CHAPTER 10
Arsenic removal using silver-impregnated PSLW activated carbon

10.1 Introduction

Ground water is the prime source of drinking water and meets the needs of households’ worldwide. Arsenic is known to be one of the naturally occurring elements in ground water which is associated with adverse health effects. Arsenic concentration in water varies from less than 0.05 µg/L to more than 5000 µg/L depending on the source of arsenic [1]. The arsenic concentration in drinking water is of great human health concern in some regions of Bangladesh, India, Nepal, Mexico and Argentina. Recent literature reveals that As(III) and As(V) oxyanions with varying concentrations have been distributed regionally across the United States (USA) [2]. The potable water is considered to be safe for human consumption if the concentration of arsenic in water is less than 10 µg/L [3,4]. Therefore it is essential to remove arsenic from potable water resources.

The important processes listed for the removal of arsenic are oxidation-reduction, precipitation, co-precipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, ion floatation and biological processing [5-11]. Among the techniques, adsorption by activated carbon is accepted to be the best available technology for the removal of pollutants. The main disadvantage of using activated carbon adsorption technology is its high cost. This can be overcome by preparing activated carbon from renewable biomass in nature [12,13] and tailoring the carbon surface to enhance the removal capacity [14].

In the present work, the PSLW carbon impregnated with silver known as silver-impregnated carbon (SIC) is employed to remove arsenic from aqueous solution.
This Chapter reports the results of the investigation on the adsorption and kinetics of removal of arsenic from aqueous solution by SIC.

10.2 Batch adsorption studies

10.2.1 Effect of pH

Arsenic adsorption onto any adsorbent depends on the pH of the solution [15,16]. Figure 10.1 depicts the effect of pH on adsorption over a range of 1-10.0. Though no regular trend in adsorption is seen with pH, the figure shows interesting feature of with two maxima, one at pH 4.0 and another at about pH 10.0. For an initial As(III) concentration of 1000 mg/L the maximum adsorption capacity of As(III) at pH 4.0 is 98.2 mg/g and at pH 10.0 it is found to be 207.5 mg/g.

It was postulated that in acidic conditions, the metallic silver gets oxidized in aqueous solution according to the following reaction [14].

\[
O_2(aq) + 4H^+(aq) + Ag^0(s) \rightarrow 4Ag^+(aq) + 2H_2O(l) \quad \Delta G^0 = -182.2 \text{ kJ/mole}
\]

From the SEM (Figure 10.2) and EDX analyses (Figure 10.3) it is evident that on the surface of SIC the silver exists as metallic silver (i.e. Ag\(^{0}\)). Therefore it is assumed that at pH 4.0, Ag is oxidized to Ag\(^{+}\) ion which reacts with AsO\(_3^-\) to give Ag\(_3\)AsO\(_3\) precipitate and gets adsorbed on the surface of SIC. As the pH rises the formation of Ag\(^{+}\) is diminished and at alkaline pHs silver exists as AgOH and the following reaction may occur.

\[
C \rightarrow AgOH + H_2AsO_3^- \rightarrow C \rightarrow AgH_2AsO_3
\]

\[
2 C \rightarrow AgOH + HAsO_3^{2-} \rightarrow (C \rightarrow Ag)_2 HAsO_3
\]

Further, at alkaline pHs, the Na\(^{+}\) ions may also bind to the negatively charged surface of SIC and neutralize the charges partially. Therefore in the alkaline pH range the H\(_2\)AsO\(_3^-\) and HAsO\(_3^{2-}\) species may also be bound to the surface of SIC carbon by
van der Waals forces in addition to the above process. Further, the FT-IR study shows that the surface of SIC consists of lactone and phenolic groups. These surface groups may form complexes with As(III) which is evident from the FT-IR spectra.

Figure 10.1-Adsorption of As(III) on SIC as a function of pH

Figure 10.2-SEM images of (a) PSLW carbon; (b) SIC and (c) As(III)-loaded SIC
The in-plane bending of -OH group occurs at 2273 cm\(^{-1}\) is blue shifted and C-O stretching at 1160 cm\(^{-1}\) in SIC disappeared at As(III)-loaded SIC (Figure 10.4).
10.2.2 Effect of contact time

Contact time is an important parameter to determine the equilibrium time of adsorption process. The available adsorption sites on SIC affect the course of time to reach the equilibrium. As shown in Figure 10.5, As(III) removal increases with increase in contact time; an initial rapid uptake of As(III) followed by a gradual uptake at later stages. The removal rate gradually slows down and equilibrium reaches at 120 min. After reaching the state of equilibrium, there is no remarkable increase in the adsorption capacity. The maximum adsorption capacity of As(III) is found to be 196.43 mg/g for an initial concentration of 1000 mg/L.
10.2.3 Effect of temperature

Temperature plays a key role in determining the adsorption capacity. In this study temperature was varied from 30 °C to 45 °C. Figure 10.6 shows the variation of adsorption capacity with temperature that increases with increase in temperature (Table 10.1). Thus, increase in adsorption capacity with temperature clearly demonstrates that the adsorption of As(III) on SIC is an endothermic process.

**Table 10.1-Effect of temperature on adsorption of As(III) on SIC**

<table>
<thead>
<tr>
<th>As(III) conc. (mg/L)</th>
<th>Temperature (°C)</th>
<th>Adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>30</td>
<td>196.43</td>
</tr>
<tr>
<td>1000</td>
<td>35</td>
<td>199.15</td>
</tr>
<tr>
<td>1000</td>
<td>40</td>
<td>224.58</td>
</tr>
<tr>
<td>1000</td>
<td>45</td>
<td>233.05</td>
</tr>
</tbody>
</table>
10.3 Thermodynamic behaviour

The thermodynamic parameters such as free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) are the actual indicators to determine whether a process proceeds spontaneously or not and to ascertain the practical applicability of the process. The thermodynamic equilibrium constants (K) were deduced by the method of Khan and Singh by plotting $\ln (q/C_f)$ versus q and extrapolating to zero q. The values of change in standard free energy, enthalpy and entropy were calculated (Table 10.2) using equations 3.12 and 3.13 (Chapter 3) and from the corresponding linear plots of log K versus 1/T at different temperatures. The negative values of $\Delta G^o$ (Table 10.2) indicate the spontaneous nature of adsorption process. The increase in adsorption capacity with increase in temperature from 30 ºC to 45 ºC (Table 10.1) demonstrates the endothermic nature. Therefore $\Delta H^o$ needs to be positive for a spontaneous process and the same has been observed (Table 10.2). The positive value of $\Delta S^o$ shows the affinity of the adsorbent towards As(III) species and suggests the possibility of some structural changes in the solvent cluster around the As(III)-SIC complex.
10.4 Isotherm analysis

The adsorption data were analyzed with two well-known adsorption isotherm models namely Langmuir and Freundlich models which are explained in Chapter 3 (Sec. 3.11.1; equations 3.10 and 3.11). The adsorption characteristic of SIC for As(III) removal was determined using Langmuir adsorption isotherm. The linear plots of $C_f/q$ versus $C_f$ at different temperatures (Figure 10.7) point out the applicability of Langmuir isotherm. The values of $Q_o$ and $b$ are obtained from the slope and intercept of the plots. All these facts prove that As(III) is adsorbed as a monolayer on the surface of the adsorbent. The essential characteristic of the Langmuir isotherm is expressed in terms of the dimensionless separation factor ($R_L$), which is defined by

$$R_L = \frac{1}{1 + bC_0}$$ (10.1)

Table 10.3 compiles $Q_o$, $b$ and $R_L$ values as a function of different temperatures. Langmuir constants, $Q_o$ and $b$ are used to assess the affinity between the adsorbate and adsorbent which steadily increase with temperature. This demonstrates that the adsorption is favourable at higher temperatures. It is observed that the $R_L$ values (Table 10.3) lie between 0 and 1 which establishes the truth that the adsorption is favourable under the experimental conditions.
Table 10.3-Langmuir isotherm constants at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$Q_o$ (mg/g)</th>
<th>$b(10^3)$ (L/mg)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>32.39</td>
<td>1.90</td>
<td>0.3448</td>
</tr>
<tr>
<td>35</td>
<td>34.77</td>
<td>1.93</td>
<td>0.3415</td>
</tr>
<tr>
<td>40</td>
<td>44.57</td>
<td>2.15</td>
<td>0.3174</td>
</tr>
<tr>
<td>45</td>
<td>59.17</td>
<td>2.40</td>
<td>0.2920</td>
</tr>
</tbody>
</table>

Figure 10.7-Langmuir isotherm plots at different temperatures

10.5 Adsorption kinetics

The kinetics of As(III) adsorption on SIC was examined with pseudo-first order and pseudo-second order kinetic models which is described in Chapter 3 (Sec. 3.11, equations 3.8 and 3.9). In the present adsorption process linear plots are obtained by plotting log ($q_e - q$) versus $t$ at all the temperatures studied (Figure 10.8). The $k_1$ and $q_e$ values determined from the slope and intercepts of the linear plots at different temperatures are given in Table 10.4. The $k_1$ values increase with increase in
temperature. This observation indicates the enhanced rate of adsorption at higher temperature.

For pseudo-second order model, the linear plots obtained by plotting \( \frac{t}{q_t} \) versus \( t \) at different temperatures are illustrated in Figure 10.9. The \( k_2 \) and \( q_e \) values determined from the intercept and slope of the plots at different temperatures are given in Table 10.4. An analysis of the values in Table 10.4, particularly the agreement between \( q_e \) (exp) and \( q_e \) (cal) and the value of \( R^2 \) towards unity between pseudo-first order and pseudo-second order models clearly reveal that the pseudo-second order model fits better to the data than the pseudo-first order model. Therefore it is inferable that the adsorption of As(III) on SIC is a second order process.

| Table 10.4-Comparison of pseudo-first order and pseudo-second order model parameters |
|-----------------------------------|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| As(III) conc. (mg/L) | Temp. (°C) | \( q_e \) (exp) (mg/g) | Pseudo-first order | Pseudo-second order |
| | | | \( k_1 \) (min\(^{-1}\)) | \( q_e \) (cal) (mg/g) | \( R^2 \) | \( k_2 \times 10^4 \) (g/mg/min) | \( q_e \) (cal) (mg/g) | \( R^2 \) |
| 1000 | 30 | 196.43 | 0.0279 | 140.79 | 0.9805 | 2.82 | 219.05 | 0.9935 |
| 1000 | 35 | 199.15 | 0.0338 | 131.00 | 0.9976 | 4.15 | 218.82 | 0.9979 |
| 1000 | 40 | 224.10 | 0.0334 | 139.74 | 0.9866 | 3.96 | 242.72 | 0.9984 |
| 1000 | 45 | 235.05 | 0.0453 | 140.47 | 0.9957 | 5.58 | 250.16 | 0.9999 |
10.6 Intraparticle diffusion

To determine whether the intraparticle diffusion is the rate determining step or not, the data were analyzed using Finkiam diffusion law [18]. The $k_i$ value is calculated from the slope of the plot of amount adsorbed (mg/g) versus $t^{1/2}$ (Figure 10.10). The plots are...
hyperbolic and do not pass through the origin, which indicate the applicability of diffusion law. The pore diffusion constants are found to be 12.41, 12.85, 17.79 and 23.04 mg/g/min$^{1/2}$ at 30, 35, 40 and 45 °C respectively. The increase in $k_i$ value with increase in temperature clearly demonstrates that the intraparticle diffusion becomes easier at high temperature. The plot also indicates that intraparticle diffusion is not the only rate-controlling step because it did not pass through the origin. The linearity of the plots demonstrates that intraparticle diffusion plays a significant role in the uptake of the As(III) by SIC.

![Figure 10.10-Plots of pore diffusion at different temperatures](image)

10.7 Column study

Column adsorption process plays a vital role in industrial processes for waste water treatment. The observed column data were analyzed using Thomas model which has been detailed in Chapter 3, Sec. 3.11.5. The Thomas model is used for describing the adsorption kinetics and to evaluate the maximum solid phase concentration ($q_o$) and the rate constant ($k$). Figure 10.11 clearly displays the break through curve for the adsorption
of As(III) on SIC. For an initial concentration of 500 mg/L of As(III), the concentrations of As(III) in effluent was found to be zero for the first 65 bed volumes, approximately 85 % of As(III) was retained for 5 bed volumes, 68 % for another 10 bed volumes and as evident from the curve, the retention of As(III) by the column gradually declines as the bed volume increases. The values of $k$ and $q_o$ are computed from the slope and intercept of the linear plot of $\log \left( \frac{C_o}{C_e} \right)$ versus $V$ and they are found as $5.311 \times 10^{-2}$ mL/min/mg and 9.36 mg/g. Thus, from the results of column analysis it is concluded that this column can be used in industrial processes for the removal of As(III) from aqueous system.

![Breakthrough curve for adsorption of As(III) on SIC](image)

**Figure 10.11**-Breakthrough curve for adsorption of As(III) on SIC

### 10.8 Desorption study

Desorption experiment was carried out by placing 0.1 g of As(III)-loaded SIC in 50 mL of 0.1 N HCl at 30 °C. The percent desorption was found to be 86.4. During the desorption experiment leaching of Ag was not observed as the solution tested with potassium chromate did not give any characteristic colouration.
10.9 Comparison of SIC with different adsorbents

Table 10.5 compares the As(III) adsorption capacity onto SIC with other adsorbents reported in the literature. From the table it is observed that the SIC has a comparable adsorption capacity with other adsorbents.

Table 10.5—Comparison of SIC with different adsorbents

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Iron oxyhydroxide impregnated activated carbon</td>
<td>32.86</td>
<td>[19]</td>
</tr>
<tr>
<td>2.</td>
<td>Calcium impregnated activated charcoal from <em>Jatropha Seed</em> residue</td>
<td>0.018</td>
<td>[20]</td>
</tr>
<tr>
<td>4.</td>
<td>Iron-modified bamboo charcoal</td>
<td>7.237</td>
<td>[22]</td>
</tr>
<tr>
<td>5.</td>
<td>Iron impregnated activated carbon</td>
<td>0.024</td>
<td>[23]</td>
</tr>
<tr>
<td>6.</td>
<td>Silver-impregnated carbon</td>
<td>32.39</td>
<td>Present study</td>
</tr>
</tbody>
</table>

10.10 Conclusion

In this study, silver-impregnated carbon (SIC) was prepared from PSLW carbon and its adsorption capacity was investigated using batch and column study. Silver content of carbon and pH play vital role in the adsorption process. The metallic silver impregnated on PSLW carbon is oxidized under acidic conditions. The adsorption at pH 4.0 is due to coulombic interaction between As(III) and Ag⁺ ion while at higher pH of 10.0 the sorption is due to van der Waals interaction and formation of complex between As(III) and surface functional groups. It was found that desorption of As(III) is possible with 0.1 N HCl. This work provides way for developing other silver impregnating adsorbents for As(III) removal.
References


