CHAPTER - 4
REDOX BEHAVIOUR OF ARSENITE/ARSENAT IN THE COLLECTED CLAY SAMPLE

4.1. Introduction:

Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry. Cyclic voltammetry is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step further than linear sweep voltammetry which ends when it reaches a set potential. When cyclic voltammetry reaches a set potential, the working electrode's potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied potential to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution\textsuperscript{282, 283, 284}.

Cyclic voltammetry is rarely used for quantitative determinations, but it is widely used for the study of redox processes and for understanding reaction intermediates, and for obtaining stability of reaction products\textsuperscript{285}. This technique is based on varying the applied potential at a working electrode in both forward and reverse directions while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential\textsuperscript{285}. At that point the scan would be reversed and run in the
negative direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed.

Arsenic toxicity strongly depends on the form in which arsenic is present. Inorganic arsenic is much more toxic than organic forms that are present in sea food. Inorganic forms of arsenic are arsenite and arsenate. Oxidation state of arsenic in arsenite is III which is more toxic than arsenate whose oxidation state is V\textsuperscript{19,286,287}. The study was carried out to see whether arsenic(III) can be oxidized to less toxic arsenate(V) with the help of cyclic voltammetry by using the natural kaolinite clay collected from Na-Dewri Gaon of Karbi Anglong district of Assam.

### 4.2. Experimental

#### 4.2.1 Apparatus and Reagents:

A computerized Cyclic voltammetric analyzer CHI 600 C fitted with a three-electrode assembly including a platinum working electrode (25 mm\textsuperscript{2} geometric surface area), a silver/silver chloride reference electrode (Ag/AgCl/saturated with 3 M KCl electrode) and a platinum counter electrode (Alfa Aesar, 99 %) was used for the cyclic voltammetric measurements. The platinum working electrode was first cleaned and sonicated before use. All the three electrodes were washed with distilled water before use. High purity nitrogen gas was bubbled through the solutions before the experiments to remove the aerial oxygen and the potentials were measured relative to the silver/silver chloride reference electrode.
4.2.2 Preparation of clay extract:

10 gm of clay sample was mixed with 100 mL of 2 M HCl solution and kept it for 24 hr. Different concentrated solutions were prepared with 5 mL of the extract prepared for further study and pH of the reaction medium was maintained at pH-7.

4.2.3 Solutions:

Solutions for all the experiments were prepared by dissolving equal amount arsenic(III) oxide (Aldrich, 99.995 %) and arsenic(V) oxide (Aldrich, 99.99 %) in the extract of the clay. Arsenite and arsenate were present in equal proportions in the resultant solutions so as to get the complete oxidation-reduction cycle. The supporting electrolyte used in this process is sodium nitrate.

4.3. Results and Discussions:

Cyclic voltammetric analysis of As(III) and As(V) were studied. Solutions having concentrations 0.1 M, 0.2 M, $1 \times 10^{-3}$ M and $1 \times 10^{-5}$ M were prepared with both arsenite(III) and arsenate(V). The results are displayed in the Fig-71. A1, A2, A3 and A4 are the anodic peaks and C1, C2, C3 and C4 are their corresponding cathodic peaks. It is observed from the Fig-71 that with the increase in the concentration of the arsenic in the solutions the oxidation peak diminishes and the reduction peak increases.
Fig-71 Cyclic voltammogram with Pt working electrode at potential scan rate of 0.01 V/s with \(0.2 \text{ M}, 0.1 \text{ M}, 1x10^{-3} \text{ M}, 1x10^{-5} \text{ M}\) solutions of As(III)+As(V) at potential range of -0.8 to 1.0V.

Since the solutions contain both arsenite(III) and arsenate(V) the reduction peaks at the potential -0.162V(C1), -0.174V(C2), -0.180(V3) and -0.213V(C4) represents the reduction from As(V) to As(III) and the oxidation peaks at 0.315V(A1), 0.281V(A2), 0.247V(A3) and at 0.225V(A4) represents the oxidation from As(III) to As(V).

Form Fig-71 it is also observed that the anodic peak currents increased with increasing concentration of arsenic species and cathodic peaks gradually disappeared. The standard reactions and their reduction potentials are given below:\textsuperscript{285}
Ar(III) + 3H⁺ + 3e⁻ = As(0) + 2H₂O……………. (4.2)

E⁰ = 0.006 V vs SCE

As(0) + 3H⁺ + 3e⁻ = AsH₃(g)………………………… (4.3)

E⁰ = -0.482V vs SCE

Arsenate is electrochemically inactive under conditions used in the electrochemical determination of arsenite ²⁸⁸, ²⁸⁹. From Fig-71 it is observed that with the increase in the concentration of arsenic species the anodic peaks are shifted towards more positive potential and the cathodic peaks towards less negative potential.

It is observed that the collected clay can oxidize the arsenic species powerfully and the anodic peak intensity increases with increasing concentration of the resultant solution.

In further studies only arsenic(V) species were taken with the extract of natural kaolinite clay to observe whether the clay has the capacity to reduce As(V) to As(III). Solutions were ultrasonicated periodically and filtered. The filtrates were taken for the experiments. The solutions were prepared with concentrations of 1x10⁻⁵ M, 1x10⁻³ M, 1x10⁻² M, 0.1 M, 0.5 M and 1 M of As(V) solution. The CV all experiment are described in Fig-72(a-f).
Fig-72(a) Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01V/s at potential range from -1.0 V to 0 V.

Fig-72(a) represents the cyclic voltammogram of the As(V) solution having concentration $1 \times 10^{-5}$ M. In this figure the reduction peak $C_1$ appears at -0.682 V, and a small oxidation peak is also observed at -0.369 V.

Fig-72(b) Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01V/s at potential range from -1.0 V to 0 V.
Fig-72(b) represents the cyclic voltammogram of the As(V) solution having concentration $1 \times 10^{-3}$ M. In this figure the reduction peak $C_2$ appears at -0.669 V, and a small oxidation peak is also observed at -0.386 V.

![Cyclic voltammogram of As(V) solution](image)

**Fig-72(c)** Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01 V/s at potential range from -1.0 V to 0 V.

Fig-72(c) represents the cyclic voltammogram of the As(V) solution having concentration $1 \times 10^{-2}$ M. In this figure the reduction peak $C_3$ appears at -0.691 V, and a very small oxidation peak is observed at -0.365 V.

Fig-72(d) represents the cyclic voltammogram of the As(V) solution having concentration 0.1 M. In this figure the reduction peak $C_4$ appears at -0.720 V, but there is no oxidation peak in this figure.
**Fig-72(d)** Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01V/s at potential range from -1.0 V to 0 V

**Fig-72(e)** Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01V/s at potential range from -1.0 V to 0 V
Fig-72(e) represents the cyclic voltammogram of the As(V) solution having concentration 0.5 M. In this figure the reduction peak C5 appears at -0.752 V, with no oxidation peak.

Fig-72(f) Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01V/s at potential range from -1.0 V to 0 V

Fig-72(f) represents the cyclic voltammogram of the As(V) solution having concentration 1 M. In this figure the reduction peak C6 appears at -0.764 V, with no oxidation peak.

It is observed from the above discussion that at lower concentration of As(V) solutions sharp cathodic peaks appear along with one small oxidation peak. With the increase in the concentration of As(V) solution oxidation peak is disappeared and the peak current of the reduction peaks gets decreased. i.e. the clay has the capacity to reduce As(V) to As(III) at lower concentration of As(V).
Cyclic voltammograms of Pt working electrode at potential scan rate of 0.01 V/s. c1 - 1x10^{-5} M As(V) solution, c2 - 1x10^{-3} M As(V) solution, c3 - 1x10^{-2} M As(V) solution, c4 - 0.1 M As (V) solution, c5- 0.5 M As(V) solution, and c6 – 1 M As(V) solution, at potential range at -1.0 to 0 V.

Fig-73 is the overlay plot of all the figures of Fig-72. In Fig-73 it is observed that with increasing concentration of arsenic(V), reduction peaks gets depressed and the peak potentials are slightly shifted towards right i.e. towards higher potential. The potential is observed in between -0.6 V to -0.8 V.

The experiment was again performed with arsenic(III) solutions. This time CV was taken at different scan rates and the concentration of the solutions was 1mgL^{-1}. 
Fig-74 Cyclic voltammograms of Pt electrode at potential range at -0.8V to 1.0 V of 1M arsenic(III) solution at scan rates A- 0.65V/s B- 0.2 V/s and C- 0.1 V/s

Sharp anodic peaks A, B and C appear at the potential range of 0.25 to 0.3 V along with one broad peak at lower scan rates which gets disappeared with increasing scan rate. From Fig-74 it is seen that As(III) gets oxidized to As(V) and small and distinct reduction peaks that appear at potential -0.15 V indicates the reduction of As(III) to As(V).
Table-42 Observed cathodic peak potentials ($E_{pc}$), anodic peak potential ($E_{pa}$), cathodic peak current ($i^R/10^{-5}A$) and anodic peak current ($i^0/10^{-5}A$) from Pt working electrode voltammograms in $1mgL^{-1}$ of As(III) with the extract of the clay at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Sq. rt. scan rate ($\nu^{1/2}$)</th>
<th>$i^0/10^{-5}A$</th>
<th>$i^R/10^{-5}A$</th>
<th>$E_{pa}$</th>
<th>$E_{pc}$</th>
<th>$i^0 \nu^{1/2}$ AV's</th>
<th>$I^R \nu^{1/2}$ AV's</th>
<th>$(E_{1/2}) = (E_{pc}+E_{pa}/2)$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.316</td>
<td>1.029</td>
<td>-2.687</td>
<td>0.246</td>
<td>-0.183</td>
<td>3.25</td>
<td>-8.503</td>
<td>0.03</td>
</tr>
<tr>
<td>0.2</td>
<td>0.447</td>
<td>1.567</td>
<td>-3.62</td>
<td>0.277</td>
<td>-0.177</td>
<td>3.50</td>
<td>-8.09</td>
<td>0.05</td>
</tr>
<tr>
<td>0.65</td>
<td>0.806</td>
<td>2.466</td>
<td>-5.520</td>
<td>0.309</td>
<td>-0.167</td>
<td>3.05</td>
<td>-6.84</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The peak current, $I_p$, is governed by the Randle-Sevcik relationship

$$I_p = k n^{3/2} A D^{1/2} C^b \nu^{1/2}$$

(4.4)

Where, the constant $k = 2.72 \times 10^5$, $n$ is the number of moles of electrons transferred per mole of electroactive species (e.g. ferricyanide), $A$ is the area of the electrode in $cm^2$, $D$ is the diffusion coefficient in $cm^2/s$, $C^b$ is the solution concentration in mole/L, and $\nu$ is the scan rate of the potential in volt/s.
The product of peak current densities and inverse of square root of potential scan rates are included in Table-42 and from the data it is clear that the product values indicates that the presence of some complex redox reactions. $E_{1/2}$ values give the reduction potential of the overall reaction.

The $I_p$ is linearly proportional to the bulk concentration, $C^b$, of the electroactive species, and the square root of the scan rate, $v^{1/2}$. After plotting of square root of scan
rates versus oxidation and reduction current a straight line is formed indicating a linear behavior. Reduction current is decreased with the increase in the square root of scan rates (Fig-75a) and oxidation current is increased (Fig-75b). Therefore, we can say that the electrode reaction is controlled by diffusion, which is the mass transport rate of the electroactive species to the surface of the electrode across a concentration gradient. This linear behavior indicates the redox properties of the arsenic species\textsuperscript{290-292}.

### 4.4 pH dependence on the electrochemical behaviour of arsenic:

The redox reactions of arsenic totally depend on pH of the reaction medium. After several experiments it was found that oxidation of arsenite(III) to arsenate(V) increases in alkaline medium (Fig-76). The pH of the reaction medium was adjusted using small quantities of HCl and NaOH solutions.

It is observed from Fig-6 that one small reduction peak appears at potential of nearly 0.107 V in every case which may be due to the reduction of As(V) to As(III). In alkaline solution (pH-9) two cathodic peaks appear at 0.107 V and the other at 0.55 V. The peak at 0.107 V is very sharp in comparison to the other in alkaline solution. i.e. the clay can reduce As(V) up to certain extent when the pH of the solution is greater than (pH-7).
Fig-76 Cyclic voltammograms at potential range at -0.8V to 1.0 V of 1M total arsenic (As(III)+As(V)) solution at scan rate 0.1V/s for 1-pH(9), 2-pH(6), 3-pH(5), 4-pH(2).

4.5 Conclusions:

In this experiment the redox reactions of arsenic species in the extract of the clay was studied by CV with a Pt working electrode at different scan rates and at different concentrations of arsenite and arsenate solutions. Distinct current peaks are observed associated with redox reactions between As(III) and As(V). This indicates that it is not so much difficult to study the redox reactions between arsenite and arsenate. In every experiment it is found that anodic and cathodic peak current densities are different with respect to the condition of reaction medium which indicate that the redox reactions are not controlled by surface mechanism it is only controlled by ion transportation\textsuperscript{291}. Oxidation of arsenite to arsenate is very much clear but the reduction of arsenate to arsenite is not so clear. For a reversible couple the ratio between anodic peak current to cathodic peak current is near to unity, but in this experiment it is not found. From that it
was concluded that the oxidation and reduction reaction of arsenic with clay is possible but along with this some other reactions may occur which hampers the redox reaction of arsenic species.