CHAPTER V

REMOVAL OF ARSENIC(III) FROM AQUEOUS SOLUTIONS THROUGH ADSORPTION ON ACTIVATED CARBON
INTRODUCTION

Pollution is now an important problem owing to increased industrialization and population overflow, and much effort is directed towards its control. Use of adsorbents, particularly activated carbon, is of current interest in the removal of pollutants from air and water. Increasingly strict discharge limits on heavy metals and their widespread uses, threatening presence at hazardous waste sites have accelerated the search for advanced and economically attractive treatment technologies for their removal. Adsorption processes are promising in this regard as opposed to more conventional chemical precipitation in that way achieve higher level removals over a wider range of solution conditions.

Arsenic is of environmental concern due to its toxicity and carcinogenicity. It is widely distributed in the biosphere. Drinking water has identified as one of the major sources of arsenic exposure by the general population [1-2]. Concerns over possible health risks associated with the chronic ingestion of low levels of arsenic in drinking water have also been increased [3]. In natural water, arsenic is primarily present in a variety of chemical forms, including, several mono-, di-, tri methylated arsenic compounds and inorganic arsenic(III) and arsenic(V). Arsenic(V) is the major arsenic species in surface water, while arsenic(III) is the dominant species in ground water. Both elemental arsenic and arsenic(V) are markedly less toxic than arsenic(III). Further the toxicity of such compounds decreases in the order arsine > arsenite > arsenate > alkyl arsenic acids > arsonium.
compounds and metallic arsenic [4]. The toxic effects of arsenic on human beings are summarized in Table 5.1 [5].

**TABLE-5.1**

The toxic effects of arsenic on human beings

<table>
<thead>
<tr>
<th>Affected area</th>
<th>Toxic effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skin</td>
<td>Hyper pigmentation, hyperkeratosis, black foot disease, gangrene, skin cancer</td>
</tr>
<tr>
<td>Lung</td>
<td>Lung cancer (needs confirmation)</td>
</tr>
<tr>
<td>Liver</td>
<td>Cirrhosis, haemangioendothelioma</td>
</tr>
<tr>
<td>Kidneys</td>
<td>Renal read sorption problems</td>
</tr>
<tr>
<td>Blood system</td>
<td>Inhibits biosynthesis of porphyrin, effects white blood cells</td>
</tr>
<tr>
<td>Reproduction system</td>
<td>Spontaneous abortions</td>
</tr>
<tr>
<td>Peripheral nervous system</td>
<td>Peripheral neuropathy, paralysis, loss of hearing</td>
</tr>
<tr>
<td>Gastrointestinal tract</td>
<td>Damage of intestine, intestine pain</td>
</tr>
</tbody>
</table>
A variety of treatment processes have been studied for arsenic removal from water. The major technologies include precipitation-coagulation, membrane separation, ion exchange and adsorption [6-8]. The precipitation-coagulation technique is generally costly, not suitable for small water facilities, and less effective for removal of arsenic(III). Membrane separation processes are more effective in removing arsenic(V) than arsenic(III). Similarly ion-exchange is more effective in removing Arsenic(V) than arsenic(III), because arsenic(V) is normally present as an anion in the medium-pH range while arsenic(III) exists as uncharged molecules in water. Adsorption methods for the removal of arsenic are diversified according to the adsorbents used.

In recent years, the cost effective adsorbents reported for the removal of toxic metals from aqueous solution are, clay [9], sawdust [10-11], fly ash [12-13], groundnut husk [14], rice husk [15], coconut husk [16], gel sorbent [17], zeolites [18-19], ion-exchanger [20-21].

Out of them activated carbon have been successfully employed as adsorbents due to their well developed porous structures and large internal surface comprised of hydrophobic grapheme layers and hydrophilic surface functional groups. These porous materials can be used for the adsorption of a wide range of species from both gas and liquid phases. An important aspect in the treatment of aqueous systems using active carbons is that it can be used to remove both
inorganic and organic species and thus it very important in the purification of water.

Many forms of activated carbons have been used for a long time in numerous processes of gas, water, and wastewater purification. Since the compositions of activated carbon vary considerably depending upon its source and method of treatment and so does the extent of adsorption so we have selected the less used activated carbon No. E4 34011 and studies the adsorption of arsenic(III) on it and is reported here in this manuscript. The appropriate thermodynamic parameters have also been calculated and discussed.
MATERIALS AND METHODS

REAGENTS AND CHEMICALS
Activated carbon No. E4 34011 was obtained from E. Merck (INDIA) Ltd. Solid sodium arsenite, NaAsO₂ was obtained from (Merck). The characteristics of the activated carbon are summarized in Table 5.2. All other reagents used were of analytical grade.

APPARATUS
A high precession water bath incubator-shaker having a temperature variation of ±0.5°C was used for the equilibrium studies. A GBC atomic absorption spectrometer, Australia, with hydride generation facility was used to determine the concentration of arsenic(III) in solution.

PRELIMINARY TREATMENT OF ACTIVATED CARBON
The activated carbon was used after drying at 110°C for 3 hours. It was treated with 1M HCl solution for 2 hours. It was then washed with double distilled water repeatedly until free from chloride ions. Finally it was dried at 110°C. The dried activated carbon was then stored in a dessicator over anhydrous P₂O₅.

SOLUTION OF ARSENIC(III)
Analytical reagent grade solid sodium arsenite, NaAsO₂ was dissolved in limited quantity of double distilled water. Later the quantity was made up to one liter with the addition of double distilled water.
TABLE-5.2

Characteristics of activated carbon

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Characteristics</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface area*</td>
<td>910m²/g</td>
</tr>
<tr>
<td>2</td>
<td>Bulk density*</td>
<td>0.62g/Cm³</td>
</tr>
<tr>
<td>3</td>
<td>Pore volume*</td>
<td>0.75g/Cm³</td>
</tr>
<tr>
<td>4</td>
<td>Moisture</td>
<td>6.8%</td>
</tr>
<tr>
<td>5</td>
<td>Ash content</td>
<td>6.6%</td>
</tr>
<tr>
<td>6</td>
<td>Substances soluble in water*</td>
<td>1%</td>
</tr>
<tr>
<td>7</td>
<td>Substances soluble in acid*</td>
<td>3%</td>
</tr>
<tr>
<td>8</td>
<td>Ion exchange capacity</td>
<td>Nil</td>
</tr>
<tr>
<td>9</td>
<td>Lead (Pb)*</td>
<td>0.005%</td>
</tr>
<tr>
<td>10</td>
<td>Iron (Fe)*</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

* Information furnished by supplier
**ADSORPTION STUDIES**

Samples weighing 0.5 gm of the purified activated carbon were shaken with 50 ml arsenic(III) solutions of different concentration at 22, 45 and 60°C for different times using a temperature controlled shaker. Preliminary studies have shown that equilibrium is reached after 120 minutes. After the predetermined time interval the equilibrating solutions were filtered and analyzed by atomic absorption spectrometer, having the hydride generation facility, to determine the equilibrium concentration (Ce) of arsenic(III) in the solutions. The amount of arsenic(III) in mmole/gm activated carbon (Am) was calculated from the difference of initial concentration (Ci) and the final concentration of arsenic(III) in the solution.

**TREATMENT OF DATA**

A. To determine the shapes isotherms, the Am values were plotted as a function of Ce at different temperatures. The plots are shown in figure [5.3].

B. A computer simulation technique was used to fit the adsorption data for the following adsorption models-

**Langmuir model**- According to this model-

\[
\frac{Ce}{Am} = \frac{1}{k.1/b} + \frac{1}{b.Ce} \tag{1}
\]

where Ce and Am are the same parameter as mentioned earlier. k is the equilibrium constant and b is the amount of adsorbate required to form a
monolayer. Hence a plot of Ce/Am versus Ce should give a straight line with a slope $1/b$ and an intercept $1/kb$ as shown in Figure [5.4].

**Freundlich model** - According to this model:

$$\ln Am = \ln k + \frac{1}{n} \ln Ce$$  \hspace{1cm} (2)

where all the terms have their usual significance and $n$ is an empirical constant. Thus a plot of $\ln Am$ versus $\ln Ce$ should give a straight line with slope $1/n$ and intercept $\ln k$.

**C. Thermodynamic parameters** $\Delta G, \Delta S$ and $\Delta H$ were calculated from the equations given below:

The free energy change ($\Delta G$) was calculated from the relation,

$$\Delta G = -RT \ln k$$  \hspace{1cm} (3)

Similarly the enthalpy change ($\Delta H$) was calculated from the following equation,

$$\ln k = \frac{\Delta H}{RT} + C$$  \hspace{1cm} (4)

and the entropy change ($\Delta S$) was calculated from the equation

$$\Delta G = \frac{\Delta H}{T} - T \Delta S$$  \hspace{1cm} (5)
RESULTS AND DISCUSSION

TIME OF EQUILIBRIUM
The dependence of adsorption of arsenic(III) from solution on activated carbon with time is presented in Figure 5.1. The adsorption increases with increasing contact time and the equilibrium was attained after shaking for 30 minutes at 25°C in pure aqueous medium. The maximum uptake after this time is constant at a value 84%. However, the time of equilibrium used in all the following studies was set to 120 minutes for the sake of simplicity as well as to ensure the complete process of adsorption.

EFFECT OF DOSE ON THE ADSORPTION PROCESS
The effect of dose of activated carbon on the adsorption of arsenic(III) is presented in Figure 5.2. The data indicates that the adsorption increases with the increase in the dose of activated carbon probably due to its high surface area. The maximum uptake exhibited at 600 mg of adsorbent in an aqueous medium.

 ADSORPTION ISOTHERM STUDIES
The adsorption of arsenic(III) on activated carbon has been studied at different temperatures (25, 45 and 60°C) in aqueous medium. Langmuir adsorption model appears to be the best fit as shown in Figure 5.3. The values of regression coefficients are close to unity for this model as compared to those for Freundlich adsorption model. The values of k and b were calculated from the slope and intercept of the plot of Ce/Am versus Ce. The constant values obtained from
Figure 5.1. Effect of time of removal of arsenic(III) by activated carbon.
Figure 5.2. Effect of activated carbon dose on the adsorption process.
Figure 5.3. The adsorption of Arsenic(III) on activated carbon at different temperatures in aqueous medium.
Figure 5.4. Langmuir plots for the adsorption of Arsenic(III) on activated carbon in aqueous medium.
### TABLE-5.3

Related parameters for the adsorption of arsenic(III) on activated carbon in aqueous medium at different temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reg. Coeff. (R)</th>
<th>Langmuir Constant</th>
<th>Reg. Coeff. (R)</th>
<th>Freundlich Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K</td>
<td>b</td>
<td>K</td>
</tr>
<tr>
<td>25</td>
<td>0.98</td>
<td>0.34</td>
<td>2.19</td>
<td>0.76</td>
</tr>
<tr>
<td>45</td>
<td>0.99</td>
<td>0.41</td>
<td>1.60</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>0.96</td>
<td>0.30</td>
<td>2.28</td>
<td>0.74</td>
</tr>
</tbody>
</table>
Langmuir and Freundlich isotherms are listed in Table 5.3. Isotherm at 25°C and 45°C shows L₂ type isotherm and are sigmoid, and isotherms at 60°C shows steep rise in adsorption isotherm, which is of the L₃ type. The adsorption of arsenic(III) does not show a regular increasing or decreasing trend in any of the concentration of arsenic(III) in the temperature range studied. The plateaus are obtained in the adsorption isotherm at 45°C owing to the formation of a complete monolayer of arsenic(III) on the surface of the activated carbon. A critical analysis of the adsorption isotherm in aqueous system reveals that the adsorption of arsenic(III) on the activated carbon increases with a rise in temperature form 45°C to 60°C. The total adsorption at 25°C shows an abnormal value, this anomaly may be interpreted in terms of an increased adsorbate-adsorbent interaction and steep rise in the adsorption isotherm at above 60°C. This may be due to the chemisorptions of arsenic(III) species on the activated carbon surface. The rise in temperature increases the surface activity as well as saturation value.

**THERMODYNAMIC STUDIES**

The various thermodynamic parameter like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated with the adsorption of arsenic(III) ions on to the activated carbon were determined by using the equations, (3), (4), and (5). All the thermodynamic parameters are calculated and listed in Table 5.4. Heat of adsorption (ΔH), which indicates the mechanism of adsorption, was calculated by equation (4). A plot of ln k versus 1/T yields a straight line with slope $\frac{ΔH}{R}$ as
TABLE-5.4

Thermodynamic parameters for the adsorption of arsenic(III) on activated carbon in aqueous medium at different temperatures

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>Langmuir Adsorption Isotherm</th>
<th>Freundlich Adsorption Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\ln K$</td>
<td>$\Delta G$</td>
</tr>
<tr>
<td>25</td>
<td>-1.08</td>
<td>2.677</td>
</tr>
<tr>
<td>45</td>
<td>-0.89</td>
<td>2.356</td>
</tr>
<tr>
<td>60</td>
<td>-1.20</td>
<td>3.323</td>
</tr>
</tbody>
</table>

$\Delta G = \text{kJ mol}^{-1}$, $\Delta S = \text{kJ mol}^{-1} \text{K}^{-1}$, and $\Delta H = \text{kJ mol}^{-1}$
Figure 5.5. The plot of Langmuir constant ($\ln k$) versus $1/T$. 
Figure 5.6. The plot of Freundlich constant (ln k) versus 1/T.
shown in Figure 5.5 and 5.6. The $\Delta H$ values were found to -2.316 kJ/mole for Langmuir isotherm and -9.575 kJ/mole for Freundlich isotherm. The negative value of $\Delta H$ indicates the process is exothermic also the process may be due physical in nature and can be easily reversed by supplying the heat equal to calculated $\Delta H$ value to the adsorption system. Moreover, the negative values of $\Delta S$ in Langmuir isotherm point out the spontaneity in the adsorption process with reduction in molecular size and increased randomness at solid liquid interface.
REFERENCES


