Effectiveness of gold nanoparticle-coated silica in the removal of inorganic mercury in aqueous systems: Equilibrium and kinetic studies

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Abstract
The adsorption of inorganic mercury, Hg(II), in aqueous solution has been investigated to evaluate the effectiveness of synthesized gold (Au) nanoparticle-coated silica as sorbent in comparison with activated carbon and Au-coated sand. The synthesis of the Au-coated silica was confirmed by x-ray diffraction (Bragg reflections at 38.2°, 44.4°, 64.6°, and 77.5°) and the Au loading on silica surface was 6.91 ± 1.14 mg g⁻¹. The synthesized Au-coated silica performed an average Hg adsorption efficiency of ~96 (± 2.61) % with KD value of 9.96 (± 0.32) L g⁻¹. The adsorption kinetics of Hg(II) on to Au-coated silica closely follows a pseudo-second order reaction where it is found out to have an initial adsorption rate of 4.73 µg g⁻¹ min⁻¹ and overall rate constant of 4.73 x 10⁻⁴ g µg⁻¹ min⁻¹. Au-coated silica particles are effective in removing Hg(II) in aqueous solutions due to their relatively high KD values, rapid adsorption rate, and high overall efficiency that can even decrease mercury levels below the recommended concentrations in drinking water.

Keywords: Adsorption, Gold-nanoparticles, Mercury, Silica, Sorbents, Synthesis
1. Introduction

Mercury contamination and its removal in ecosystems constitute the core of various research studies in the past decades. Among the trace heavy metal contaminants, mercury has caught much attention because it is readily and persistently distributed in all media, such as air, water, particles, and biota with potential high toxicity [1]. The alarming increase in the presence of Hg in the environment is attributed to the increased anthropogenic activities such as large-scale combustion of coal in several power plants [2] and artisanal and small-scale gold mining [3]. Mercury exists in several states; as gaseous elemental mercury (Hg$^0$), particulate mercury (Hg$_n$), water-soluble, oxidized mercurous (Hg$_2^{2+}$) and mercuric mercury (Hg$^{2+}$) [4]. Elemental, organic, or inorganic forms of mercury are coverted to mercuric mercury when ingested, and can travel through the blood stream and may remain in the brain indefinitely instead of being slowly eliminated by the kidneys [5]. The Hg species can be present as methylmercury such as CH$_3$Hg$^+$ which can be readily bioaccumulated in organic tissues and can be biomagnified increasing the concentration of mercury to dangerous levels in organisms belonging to the higher orders in the food chain [6].

The effective removal of mercury in wastewaters and in the ecosystem has therefore been the target of several researches in the field of environmental science and engineering. The US Environmental Protection Agency has set the maximum level of mercury contamination in drinking water at 2 µg L$^{-1}$ [7]. Commercially available materials being used for Hg removal include activated carbon, zeolites, and clays [8]. These materials in general have small surface areas, and poor selectivity for mercury, not to mention costly, that is why alternative materials for Hg extraction are continuously being tested. Such materials involve chemically treated composites of zeolites, clays, and mesoporous silica, bio sorbents, MOFs and several polymers [9].
Among those sorbents, mesoporous silica is an attractive material to utilize for sorption studies owing to its surface area being available in a wide range (200-1500 m$^2$ g$^{-1}$), its highly porous structure, and high level of uniformity [9] which allows good accessibility to active centers impregnated along its inner surface. Mesoporous silica is made more effective via several methods which include impregnation, post-synthesis chemical treatment, and co-condensation in the presence of a template. The chemicals being treated onto silica surfaces vary depending on the target contaminants. Gold exhibits a unique catalytic nature and action when it is deposited as nanoparticles on a variety of metal oxides [10]. Gold also forms an amalgam with mercury and this is the principle being used in several gold extraction processes using mercury such as mining. By using the same principle, it would therefore be useful to use gold in collecting mercury from aqueous solutions.

Hence, the objectives of the study are to synthesize and perform characterization techniques on Au-coated silica and to evaluate the effectiveness of gold-coated silica for Hg (II) uptake in aqueous solutions by comparing adsorption efficiency and partition coefficients with commercially available activated carbon and synthesized Au-coated sand. The adsorption behavior of silica will also be studied in the presence of strong contending ions such as Cl$^-$ and several cations (Cu, Mg, Zn), simulating natural water conditions. A kinetic study will also be performed to further describe the rate of Hg (II) adsorption onto the sorbent systems.

2. Materials and Methods

2.1. Synthesis of Au-Coated Sand and Silica

The modified procedure for the synthesis of the Au-coated sorbents was patterned from the study of Leopold et al. [11]. Pure silica (chromatography grade, Fisher Scientific) of 60Å pore size and 70-100 µm particle diameters was acid-washed and dried. Then 5.0 g was
weighed and added to a solution of 40 mL of 1000 mg L\textsuperscript{-1} Au\textsuperscript{3+} stock solution in acid-washed amber bottles. The suspension was constantly mixed using a magnetic stirrer at room temperatures and the pH was adjusted to 7.5 using 7 M NaOH solution and 1 M HCl. pH adjustment is important since colloidal gold particles form in pH <7 while Au\textsuperscript{3+} is reduced to Au\textsuperscript{0} and agglomerates in pH >8. After the pH adjustment, 10 mL of 0.22 M NH\textsubscript{2}OH·HCl (analytical grade) was added to reduce Au\textsuperscript{3+} to Au\textsuperscript{0}. The creation of a dark and cloudy suspension indicated gold reduction on silica particles. The container was then sealed and left inside an orbital shaker for 12 hours. The container was removed and the particles were allowed to settle for 12 hours after which the supernatant was removed. The particles were re-suspended in deionized water and the supernatant was decanted. This was done a total of 10 times to ensure the removal of colloidal particles and excess ions from the pH adjustment reagents. The purple-red particles were then collected in a clear, glass container and oven-dried at 260\textdegree C for 4 h.

The same synthesis method was used for making the Au-coated sand particles. Silica sand (general purpose grade) was utilized in this study to observe if the structure and particle size of sorbents with similar chemical composition has a significant effect on Hg (II) removal. Sand has been used as an adsorbent particularly in dye removal due to its availability in nature [12]. The almost spherical sand, roughly around 500 – 1000 µm, was acid-washed for 24 hours, rinsed with deionized water, and oven-dried. After treatment, the au-coated sand particles were observed to be coarser and have a less intense purple-red color.

The synthesized Au-coated silica and untreated silica were then characterized using X-ray diffraction to confirm the presence of Au. The sample was ground and pressed into the sample holder to get a plain, uniform surface. The diffraction pattern was taken over 20 range of 0-90\degree, using RINT2000 wide angle goniometer in continuous scanning mode. SEM analysis was performed using a Hitachi S-4300 scanning electron microscope. A small
amount of the pure and gold-coated silica was spread on a carbon film strip which was placed on a small metal cylinder. The sample-loaded cylinder was then coated with metal film at a coating rate of 6.5 nm min\(^{-1}\). The coated sample was then loaded in the SEM chamber. The SEM was vacuum-treated to remove gas and the samples were viewed at different magnifications.

The concentration of Au deposited onto the sorbent surface was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave digestion. One hundred mg of the synthesized sorbents is added to 10 mL of concentrated HCl and HNO\(_3\) (7:1 v/v) solution in sample vessels. The samples underwent microwave digestion for 20 min. at 200 \(^\circ\)C and cooling time of 10 min. Dilution was then performed using 2\% HNO\(_3\) solution after which the samples were analyzed using ICP-OES.

### 2.2. Hg (II) Adsorption and Kinetic Study

Several working solutions were prepared with increasing Hg\(^{2+}\) concentrations (100 \(\text{ug L}^{-1}\) up to 300 \(\text{mg L}^{-1}\)) using HgCl\(_2\)\((s)\). The pH of the solutions was kept around 7.4 using HEPES buffer solution. A 100 mg of the granular activated carbon (chemical pure, Daejung Chemicals), Au-coated sand, and Au-coated silica was added to separate 43 mL of the working solutions. The reactors were tightly capped and placed in an orbital mixer for 24 h at room temperature (22\(^\circ\)C). The solutions were then centrifuged for 5 min at 2500 rpm to separate the solid from the liquid phase.

The Hg (II) remaining in the solution was then measured using procedure described in the EPA Method 1631 using Brooks-Rand TDM-II Dual-trap Desorption Module coupled with the Brooks-Rand Model III Atomic Fluorescence Spectrometry (AFS) [13]. Four bubbler glassware were filled with 100 mL ultrapure deionized water and 500 \(\mu\)L of SnCl\(_2\) was used to reduce any trace mercury in the solution with continuous purging of high purity N\(_2\) gas for
15 minutes. Then, another 500 µL of SnCl₂ was added for further reduction and the system was purged with N₂ gas for 5 min and after that, increasing mass in 50, 100, 150, 200 pg of Hg(II) using 1 µg L⁻¹ HgCl₂ standard were introduced in the bubblers. The same volume of SnCl₂ was added to the solutions in the bubbler and the reduced mercury, Hg (0), was continuously collected in gold sand traps (BrooksRand) for 15 min. A singular peak for Hg was obtained between 1-2 min of heating the trap at 10.94 mV. The peak intensities were measured using AFS with Argon as the carrier gas (35-40 mPa) and calibration curves were established. Sample analysis was done using the same method described in the previous paragraph however 1 mL of 4 M NH₂OH·HCl was added to the bubbler with 15 min purging time.

The kinetic experiments were done at room temperatures (22 ±1 ºC) in one Hg(II) concentration (10 mg L⁻¹) and 100 mg of sorbents. Mercury concentrations were measured before addition of the sorbents and at time intervals; 60, 120, 180, 240, 300, 360, 420, 480, 540, 600, and 1440 minutes. In between measurements, the samples were placed in an orbital mixer and the samples underwent centrifugation prior to volume extraction for Hg concentration measurement.

2.3. Effect of Other Ions in Hg (II) Adsorption

For the evaluation of the effect of strong contending ions to Hg (II) adsorption, the sorption experiment set-up was replicated with 1 M Cl⁻ as NaCl solution instead of deionized water. 0.1 M solutions of Cu (II), Mg (II), and Zn (II) from CuSO₄·5H₂O, anhydrous MgSO₄, ZnSO₄·7H₂O, respectively, were used to evaluate the effect of other cations in the solution. The solutions were placed in the orbital shaker for 24 hours and all solutions underwent centrifugation prior to the analysis. The pH of the solutions containing other cations was also
measured using ThermoFisher Orion™ Star A121 pH, mV and Temperature Portable Waterproof Meter.

3. Results and Discussion

3.1. Sorbent Characterization

The X-ray diffraction patterns (XRD) for untreated and gold-coated silica are shown in Figure 1. The four Bragg reflections at 38.2°, 44.4°, 64.6°, and 77.5° correspond to diffraction values of 111, 200, 220, and 311, face-centered cubic structures. The presence of the four peaks confirms the presence of Au on the surface of the synthesized silica particles. Another parameter that can be obtained using XRD data is the actual size of the gold particles on the silica surface using Debye-Scherrer equation [14]:

\[
L = \frac{\kappa \lambda}{\beta \cos \theta}
\]  

where \( L \) is the crystallite size of gold, \( \kappa \) is a constant (0.9), \( \lambda \) is the X-ray wavelength (Cu K\( \alpha = 1.5406 \)), \( \beta \) is the true half peak width, and \( \theta \) is the half diffraction angle of the centroid of the peak in degree. The success of coating gold onto the silica surface can be supported using the calculated particle size and their percentage abundance. The peak intensity from the XRD plot corresponds to the magnitude of gold particle size distribution. Integrating the roughly estimated particle sizes of the Au nanoparticles obtained from using equation 1 with the peak intensity shows that most Au nanoparticles fall into the 3.15 nm crystallite size (43.8%), followed by 3.23 nm (23.2%), 11.52 nm (17.3%), and the least fall into 45.83 nm (15.7%). The results indicate that smaller size gold nanoparticles comprise the majority of the particles on the surface of the silica and this could be due to the generally higher surface area of the smaller Au nanoparticles. The higher surface area allows more contact between silica and Au particles.
SEM Analysis was also performed on the pure and the Au-treated materials in order to study the topography of the synthesized sorbents and to confirm the presence or absence of gold nanoparticles on the surface of the samples. SEM images at 40x magnification shows the particle size difference of silica and sand which possibly accounts for the wide difference in the observed adsorption capacity of the two sorbents. The surface of the sorbents also displays a certain degree of porosity and unevenness that have increased their surface area, allowing for greater adsorptive capacity. Comparison of the sorbents at higher magnification (1000-5000x) (refer to Figure 2) revealed the presence of small particles dotted along the surface of the gold-coated silica while no such features were found on the untreated silica surface. This finding further supports the success of the deposition of gold particles on the surface of the treated sorbents. Some of the larger gold particles captured in the SEM images correspond to the largest computed diameter of the gold nanoparticles (approx. 50 nm) using XRD data. The smaller and more abundant particles captured in the SEM images account for the smaller calculated gold nanoparticles from XRD data.

ICP-OES analysis was performed to quantify the effectiveness of gold deposition on the surface of silica and sand. The results show that Au concentration is higher in silica (69.13±11.39 mg L⁻¹) than sand (15.18 ± 5.36 mg L⁻¹). Further calculations show that there is 6.9 ± 1.1 mg and 1.5 ± 0.5 mg of Au per gram of silica and sand, respectively. These values reveal that ~86% of the Au³⁺ from the synthesis experiment was successfully deposited on the surface of silica while only ~19% was deposited on the sand surface. This findings support the color intensity difference observed between the two sorbents in which Au-coated silica has a more intense color than sand. Both the XRD and ICP-OES results validate the success of the synthesis of Au-coated sorbents used in this study.
Fig. 1. X-ray diffraction images reveal peaks that indicate the deposition of Au on the silica surface.
Fig. 2. SEM images of Au-coated silica A) silica magnified 40x to reveal diameter of silica particles at 70-200 µm, B) shows the topography of silica surface which contributes to higher surface area, C) displays gold nanoparticles on the treated silica surface as opposed to the D) surface of untreated silica.

3.2. Kinetic Studies

The effectiveness of Au-coated silica nanoparticles was further evaluated using kinetic experiments. The sorbents were added to 10 mg L⁻¹ Hg (II) solution and was analyzed at several time points within 24 hours to determine the adsorption of mercury. Figure 3 indicates that Au-coated silica nanoparticles achieved an efficiency of >90% within 3 h and 99.99% of Hg (II) was adsorbed within 6 h. This performance was superior compared to both activated carbon (>90%, 5 h) and Au-coated sand (>50%, 7 h). Furthermore the maximum adsorption on activated carbon is only 96% while Au-coated sand exhibited the least
desirable performance with just over 50%. The adsorption of Hg (II) on to the sorbent surface was compared to theoretical models.

Pseudo-first order reaction kinetics model describes the adsorption capacity from solution concentration. It is often used to describe the removal of pollutants from wastewater. The equation is described below where \( k \) is the rate constant (s\(^{-1}\)), \( q_e \) and \( q_t \) are the equilibrium concentrations (µg g\(^{-1}\)) and concentration at time (t), respectively [15].

\[
\ln (q_e - q_t) = -kt + \ln q_e
\]  

(2)

The pseudo-second order reaction rate was also used since it describes the adsorption of metal ions, dyes, herbicides, oils, and organic matter in aqueous solutions [16]. This relationship is described by the equation below where \( k_2 \) is the second-order rate constant in g µg\(^{-1}\) min\(^{-1}\).

\[
\frac{t}{q_e} = \frac{1}{V_0} + \frac{1}{q_e} t
\]

(3)

The initial sorption rate is taken from \( V_0 = k_2 q_e^2 \) in µg g\(^{-1}\) min\(^{-1}\). The pseudo-second order fitted the best to describe the kinetics of Hg (II) similar to the results obtained from Hg (II) adsorption by aerogel studies by Ramadan et al [17]. The obtained rates (µg g\(^{-1}\) min\(^{-1}\)) are; 1.89, 0.24, and 4.72 for activated carbon, Au-coated sand, and Au-coated silica, respectively.

The greater initial adsorption rate and overall reaction rate (\( k_2 \)) in Au-coated silica could be attributed to the affinity of Hg (II) for the Au on the silica surface and the larger surface area of the silica base that can accommodate more gold particles. Only Au-coated silica was able to reach 99.999% adsorption efficiency among the sorbents studied. This adsorption efficiency exceeded the maximum efficiency observed in the sorption experiment. The equilibrium concentration of Hg (II) on the surface of the sorbents was obtained by plotting the \( q_s \) with time shown in Figure 3, while the best-fit model, pseudo-second order kinetics, is shown in Figure 4. Kinetic values are summarized in Table 1.
Fig. 3. The first-order adsorption kinetics of Hg (II) on the surface of activated carbon, Au-coated sand, and Au-coated silica.
Fitting the equilibrium concentrations to a pseudo-second order rate kinetics model revealed a highly linear correlation ($R^2 > 0.98$).

**Table 1.** Summary of Pseudo-Second Order Constants Obtained from Kinetic Study Experiments

<table>
<thead>
<tr>
<th>Sorbent System</th>
<th>Initial Adsorption Rate (µg g$^{-1}$ min$^{-1}$)</th>
<th>$k_2$ (g µg$^{-1}$ min$^{-1}$)</th>
<th>Max. Adsorption Capacity (µg g$^{-1}$)</th>
<th>$R^2$</th>
<th>Max. Adsorption Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>1.89</td>
<td>$1.81 \times 10^{-4}$</td>
<td>$1.0 \times 10^4$</td>
<td>0.973</td>
<td>98</td>
</tr>
<tr>
<td>Au-coated Sand</td>
<td>0.24</td>
<td>$4.73 \times 10^{-4}$</td>
<td>$2.7 \times 10^3$</td>
<td>0.997</td>
<td>55</td>
</tr>
<tr>
<td>Au-coated Silica</td>
<td>4.72</td>
<td>$4.72 \times 10^{-3}$</td>
<td>$1.0 \times 10^4$</td>
<td>0.997</td>
<td>100</td>
</tr>
</tbody>
</table>
3.3. Hg (II) Sorption Studies

The three sorbent systems were investigated for their effectiveness in removing Hg (II) from the solution. A plot of concentration (Ce, ug L\(^{-1}\)) of Hg (II) in the solution at equilibrium and the amount of Hg (II) adsorbed (qe, ug g\(^{-1}\)) on the surface of the sorbent at equilibrium yielded a linear equation:

\[
K_D = \frac{q_e}{C_e} \quad (4)
\]

Where the partition coefficient, \(K_D\), is the measure of the sorbent’s affinity for the target metal ion, in this case Hg (II) [18]. The summary of the adsorption parameters is indicated in Table 2.

Among the three sorbent systems under investigation, the synthesized Au-coated silica exhibited the highest affinity (\(K_D\)) to Hg (II), 9.96 ± 0.32 L g\(^{-1}\), and demonstrated the highest average efficiency, 96 ± 2.61%. The relatively good performance of the synthesized sorbent could be attributed to the surface topography of the silica base, a relatively higher surface area, and the affinity of gold towards the target metal ion. Au-coated sand showed the weakest response among the sorbent systems even though it has been treated with gold and this behavior could be brought upon by the possible difference in the surface topography of sand particles and in the silica particles. It is important to note that the qualitative assessment of the synthesized Au-coated sorbents shows that the red-purple color of gold-coated sand is less intense than the red-purple of the synthesized silica as further illustrated in Figure 5.

The result of the ICP-OES yielded Au concentrations that are four times less in sand than in silica which supports the qualitative assessment. It is suggested that 1.0 x 10\(^2\) L g\(^{-1}\) values for \(K_D\) indicate excellent sorbent affinity whereas this study yielded a far less value. This behavior could be due to the Au deposition on the surface of silica (86%) and sand (19%) resulting in a less than unity Au-Hg ratio. This is particularly problematic for metal
adsorption which predominantly follows a 1:1 ratio. Despite this, the synthesized Au-coated silica can decrease ambient Hg (II) levels well below the acceptable limits in drinking water (<2 µg L⁻¹) based on kinetics and sorption experimental results.

It is also well to include the surface physical chemistry of the attachment and distribution of the adsorbate, Hg (II), on the Au-coated silica particles. This behavior can be described by the Langmuir and Freundlich adsorption isotherm models using equilibrium concentration of Hg (II) remaining in the solution and concentration on the surface of the sorbents. The Langmuir isotherm model:

\[
\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m}
\]  (5)

Where \(K_L\) represents the Langmuir equilibrium constant (L g⁻¹) and \(S_m\) is the monolayer capacity of the adsorbent (µg g⁻¹). The Freundlich isotherm model is described by:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]  (6)

Where \(K_F\) is the Freundlich constant related to adsorption capacity µg g⁻¹ (µg L⁻¹)⁻¹ [19], [20], [21] and \(1/n\) corresponds to the degree of heterogeneity. Table 3 summarizes the values for these parameters as well as their \(R^2\) values to evaluate the degree of agreement of the adsorption behavior to the isotherm models.

Activated carbon displayed the highest maximum adsorption capacity (2500 µg g⁻¹) over the other sorbent systems (Au-silica 1429 µg g⁻¹, Au-sand 833 µg g⁻¹) and this could be due to the collection of Hg on its external surface and in the spaces available in the porous network. Moreover, the lesser value obtained from the Au-coated sorbents could be due to the one-to-one metal-metal interaction of gold and mercury and that the sorbent synthesis method might have limited the deposition of mercury on to the external surface of silica. Other methods of chemical treatment such as immersion of pure silica in a solution of Au³⁺ for
longer durations to allow the attachment of gold in to the inner surfaces of the silica might increase the maximum adsorption capacity of the sorbent. Sorption experiments could also be performed using untreated silica to know its Hg (II) adsorption capabilities. Activated carbon and Au-coated sand fitted the Freundlich isotherm model which suggests a multiple layer interaction while a more monolayer distribution describes the attachment of Hg (II) on the Au-coated silica which indicates that the adsorption of Hg (II) has reached a saturation point.

Au-coated silica also displayed the highest degree of heterogeneity.

**Fig. 5.** The materials and synthesized sorbents pure silica, pure sand, Au-coated sand, Au-coated silica (from left to right). Au-coated silica has a more intense purple-red color than Au-coated sand.

<table>
<thead>
<tr>
<th>Sorbent System</th>
<th>$K_D$ (L/g)</th>
<th>$R^2$</th>
<th>Average Adsorption Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>6.2±0.32</td>
<td>0.9817</td>
<td>95%</td>
</tr>
<tr>
<td>Au-coated Sand</td>
<td>0.13±0.006</td>
<td>0.9841</td>
<td>21%</td>
</tr>
<tr>
<td>Au-coated Silica</td>
<td>9.7±0.32</td>
<td>0.9960</td>
<td>96%</td>
</tr>
</tbody>
</table>
Table 3. Summary of Langmuir and Freundlich Isotherm Derived Values in DI Water System

<table>
<thead>
<tr>
<th>Sorbent System</th>
<th>$S_m$ (µg g$^{-1}$)</th>
<th>$K_L$ (L g$^{-1}$)</th>
<th>$R^2$</th>
<th>$K_F$ (µg 1-N g$^{-1}$ L$^N$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>2500</td>
<td>$2 \times 10^{-2}$</td>
<td>0.93</td>
<td>21</td>
<td>1.3</td>
<td>0.96</td>
</tr>
<tr>
<td>Au-coated Sand</td>
<td>833</td>
<td>$5 \times 10^{-4}$</td>
<td>0.73</td>
<td>0.44</td>
<td>1.3</td>
<td>0.84</td>
</tr>
<tr>
<td>Au-coated Silica</td>
<td>1429</td>
<td>$7 \times 10^{-3}$</td>
<td>0.99</td>
<td>15</td>
<td>1.5</td>
<td>0.91</td>
</tr>
</tbody>
</table>

3.4. Effect of Other Ions in Hg (II) Adsorption

Actual wastewater effluent is frequently comprised of dissolved inorganic and organic compounds, several of which form stable complexes with Hg (II), such as Hg-SO$_3$-NO$_2$-Cl in wet flue gas desulfurization device (WFGD)[22], that is why it is important to assess the performance of sorbents in aqueous solutions containing several of these interfering ions.

Chloride dominates inorganic speciation of Hg (II) in natural waters [23] and is known to form the stable complex HgCl$_2$ with Hg (II) [22]. The equilibrium concentration in the batch solution of 1 M Cl$^-$, pH 7.2, was measured after 24 hours of constant mixing. The results indicated that there is a decrease in Hg (II) uptake in all sorbent systems. Figure 6 illustrates the decrease in adsorption efficiency when the adsorption study was done in 1 M Cl$^-$ solution while Figure 7 illustrates the Freundlich isotherms in DI and Cl$^-$ rich systems. Interestingly, Hg (II) adsorption on all sorbent surfaces in the presence of Cl$^-$ favored the Freundlich isotherm model ($R^2 = 0.97$ in Au-coated silica and Au-coated sand, 0.94 for activated carbon).

This indicates that the attachment of Hg (II) onto the sorbent surface of Au-coated silica reached a saturation point which is characteristic of a monolayer distribution in the Cl$^-$ free set-up. The presence of chloride decreased the free Hg (II) concentration in the solution by forming stable complexes, shifting the adsorption behavior to the more linear portion of the adsorption isotherm which is best described by the Freundlich isotherm. The adsorption isotherm values are summarized in Table 4.
The general decrease in Hg (II) uptake among the sorbents agrees to the predicted Hg-Cl interactions however the much lower removal efficiency experienced by the Au-coated silica than activated carbon suggests that Hg-Cl interaction is not the only occurring process but it could be due to interactions between Au and Cl\(^{-}\) as well as SiO\(_2\) and Cl\(^{-}\). These possible chemical interactions did not make a significant impact on the Au-coated sand however, which means that the process is more complicated. Au-coated silica experienced an increase in heterogeneity factor however the other sorbents showed the opposite behavior. Although the adsorption capacity, K\(_F\), decreased in all sorbents, Au-coated silica exhibits the highest value in the chloride rich solution.

Hg (II) adsorption was also studied in the presence of cations in the solution. The effect of copper was studied since it belongs to Group 11 of the periodic table in which gold is also a member therefore these two metals share similar properties and possible binding capabilities with Hg. The effect of magnesium was studied since it is one of the more common metals naturally present in water along with calcium, potassium, and sodium [24]. The effect of zinc was also studied since it belongs to the same group as mercury in the periodic table therefore it could behave similarly when exposed to gold nanoparticles. The effect of 0.1 M of these cations on the sorption performance of activated carbon and Au-coated silica was studied in low (0.1 mg L\(^{-1}\)) and high (100 mg L\(^{-1}\)) concentrations of Hg (II) in the solution. The results are shown in Figure 8.

The presence of these metal salts caused a general decrease in pH however this decrease was minimal in low and high Hg (II) concentrations for both sorbent systems however a significant decrease in Hg adsorption was observed in the 0.1 M Mg (II) solution in the activated carbon set-up at 100 mg L\(^{-1}\) Hg. A somehow similar findings was observed by Lim et al. (2008) [25], regarding the partially depressed adsorption of Pb (II) on sawdust in the presence of Mg (II) while calcium, magnesium and sodium show a significant influence in
fulvic acid adsorption on activated carbon [26]. Further research is needed to describe this behavior in more detail. Au-coated silica displayed <90% efficiency in the presence of these cations. This behavior favors the use of Au-coated silica in effluent waters where dissolved ions are present.

**Fig. 6.** A comparison of adsorption efficiency of the three sorbent systems in and without the presence of chloride ions.
Fig. 7. The Freundlich isotherm models for the adsorption of Hg (II) on the surface of the three sorbents in DI water and 1 M Cl⁻ solution.
Fig. 8. The concentration of Hg (II) adsorbed on the sorbent surfaces in the presence of other cations at equilibrium was measured and there is minimal change observed for Au-coated silica.
Table 4. Summary of Langmuir and Freundlich Isotherm Derived Values in 1 M Cl- Solution

<table>
<thead>
<tr>
<th>Sorbent System</th>
<th>$S_m$ (µg g$^{-1}$)</th>
<th>$K_L$ (L g$^{-1}$)</th>
<th>$R^2$</th>
<th>$K_F$ (L g$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>833</td>
<td>$2 \times 10^{-3}$</td>
<td>0.42</td>
<td>2.9</td>
<td>1.2</td>
<td>0.94</td>
</tr>
<tr>
<td>Au-coated Sand</td>
<td>204</td>
<td>$6 \times 10^{-4}$</td>
<td>0.28</td>
<td>0.07</td>
<td>0.89</td>
<td>0.97</td>
</tr>
<tr>
<td>Au-coated Silica</td>
<td>770</td>
<td>$3 \times 10^{-3}$</td>
<td>0.84</td>
<td>5.5</td>
<td>1.8</td>
<td>0.97</td>
</tr>
</tbody>
</table>

4. Conclusions

The synthesis of the target sorbent, Au-coated mesoporous silica, has been established using qualitative assessment, X-ray diffraction data which shows Au peaks in 2θ=38.2º, 44.4º, 64.6º, 77.5º and ICP-OES Au concentration measurements which yielded (69.13± 11.39 mg L$^{-1}$) in silica and (15.18 ± 5.36 mg L$^{-1}$) for sand. The presence of gold particles on the sorbent surface was further confirmed by comparing treated and untreated silica SEM images. The amount of Au per gram of sorbent was derived from the ICP-OES data which yielded the values of 6.9 ± 1.1 mg g$^{-1}$ for silica and 1.5 ± 0.5 mg g$^{-1}$ for sand. This indicates that ~86% of the Au$^{3+}$ in the synthesis step was reduced and deposited on to the surface of silica. There is only ~19% of Au$^{3+}$ reduced and deposited on the surface of sand. It was also found out that most of the gold nanoparticles found on the silica surface are around 3-4 nm in diameter. The effectiveness of the synthesized Au-coated silica was determined using Hg (II) sorption data in DI water and in 1 M Cl- solution systems and using kinetic experiments. The results were compared to commercially available activated carbon and another Au-coated sorbent, sand. Au-coated silica was found out to have outperformed the other sorbents in study with average adsorption over a 100 µg L$^{-1}$-300 mg L$^{-1}$ Hg (II) concentration range of 96% and has the fastest initial rate of adsorption of 4.72 µg g$^{-1}$ min$^{-1}$ however it also experienced the greatest decrease (30%) in performance in the presence of interfering ions such as Cl$^-$. There is minimal effect to the Hg (II) adsorption of the sorbents in the presence of cations Cu (II), Mg
(II), and Zn (II). The adsorption on the surface of Au-coated silica follows a Langmuir isotherm behavior where a saturation point was reached due to the Au-Hg ratio being less than 1. However, the presence of chloride ions in the solution decreased the amount of free Hg (II) ions that can adsorb on the sorbent surface. The shift in adsorption behavior to the linear portion of the adsorption isotherm is best described by the Freundlich isotherm.

The study could further consider the effects of temperature, other ions in the solution such as NOx, sulfur-containing compounds, the presence of dissolved organic materials (DOM) to the adsorption behavior, and to perform more characterization tests for the synthesized Au-coated sand and Au-coated silica such as scanning and transmission emission microscopy. The experiment could also use other methods of coating gold onto the silica surface including the inside surfaces of the pore structures to increase the maximum adsorption capacity of the synthesized sorbent. Other metals could also be coated onto silica surfaces (Ag, Cu) and their adsorption efficiency could be studied in comparison to Au. Methyl mercury experiments could also be performed to assess the total effectiveness of the synthesized nanoparticles in removing a wider range of mercury species from the solution system.

This study established that Au-coated silica is a more rapid and viable alternative to commercially available sorbents for the removal of Hg (II) in aqueous solutions particularly during initial Hg adsorption.
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References


