Mercury (II) adsorption from aqueous solution using nitrogen and sulfur co-doped activated carbon
Hangdao Qin, Rong Xiao, Lei Guo, Jianling Meng and Jing Chen

ABSTRACT

Activated carbon (AC) was modified with urea, thioglycolic acid and thiourea to obtain nitrogen doped activated carbon (ACN), sulfur doped activated carbon (ACS) and nitrogen and sulfur co-doped activated carbon (ACNS), respectively. The AC samples were characterized by elemental analysis, N₂ adsorption-desorption, determination of the pH of the point of zero charge (pHₚζ) and X-ray photoelectron spectroscopy, and tested for adsorption behaviors of Hg(II) ions. The experimental data of equilibrium isotherms fitted well with the Langmuir model. ACNS showed the highest adsorption capacity of 511.78 mg/g, increasing more than 2.5 times compared to the original ACA. The adsorption process followed pseudo-second-order kinetics. The thermodynamic parameters of ΔΗ°, ΔS°, and ΔG° at 30 °C were −20.57 kJ/mol, −0.032 kJ/mol K and −10.87 kJ/mol, respectively.

It was concluded that the Hg(II) ions’ adsorption on ACNS was exothermic, spontaneous and physisorptive in nature. Finally, the adsorption capacity of ACNS reduced by just 8.13% even after the sixth cycle compared to the initial cycle.

Key words | Hg(II) ions, isotherms, kinetics and equilibrium studies, water treatment

INTRODUCTION

Mercury-containing wastewater, generated from combustion of fossil fuels, the chlorine-alkali industry, pulp and paper industry and PVC industry, is highly toxic and harmful (Yardim et al. 2003). Treatment approaches, such as membrane filtration, chemical precipitation, ion exchange, biological treatment and adsorption have been extensively investigated in the treatment of mercury-containing wastewater. Among them, adsorption is an effective technology for removal of Hg(II) ions from wastewater or other aqueous solutions (Denizli et al. 2003; Miretzky & Cirelli 2009; Zabibi et al. 2009).

Activated carbon (AC) is an excellent adsorbent due to its high surface area, well-developed internal pore structure and tunable surface chemistry (Deryio-Marczewska et al. 2004). Ion exchange, electrostatic interaction and coordination of functional groups on the activated carbon surface were considered as the main factors in the adsorption of metal ions by AC (Huang & Blankenship 1984; Natale et al. 2006; Hassan et al. 2008). However, a significant drawback of AC adsorption, presenting a low level of selectivity and adsorption saturation, was revealed by several studies. Halogen and sulfhydryl groups were introduced into adsorbent surface to enhance the Hg(II) ions adsorption capacity (Zhang et al. 2005; Danwanichakul et al. 2008; Hadavifar et al. 2014). Non-modified magnetic iron oxide nanoparticles can adsorb up to 43.47% of 50 mg/L of Hg(II) ions from polluted water, but magnetic iron oxide nanoparticles modified by 2-mercaptobenzothiazole improved the efficiency up to 98.6% for the same concentration (Parham et al. 2012). Besides, Hg(II) adsorption capacity was improved when amino was introduced into the surface of the adsorbent (Sreedhar & Anirudhan 2000; Zhu et al. 2008).

Actually, nitrogen-containing AC has been developed to remove heavy metals (Shang et al. 2014) and organic pollutants (Yang et al. 2014; Qin et al. 2014, 2015; Qin & Chen 2016) from aqueous media. The nitrogen-containing functional groups were introduced onto the AC surface, which increased the adsorption capacity, selectivity and removal efficiency of heavy metals and organic compounds due to the strengthened (~π~) electrostatic interactions as well as the coordination of surface functional groups. This prompted us to investigate the use of nitrogen and sulfur dual-doped carbon materials for the adsorption of Hg(II) ions.

In the present work, AC samples were modified with urea, thioglycolic acid and thiourea to obtain nitrogen
doped activated carbon (ACN), sulfur doped activated carbon (ACS) and nitrogen and sulfur co-doped activated carbon (ACNS), respectively. AC samples before and after modification were characterized by elemental analysis, N$_2$ adsorption-desorption, determination of the pH of the point of zero charge (pH$_{pzc}$) X-ray photoelectron spectroscopy (XPS). The isotherm data for adsorption of Hg(II) ions were fitted with the Langmuir and Freundlich models. The effect of pH and temperature on the adsorption of Hg(II) ions was investigated. The kinetics and thermodynamic properties were determined from the experiment data. Based on the thermodynamic parameters, the adsorption mechanism of ACNS was proposed. In addition, desorption and regeneration cycles were carried out to prove the renewability of the doped adsorbent.

**EXPERIMENTAL**

**Modification of activated carbon**

The original AC (20 g, 16–40 mesh) was treated with 1 mol L$^{-1}$ HCl solution for 3 h to remove metal ions, and then the sample was filtered and washed with distilled water and dried. The acid-treated AC was denoted as ACA. ACA was suspended in 300 mL 50% HNO$_3$ and refluxed at 80 °C for 3 h in a three-necked flask, then filtered and washed with hot distilled water and dried at 120 °C for 12 h. The oxidized AC was denoted as ACO. A mixture of ACO (5 g), urea (3.6 g)/thioglycolic acid (4.55 g)/thiourea (3 g) and distilled water (50 mL) was stirred to obtain carbon slurry. The molar ratio of urea, thioglycolic acid and thiourea was 1:1:1. The solution was filtered, dried and heat-treated under a flow of Ar for 3 h at 900 °C, with a heating rate of 10 °C min$^{-1}$. Finally, the samples were cooled to room temperature and stored in a desiccator until their use. The resulting samples were denoted as ACN, ACS and ACNS, respectively.

**Characterization**

The C, H, N, S and O (by difference) elemental composition of the AC was determined using a Carlo Erba EA 1108 Elemental Analyzer. Prior to the analysis, the samples were dried at 110 °C in the oven overnight. The specific Brunauer-Emmett-Teller (BET) surface area and pore volume of activated carbon samples were determined from the adsorption and desorption isotherms of N$_2$ at −196 °C using a Builder SSA-420 instrument. The sample was separately degassed at 300 °C for 2.5 h in a vacuum environment before measurements. The pH of the point of zero charge (pH$_{pzc}$) was determined by the pH drift method according to the procedure proposed by Yang et al. (2014). XPS measurements were performed with a Kratos XSAM800 using an Al Kα (1,486.6 eV, anode operating at 12 kV, and 15 mA) radiation source. The binding energies were calibrated based on the graphite C 1 s peak at 284.5 eV. XPS data corresponding to N 1 s and S 2p spectra were fitted using the software CasaXPS.

**Adsorption isotherms**

A stock solution of 1,000 mg/L of Hg(II) was prepared by dissolving solid Hg(NO$_3$)$_2$ in distilled water. The stock solution was then diluted to required concentrations for performing adsorption studies. To determine the adsorption isotherms, 50 mg of adsorbent was placed in a series of conical flasks containing different concentrations (10–200 mg/L) of 50 mL solution of Hg(II) ion solution, stirring at 150 rpm and 30 °C. When reaching equilibrium, the Hg(II) ion solution was separated from the adsorbent for further analysis. The final concentration of Hg(II) ions was determined employing an atomic fluorescence spectrometer (AFS, Al3200, Auros). The amount of uptake capacity at equilibrium was calculated by Equation (1).

$$ q_e = \frac{(C_0 - C_e) \times V}{m} $$

where $q_e$ (mg/g) is the amount of uptake capacity at equilibrium; $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations of the solution, respectively; $m$ (g) is the mass of activated carbon and $V$ (L) is the volume of the solution.

The experimental data were fitted with the Langmuir and Freundlich models. The Langmuir equation and Freundlich equation were formulated as Equations (2) and (3), respectively.

$$ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} $$

where $q_m$ (mg/g) is the maximum adsorption capacity to form a complete monolayer on the surface of adsorbate; $K_L$ (L/mg) is the Langmuir constant.

$$ q_e = K_F C_e^{1/n} $$

where $K_F$ ((mg/g)(L/mg)$^{1/n}$) is the Freundlich constant that represents the quantity of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration; $n$ is the...
dimensionless exponent of the Freundlich equation, depicting an indication of how favorable the adsorption process is.

The amount of metal ions released in supernatant was studied over a pH range of 2–10 at 30 °C. The pH of the solutions was modified by using 0.1 mol/L HNO₃ or 0.1 mol/L NaOH solution and monitored by a PHC-3C pH meter. The Hg(II) ion concentration was fixed at 50 mg/L and the adsorbent dose was 50 mg.

**Adsorption kinetics**

The kinetics studies were carried out using 50 mg of adsorbent in 50 mL of 50 mg/L Hg(II) ion solution at pH 6 and 30 °C. The samples were separated at predetermined time intervals.

In this study, the pseudo-first-order kinetic model (Yang et al. 2010) and the pseudo-second-order model (Yan et al. 2007) were used to investigate the adsorption of Hg(II). The pseudo-first-order kinetic model was described as Equation (4). When ln(qe/qt) was plotted against time t, data fitted a straight line and k₁ and qe corresponded to the slope and intercept of the line, respectively.

\[
\ln \left( q_e - q_t \right) = \ln q_e - k_1 t 
\] (4)

where qe and qt (mg/g) are the amount of Hg(II) ions adsorbed at equilibrium and at time t, respectively; k₁ (1/h) is the first-order rate constant.

The pseudo-second-order kinetic model was described as Equation (5). The plot of t/qt against t should give a linear relationship. The rate constants k₂ and adsorption capacity at equilibrium qe were calculated from the values of the slopes and the intercepts.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\] (5)

where qe and qt (mg/g) are the amount of Hg(II) ions adsorbed at equilibrium and at time t, respectively; k₂ (g/mg h) is the second-order rate constant.

**Adsorption thermodynamics**

The adsorption studies were carried out at different temperatures (30, 40, 50 and 60 °C) with 50 mg/L Hg(II) ions concentration. 50 mg adsorbent was added to 50 mL of Hg(II) solution at pH 6. The enthalpy change (ΔH°) and entropy change (ΔS°) for Hg(II) ion adsorption by AC were determined using Equations (6) and (7) (Bessbousse et al. 2009). When lnKd was plotted against temperature 1/T, the data fitted a straight line and ΔH° and ΔS° corresponded to the slope and intercept of the line, respectively.

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} 
\] (6)

\[
K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} 
\] (7)

where Kd (mL/g) is the distribution coefficient; R (8.314 \times 10^{-3} kJ/mol K) is the universal gas constant; T (K) is the absolute temperature. The ΔG° is the change in Gibbs free energy, calculated according to the following equation (Bessbousse et al. 2009):

\[
\Delta G^o = \Delta H^o - T\Delta S^o 
\] (8)

**Desorption and regeneration study**

Ethylenediaminetetraacetic acid (EDTA) was used for desorption of Hg-loaded ACNS due to the ability of EDTA to form strong complexes with Hg ions. 50 mg adsorbent was added to 50 mL of 50 mg/L Hg(II) ion solution at pH 6. Adsorption was allowed for 24 h, followed by desorption with 0.05 mol/L EDTA solution. The concentrations of Hg(II) at both the adsorption and desorption stages were determined. After each cycle, the regenerated adsorbent was washed twice with distilled water and centrifuged to remove the remaining ions, followed by drying under vacuum conditions. Reusability of ACNS was determined in six adsorption–desorption cycles. The desorption capacity was calculated by the following equation:

\[
\text{Desorption} = \frac{\text{Amount of metal ions released in supernatant}}{\text{Amount of metal ions adsorbed}} \times 100\% 
\] (9)

**RESULTS AND DISCUSSION**

Activated carbon characterization

The C, H, N, S and O contents obtained by elemental analysis are summarized in Table 1. After treatment with HNO₃, amounts of oxygen were significantly introduced onto the ACO surface. In the case of ACN, ACS and ACNS, the amount of oxygen decreased compared to ACO, which indicated that urea, thioglycolic acid or thiourea had reacted with oxygen-containing surface groups. As a result of the modification, the nitrogen and sulfur contents substantially increased.
To further understand the chemical state of N and S in the doped AC, as showed in Figure 1, the N 1 s and S 2p peaks were analyzed in detail. The calculated atomic percentages of different N and S functionalities in the doped AC are also presented in Figure 1. The deconvolution of the XPS spectra corresponding to the N 1 s regions was carried out following the procedure proposed by several authors (Burg et al. 2002; Raymundo-Pinero et al. 2002). As shown in Figure 1(a) and (c), the N 1 s peak was deconvoluted into three different types of N-containing species: pyridinic-N (N1, 398.5 eV), pyrrolic-N (N2, 400.4 eV) and graphitic-N (N3, 401.8 eV). The results indicated that ACN was characterized by a high concentration of pyridine groups, whereas ACNS showed a high concentration of pyrrolyl groups. For the S 2p region, the peak was resolved into three different peaks at the binding energies of 164.0, 165.2 and 168.8 eV, corresponding to thiolate (S1), thio-phenene-S (S2) and sulphate (S3), respectively (Su et al. 2013; Liu et al. 2016). It was noted from Figure 1(b) and 1(d) that there was no significant difference in the content of thiophene-S between ACS and ACNS; however, ACNS presented a high concentration of thiolate species.

Adsorption isotherms

Adsorption isotherms contain certain constant parameters expressing the surface properties and affinity of the adsorbent, making it possible to evaluate the adsorption capacity of the adsorbent for metal ions. The Langmuir and Freundlich adsorption isotherms of the Hg(II) ions are shown in Figure 2. The parameters of the Langmuir and Freundlich models ($q_m$, $K_L$, $K_F$ and $n$) and the nonlinear regression correlation coefficients ($R^2$) are listed in Table 3. The correlation coefficient ($R^2$) was greater than 0.987 in the Langmuir model, suggesting that the Langmuir model fitted well to the data. Comparing the fitted curves in Figure 2 and the $R^2$ values listed in Table 3, the Langmuir model fitted the Hg(II) ion adsorption equilibrium data better than the Freundlich model. Similar results were reported by other authors (Hadjivaf et al. 2014; Deb et al. 2007).

It can be observed from Table 3 that the adsorption capacity of AC was slightly decreased after the treatment with HNO3, which indicated that the acidic surface groups were not favorable to the adsorption of Hg(II). The introduction of nitrogen-containing and sulfur-containing functional groups onto the AC surface enhanced the adsorption performance, and ACNS showed the highest adsorption capacity of 511.78 mg/g, increasing more than 2.5 times compared to the ACA. The values of $q_m$ indicated that the

### Table 1 | Elemental analysis of AC samples

<table>
<thead>
<tr>
<th>AC</th>
<th>C (wt.%)</th>
<th>H (wt.%)</th>
<th>N (wt.%)</th>
<th>S (wt.%)</th>
<th>O (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACA</td>
<td>89.95</td>
<td>0.92</td>
<td>0.16</td>
<td>0</td>
<td>8.97</td>
</tr>
<tr>
<td>ACO</td>
<td>85.88</td>
<td>0.28</td>
<td>0.56</td>
<td>0</td>
<td>13.28</td>
</tr>
<tr>
<td>ACN</td>
<td>85.56</td>
<td>0.36</td>
<td>3.56</td>
<td>0</td>
<td>10.52</td>
</tr>
<tr>
<td>ACS</td>
<td>84.34</td>
<td>0.34</td>
<td>0.48</td>
<td>3.26</td>
<td>11.58</td>
</tr>
<tr>
<td>ACNS</td>
<td>82.47</td>
<td>0.32</td>
<td>3.24</td>
<td>3.12</td>
<td>10.85</td>
</tr>
</tbody>
</table>

The results of porosity characterization together with pH$_{pzc}$ are presented in Table 2. The acid-treated activated carbon (ACA) was a highly mesoporous carbon with large specific surface area ($S_{BET}$, 1,318 m$^2$/g), pore volume ($V_t$, 1.12 cm$^3$/g) and high percentage of mesoporous structure (42.8% for $V_{micro}$ and 57.2% for $V_{meso}$). A slight decrease of $S_{BET}$ and $V_t$ was observed after treatment with HNO3. It was noted that the $S_{BET}$ and $V_t$ of ACN displayed an appreciable increase compared to ACO, which may due to decomposition of urea during the treatment into highly reactive nitrogenising agents, which could react with the activated carbon surface and produce its gasification (Rivera-Utrilla & Sanchez-Polo 2004). On the contrary, when ACO was treated with thioglycolic acid or thiourea, an obvious decrease in $S_{BET}$ and $V_t$ was observed, which can be explained by the introduction of sulfur-containing groups. A similar result was reported in other literature (Messele et al. 2014; Qin et al. 2018).

In addition, whereas ACA had slightly acidic properties, ACO showed a low pH$_{pzc}$ due to the introduction of oxygen-containing surface groups having acidic properties, mainly carboxylic acids. After the treatment with urea, ACN presented slightly basic properties. This result could be explained by the presence of nitrogen groups having basic properties. In the case of ACS, the enhancement of pH$_{pzc}$ was attributed to the reduction of the acidic oxygen-containing surface groups. Treatment with thiourea led to an increase of pH$_{pzc}$ since nitrogen-containing and sulfur-containing functional groups were introduced onto the ACNS surface.

### Table 2 | Porous properties and pH$_{pzc}$ of AC before and after modification

<table>
<thead>
<tr>
<th>AC</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$V_{micro}$ (cm$^3$/g)</th>
<th>$V_{meso}$ (cm$^3$/g)</th>
<th>pH$_{pzc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACA</td>
<td>1,318</td>
<td>1.12</td>
<td>0.48</td>
<td>0.64</td>
<td>6.24</td>
</tr>
<tr>
<td>ACO</td>
<td>1,256</td>
<td>0.98</td>
<td>0.35</td>
<td>0.63</td>
<td>2.66</td>
</tr>
<tr>
<td>ACN</td>
<td>1,365</td>
<td>1.08</td>
<td>0.44</td>
<td>0.64</td>
<td>7.84</td>
</tr>
<tr>
<td>ACS</td>
<td>1,118</td>
<td>0.82</td>
<td>0.28</td>
<td>0.54</td>
<td>5.58</td>
</tr>
<tr>
<td>ACNS</td>
<td>1,106</td>
<td>0.80</td>
<td>0.26</td>
<td>0.54</td>
<td>6.85</td>
</tr>
</tbody>
</table>
adsorption capacity of AC samples increased in the order ACO < ACA < ACN < ACS < ACNS. It was noted that there was no linear relation between the adsorption capacity and \( S_{BET} \) (Table 2), suggesting the N-containing and S-containing functional groups introduced by modification played an important role in the adsorption of Hg(II). According to the Hard-Soft-Acid-Base theory, the Hg(II) was considered as a soft acid that form strong covalent

Figure 1 | (a) N 1 s XPS spectra of ACN, (b) S 2p XPS spectra of ACS, (c) N 1 s XPS spectra of ACNS and (d) S 2p XPS spectra of ACNS.

Figure 2 | Langmuir (a) and Freundlich (b) adsorption isotherms for Hg(II) ions on AC samples at 30 °C and pH 6.0.
bonds to soft bases such as –NH₂, –CN, –SH and –RS groups (Sinner et al. 1998; Namasivayam & Kadirvelu 1999; Reddy & Francis 2001). Therefore, the interactions of Hg(II) with surface nitrogen and sulfur ligands were favored. According to the results of XPS analysis, the greater adsorption capacity of ACNS versus ACN may be due to the higher concentration of pyrrol groups and versus ACS may be due to the higher concentration of thiolate species in ACNS. These results appear to indicate that pyrrol and thiolate groups increased the adsorption capacity of the carbon. The presence of pyrrol groups on the AC surface increased the electronic density of its basal plane, while thiolate groups showed great binding capacity with Hg(II) ions.

**Effect of solution pH**

According to the results of adsorption isotherms, the nitrogen and sulfur co-doped ACNS showed the highest adsorption capacity. Therefore, the unmodified ACA and the optimal ACNS were chosen for investigating the adsorption of Hg(II) ions at a pH range of 2–12, since the pH of the solution played an important role in the adsorption of metal ions. The results are illustrated in Figure 3. It was observed that the adsorption capacity reached a plateau value at the pH range of 4–10 and decreased sharply at higher or lower initial pH values. ACNS showed a wider pH range for maximum adsorption than the parent ACA. Under the pH range of 2–4, the carbon surface was positively charged because the pH<sub>pzc</sub> of ACA and ACNS was found to be 6.24 and 6.85, respectively. Significant adsorption of Hg(II) did not occur due to electrostatic repulsion (Manohar et al. 2002). In addition, the competition between hydrogen and metal ions for the surface sites decreased the adsorption capacity (Hadaafifar et al. 2014). Maximum sorption efficiency in the pH range 4–10 for ACNS was explained well by the Hard-Soft-Acid-Base theory. The predominant species of mercury was Hg(OH)<sub>2</sub> at this pH range (Anoop & Anirudhan 2002; Manohar et al. 2002). Neutral molecules were softer acids than metal cations, and the interaction of Hg(OH)<sub>2</sub> with N-containing and S-containing functional groups was likely favored. Furthermore, Hg(OH)<sub>2</sub> had smaller effective size and higher mobility than Hg(II) (Zhang et al. 2015; Pillay et al. 2013). The decrease in adsorption beyond pH 10 may be attributed to the predominant formation of Hg(OH)<sub>3</sub> species, which had less affinity for binding with ACNS because the surface was negatively charged (Deb et al. 2017).

**Adsorption kinetics**

The experimental kinetic data were fitted with the pseudo-first-order and pseudo-second-order kinetic models. The corresponding parameters were calculated and listed in Table 4. The theoretical uptakes <i>q</i><sub>e, cal</sub> departed from the experimental values <i>q</i><sub>e, exp</sub> and all correlation coefficients <i>R</i><sup>2</sup> were smaller than 0.9, indicating that the pseudo-first-order equation was ruled out from describing the kinetics of the adsorption. However, all the correlation coefficients <i>R</i><sup>2</sup> for the pseudo-second-order kinetic model were above 0.98. Moreover, the theoretical uptakes <i>q</i><sub>e, cal</sub> were in good agreement with the experimental uptakes <i>q</i><sub>e, exp</sub> for the pseudo-second-order expression. These results indicated that the pseudo-second-order kinetic model was the suitable equation to describe the adsorption kinetics of benzoic acid on AC. The fact that the kinetics of Hg(II) ion adsorption on AC followed the pseudo-second-order kinetic model suggested Hg(II) adsorption probably occurred via surface complexation (Deb et al. 2017).
Adsorption thermodynamics

The effect of temperature on the adsorption of Hg(II) ions on ACNS has been illustrated by a linear plot of \( \ln K_d \) versus \( 1/T \) in Figure 4. The evaluated thermodynamic parameters and correlation coefficient are summarized in Table 5. The negative value of \( \Delta H^\circ \) with a decreasing trend of \( K_d \) with increasing temperature revealed that the adsorption process was exothermic in nature. The negative value of \( \Delta G^\circ \) indicated that the adsorption of Hg(II) on ACNS was spontaneous. Moreover, the value of \( \Delta G^\circ \) increased from \(-10.87\) to \(-9.91\) kJ/mol for the temperature range 30 °C to 60 °C, which implied that the adsorption was more favorable at lower temperatures. According to the previous work (Liu et al. 2003), the change in \( \Delta G^\circ \) for physisorption happened within the range of \(-20\) to 0 kJ/mol, while the physisorption and chemisorption together occur at between \(-80\) and \(-20\) kJ/mol with chemisorption being at between \(-400\) and \(-80\) kJ/mol. The obtained values of \( \Delta G^\circ \) suggested that interactions between Hg(II) ions and ACNS can be considered as a physisorption mechanism.

In addition, the negative value of \( \Delta S^\circ \) indicated that no ion replacement reactions occurred in the adsorption process, because the increase of entropy of the system could have happened due to release of the ions from the solid surface to the solution (Dujardin et al. 2000). On the other hand, the release of water molecules produced by the interaction of Hg(II) ions with functional groups and surface sites of the adsorbent resulted in the positive \( \Delta S^\circ \) value (Deb et al. 2017).

Desorption and regeneration

In order to be used at an industrial scale, an adsorbent should possess the ability to be regenerated so that it can be used multiple times. ACNS was reused in six successive adsorption–desorption cycles. It was found that the desorption capacity reached 95% in a single cycle of desorption, revealing good regeneration capacity of the adsorbent. These results were consistent with the report that above 90% of adsorbed mercury had been recovered for carbons which were activated at high temperature (Ranganathan 2003). The variation in the equilibrium adsorption capacities with the number of adsorption-desorption cycles is shown in Figure 5. It was evident that the ACNS could be used multiple times, as the adsorption capacity reduced by just 8.13% even after the sixth cycle compared to the initial cycle. Therefore, ACNS showed

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**Table 4** Parameters of the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of Hg(II) ions on AC

<table>
<thead>
<tr>
<th>AC</th>
<th>( q_e, \text{exp} ) (mg/g)</th>
<th>( q_e, \text{cal} ) (mg/g)</th>
<th>( k_1 ) (1/min)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACA</td>
<td>80.88</td>
<td>48.24</td>
<td>0.028</td>
<td>0.828</td>
</tr>
<tr>
<td>ACO</td>
<td>61.61</td>
<td>31.45</td>
<td>0.021</td>
<td>0.858</td>
</tr>
<tr>
<td>ACN</td>
<td>105.24</td>
<td>55.28</td>
<td>0.052</td>
<td>0.786</td>
</tr>
<tr>
<td>ACS</td>
<td>128.22</td>
<td>78.52</td>
<td>0.035</td>
<td>0.856</td>
</tr>
<tr>
<td>ACNS</td>
<td>141.48</td>
<td>91.42</td>
<td>0.038</td>
<td>0.825</td>
</tr>
</tbody>
</table>

*Figure 4* Plots of \( \ln K_d \) versus \( 1/T \) for Hg(II) ion adsorption on ACNS.

<table>
<thead>
<tr>
<th>( q_e, \text{cal} ) (mg/g)</th>
<th>( k_2 ) (g/mg min)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.12</td>
<td>0.0035</td>
<td>0.988</td>
</tr>
<tr>
<td>62.68</td>
<td>0.0028</td>
<td>0.986</td>
</tr>
<tr>
<td>104.85</td>
<td>0.0043</td>
<td>0.989</td>
</tr>
<tr>
<td>126.82</td>
<td>0.0046</td>
<td>0.988</td>
</tr>
<tr>
<td>143.15</td>
<td>0.0052</td>
<td>0.988</td>
</tr>
</tbody>
</table>

**Table 5** Thermodynamic parameters for the adsorption of Hg(II) ions on ACNS

<table>
<thead>
<tr>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>( \Delta S^\circ ) (kJ/mol K)</th>
<th>( \Delta G^\circ ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td>313 K</td>
<td>323 K</td>
</tr>
<tr>
<td>(-20.57)</td>
<td>(-0.032)</td>
<td>(-10.87)</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Nitrogen doped, sulfur doped and nitrogen and sulfur co-doped activated carbon were successfully prepared and their performances in the adsorption of Hg(II) ions from aqueous solution were investigated. The adsorption experiments revealed that the adsorption process followed the Langmuir isotherm model and pseudo-second-order kinetics. ACNS presented the best capability for Hg(II) ion removal at pH 6 and 30°C. The values of thermodynamic parameters $\Delta H$, $\Delta S$, and $\Delta G$ were obtained as $-20.57$ kJ/mol, $-0.032$ kJ/mol K and $-10.87$ kJ/mol, respectively, suggesting an exothermic and spontaneous nature for the adsorption. The desorption and regeneration study showed a small loss in the adsorption capacity of 8.13% for Hg(II) ions after six cycles, demonstrating a prospective application of ACNS for treating mercury-containing wastewater.

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