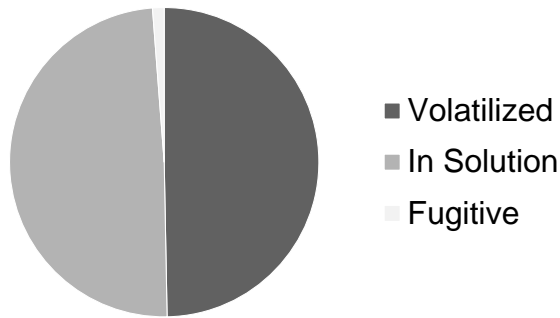
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13 In the modification of WPH with nitric acid, as the concentration increased, the oxygen content and  
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15 total acidity increased while the  $\text{pH}_{\text{pzc}}$  fell. Relative to 10 M  $\text{HNO}_3$  treatment, the 10 M  $\text{H}_2\text{SO}_4$  treatment  
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17 was less effective at adding surface oxygen groups, seen in the reduced oxygen content and the lower  
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19 total acidity. Interestingly, the  $\text{pH}_{\text{pzc}}$  of SAC-10M was slightly lower than NAC-10M for both WPH and  
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21 CASPF carbons. Also note the lack of response in SAC carbons to acid concentration: total acidity,  $\text{pH}_{\text{pzc}}$ ,  
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23 and oxygen content remain relatively stable. Modification with NaOH exerted little influence on the  $\text{pH}_{\text{pzc}}$ ,  
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25 oxygen content, and total acidity.  
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31 The CASPF modified carbons interestingly showed an increase in the  $\text{pH}_{\text{pzc}}$  upon modification  
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33 though the values remained very acidic. Modification with 10 M  $\text{HNO}_3$  resulted in an oxygen content of  
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35 21.2% and a high total acidity of 425 meq/g, a 37% increase from raw CASPF carbon. Modification with  
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37 10 M  $\text{H}_2\text{SO}_4$  actually reduced the oxygen content and total acidity relative to the raw CASPF carbon.  
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40 **3.3 Batch Testing of Synthetic Waters.** Prior to performing the Hg adsorption experiments, it was  
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42 imperative to identify potential sources of error. An air blank was performed on the test stand with only  
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44 ultrapure water in the mercury-carbon contact chamber to verify that the batch reactor was free from  
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46 residual Hg contamination. Reagent blanks verified all solutions and ultrapure water were free from trace  
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48 levels of mercury. A sorbent blank identified trace levels of Hg present in the virgin carbons with WPH  
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50 containing 0.13  $\mu\text{g}$  Hg/g and CASPF containing 0.071  $\mu\text{g}$ /g. This background level was not shown to  
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52 influence aqueous or volatilized Hg levels.  
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56  
57 Due to the volatile nature of  $\text{Hg}(0)$ , it was important to understand the rate of volatilization in the  
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59 absence of carbon.  $\text{Hg}(0)$  adsorption experiments were performed at a 30 s contact time rather than  
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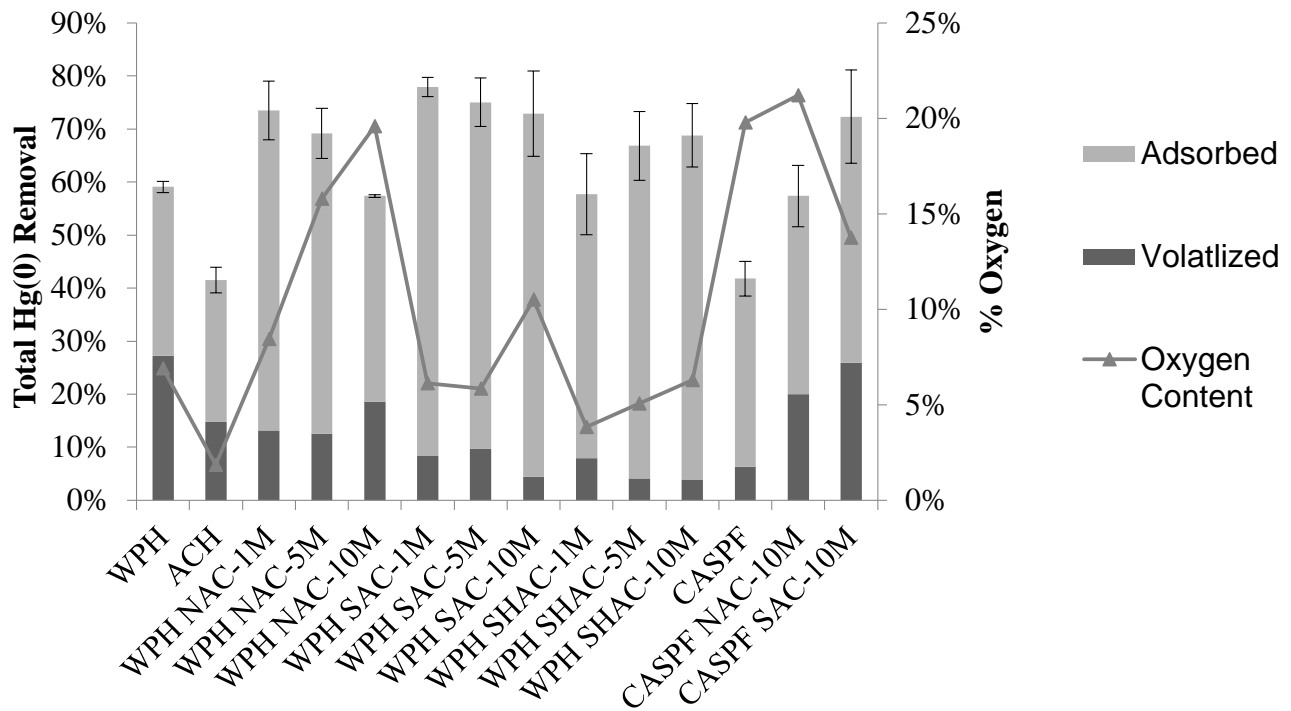
1 pseudo-equilibrium. Figure 2 demonstrates the highly volatile nature of the elemental Hg, with nearly  
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 3 50% volatilizing within the 30 s contact time. Only 1.2 % of the Hg(0) remained fugitive.  
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 19 Figure 2. Background Hg(0) mass balance for a 30 s contact time  
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22 The effects of the various modifications are reported in Fig. 3, where Fig. 3A shows the results with  
 23 aqueous Hg(II) and Fig. 3B shows the results with aqueous Hg(0).  
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27 A.



B.

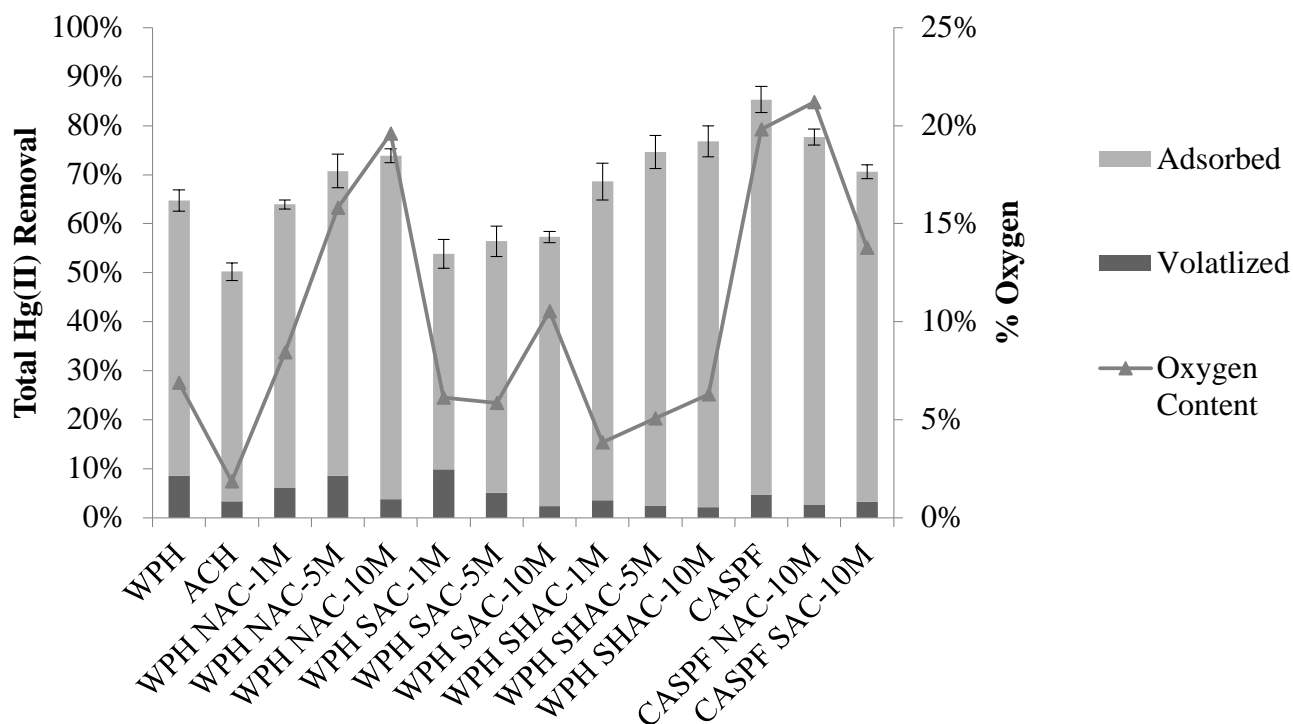
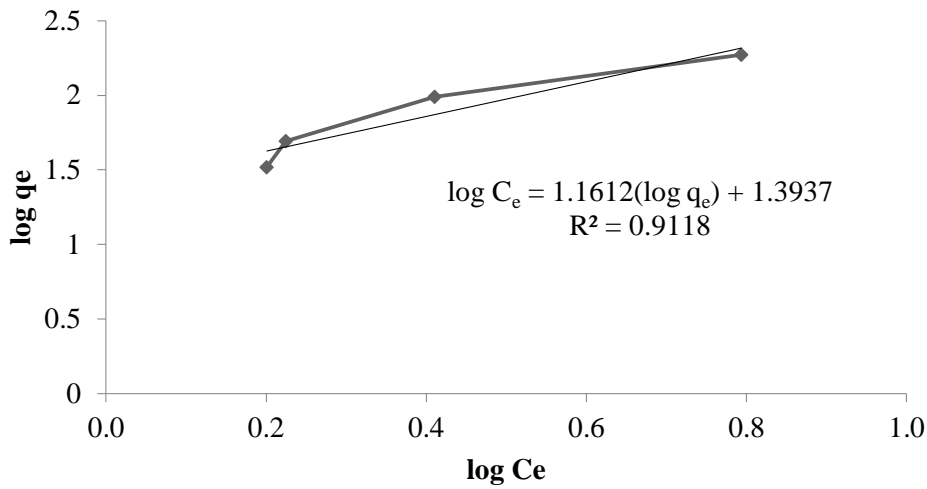


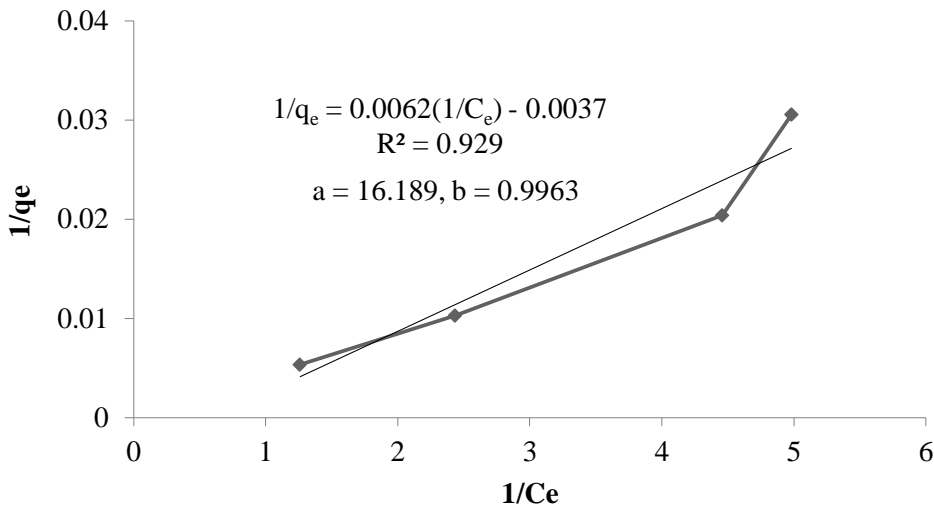
Figure 3. Hg(0) and Hg(II) removal through adsorption and volatilization for various surface-modified carbons

The effect of the dose of C(O) modified carbons on Hg(II) adsorption was investigated by varying the carbon dose (Figure 4). The good fitting of the experimental data to both models implied that both chemisorption and physisorption mechanisms took place in the adsorption system. The Freundlich term  $1/n$  was 0.86, indicating heterogeneity of the carbon surface and affinity of the adsorbate for the adsorbent, resulting in favorable adsorption of Hg(II).





A.



B.

Figure 4. A) Freundlich and B) Langmuir isotherms of Hg(II) adsorption by NAC-1M

The mobility of Hg(II) once adsorbed to the surface modified carbons was investigated using the standardized TCLP test (Table 2). After loading the carbons with 100  $\mu\text{g Hg/g C}$ , the effluent remained well under the regulated limit of 200  $\mu\text{g/L}$  for all carbons tested.

Table 2. Hg leaching from various carbons under landfill conditions

Sample	Effluent ( $\mu\text{g Hg}$ )	Hg leaching ( $\mu\text{g Hg/g C}$ )

1	ACH	8.4	16.7
2			
3	WPH	6.9	13.8
4			
5	CASPF	31.2	62.2
6			
7	NAC-10M	36.1	72.2
8			
9	SAC-10M	54.1	107.8
10			
11	SHAC-10M	11.4	22.7
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16 The unadjusted matrix pH ranged between 4.4 and 4.7. Using Visual MINTEQ 2.61, the mercury

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18 speciation in the given matrix conditions was predicted to be 96.5-99%  $\text{Hg}(\text{OH})_2$  and 1-3.5%  $\text{HgOH}^+$ .

19

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21 The pH of the aqueous solution varied by the modification of the carbon (Table 3). The more basic systems

22

23 contained Hg primarily as  $\text{Hg}(\text{OH})_2$  while the more acidic systems contained Hg in various states of

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25 hydrolysis, including  $\text{Hg}^{2+}$ ,  $\text{HgOH}^+$ , and  $\text{Hg}(\text{OH})_2$ .  $\text{Hg}(\text{OH})_2$  was likely removed due to preferential

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27 precipitation onto the carbon surface. For the systems with a pH below the point of zero charge, the carbon

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29 surface was positively charged Hg cations had to overcome electrostatic repulsion in order to ion exchange

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31 with  $\text{H}^+$  on the carbon surface. All Hg species had the potential to undergo physisorption.

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36 Table 3. Variation of Hg-DI contact pH with  $\text{pH}_{\text{pzc}}$  of C(O) modified carbons

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38	Sample	Hg-DI Contact
39		pH
40	CASPF	2.86
41		
42	WPH	5.90
43		
44	ACH	7.20
45		
46	NAC 1M	4.50
47		
48	NAC 5M	3.40
49		
50	NAC 10M	3.10
51		
52	SAC 1M	3.08
53		
54	SAC 5M	3.11
55		
56	SAC-10M	2.99
57		
58	SHAC 1M	5.50
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1	SHAC 5M	5.36
2		
3	SHAC 10M	5.21
4		
5	CASPF SAC10M	2.86
6		
7	CASPF NAC10M	2.89
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#### 4. Discussion

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Increasing concentration of the reagent for wet chemical oxidation of WPH increased Hg(II) adsorption (Figure 3). Virgin WPH carbon performed fairly well for Hg(II) removal, with this performance being reduced by several of the modifications investigated. This could be due, in part, to water cluster formation. Acidic C(O) groups tend to adsorb water by hydrogen bonding and dispersion forces, followed by clustering of additional water molecules at these adsorption sites [43]. These water clusters can block adsorbate access to the activated carbon porosity [44]. Studies have shown a drop in adsorption capacity with an increase in the amount of C(O) groups, evidence of the water adsorption effect [45,46]. As a basic carbon low in surface oxygen functionality, water cluster formation would be minimal for virgin WPH.

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When virgin WPH was applied to Hg(0) adsorption, relatively high levels of volatilization occurred. SAC and SHAC carbons achieved high levels of Hg(0) adsorption with minimal losses through volatilization. Volatilization from NAC systems was intermediate. The annealed carbon, with the lowest oxygen content, displayed the lowest Hg (0) and Hg(II) removal.

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Due to the multitude of variables that can influence adsorption, the influence of one specific variable requires regression analysis. A t-test with a significance level of  $\alpha = 0.05$  revealed oxygen content as a good regression parameter for Hg(II) adsorption (p-value = 0.00328) but the same does not hold true for Hg(0) adsorption (p-value = 0.28850). As Hg(0) is uncharged, it is possible that there are not sufficient attractive forces to overcome the pore blocking effect due to water cluster formation. Although the speciation in the Hg(II) system exists primarily as the uncharged Hg(OH)<sub>2</sub>, the carbon particles serve as nucleation points for the precipitation of solid Hg(OH)<sub>2</sub> which may be able to overcome the pore blocking of the water clusters.

1 Hg(II). A t-test revealed that surface area alone was poorly correlated to Hg(II) removal, with an R<sup>2</sup>  
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3 value of 0.004. An ANOVA test on the influence of surface area, pore size, and pore volume on Hg(II)  
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5 removal revealed that pore volume had significantly more influence than surface area and pore size, with  
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7 a sums of squares value of 569.75 compared to 5.31 and 97.47, respectively.  
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10 The two-variable model that best fits the Hg(II) removal data indicates oxygen content and pH<sub>pzc</sub> as  
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12 important variables, resulting in an R<sup>2</sup> value of 0.499. An ANOVA test indicated oxygen content to be the  
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14 primary variable influencing adsorption with sums of squares of 666.82 while the pH<sub>pzc</sub> sums of squares  
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16 was only 62.06.  
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20 Surface area also poorly correlated to Hg(0) removal, with an R<sup>2</sup> value of 0.093. A t-test analysis of the  
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22 influence of surface area, pore size, and pore volume on Hg(0) removal resulted in a negative adjusted  
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24 R<sup>2</sup>, making an ANOVA test impractical.  
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28 The best regression model to fit the Hg(0) data indicates that surface area, pore volume, surface oxygen  
29  
30 functionality, and the point of zero charge as important variables, resulting in an R<sup>2</sup> value of 0.5886. The  
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32 t-test identified the pH<sub>pzc</sub> as a good regression parameter (>95% confidence). An ANOVA test indicated  
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34 the point of zero charge as the primary variable influencing adsorption with sums of squares of 1041.72.  
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36 As no model using the measured variables achieved a strong R<sup>2</sup> value, it is possible that an unquantified  
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38 variable was influencing the results of both Hg(II) and Hg(0) adsorption.  
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42 Three kinetic models were investigated for Hg(II) adsorption by NAC-1M (Figure 5). The plot of q<sub>t</sub> vs  
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44 t<sup>1/2</sup> is fairly linear for ACH, NAC-1M, SAC-1M, and SHAC-1M, with R<sup>2</sup> values of 0.7596, 0.7892,  
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46 0.8938, and 0.8322, respectively. The linearity of the experimental data indicated that intraparticle  
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48 diffusion may be a rate limiting step in these systems. The ACH carbon demonstrated immediate uptake  
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50 of Hg(II) at a much higher capacity than the other carbons, likely due to the absence of surface oxygen  
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52 groups and therefore an absence of water clusters on the adsorbent surface. Interestingly, the adsorption  
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54 capacity decreased as time progressed. This may be due to competitive adsorption between Hg(II) and  
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56 H<sub>2</sub>O for the available adsorption sites on the carbon surface where equilibrium with water proceeds slower  
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58 than with Hg, thus the decrease in Hg adsorption capacity as equilibrium is approached.  
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1 The applicability of the pseudo-first order and pseudo-second order models was assessed by comparing  
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3 the  $R^2$  values of the linear plots. Due to the negative slope of ACH, it could not be assessed for pseudo-  
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5 first order kinetics. NAC-1M, SAC-1M, and SHAC-1M all fit the pseudo-first order model with  $R^2$  values  
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7 of 0.9188, 0.9822, and 0.8975, respectively. Even so, the data showed a stronger fit with the pseudo-  
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9 second order kinetic model, with  $R^2$  values higher than 0.99, indicating that chemisorption played a large  
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11 role in Hg(II) removal. The p-values for the slopes were very low, ranging from  $1.2 \times 10^{-5}$  to  $6.7 \times 10^{-7}$ .  
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15 Aqueous Hg(0) can undergo physisorption. Literature indicated that C(O) groups influenced vapor  
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17 phase Hg(0) adsorption. The lack of correlation of Hg adsorption with C(O) does not support this  
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19 occurrence in the aqueous phase. Ideally, individual surface oxygen groups would be quantified in order  
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21 to determine their specific relationship, if any, to adsorption.  
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## 25 **5. Conclusions**

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27 Acidic surface oxygen functionality was increased on activated carbon surfaces by wet chemical  
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29 oxidation using HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and NaOH. Nitric acid modification produced the most surface oxygen  
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31 groups but resulted in slight damage to porosity. Sulfuric acid and sodium hydroxide modification did not  
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33 damage porosity but were less effective than nitric acid at increasing the surface oxygen functionality.  
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38 Oxygen content and pH<sub>pzc</sub> were shown to be important variables in Hg(II) adsorption. Hg(0) adsorption  
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40 data best fit a four variable model, indicating that surface area, pore volume, surface oxygen functionality,  
41  
42 and the pH<sub>pzc</sub> as good regression parameters, with the pH<sub>pzc</sub> as the primary variable influencing the results  
43  
44 rather than oxygen functionality. As neither model achieved a strong  $R^2$  value, it is possible that an  
45  
46 unquantified variable influenced these results. Due to the uncharged nature of Hg(0), water cluster  
47  
48 formation due to C(O) groups, may have limited adsorption. It appears that a moderate amount of surface  
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50 oxygen groups are optimal for Hg(0) adsorption from aqueous solution.  
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55  
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57  
58 the success of this project. For assistance in the laboratory, we thank Andrew Nelson.  
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