6.7. Introduction

Nickel bearing compounds exhibit excellent electrochemical properties in an alkaline medium due to the reversible one-electron redox process of the couple Ni (III)/Ni (II). Nickel (II) ions were investigated in the compounds like nickel chloride and nickel sulfate at carbon paste electrode by using cyclic voltammetric technique. The well defined redox peaks were observed for both nickel chloride and nickel sulfate compounds in 0.1 M KOH solution as supporting electrolyte at scan rate of 100 mV/s. The effect of scan rates and concentrations were studied and the effects show good linear relationship with the peak currents. The cyclic voltammetric behavior of Ni (II) ions were also examined in 1 M KCl solution as supporting electrolyte. The Ni (II) ions shows well defined redox peaks in presence of potassium ferricyanide as a mediator.

6.8. Review of Literature of Nickel and Carbon Paste Electrode

Metal ions are generally non-degradable. They have infinite lifetimes, and build up their concentrations in food chains to toxic levels. In recent years, arrays of industrial activities have been disturbing the geological equilibrium of metal ions through release of large quantities of toxic metal ions into the environment [1].

Metallic nickel is not affected by water but is slowly attacked by dilute hydrochloric or sulfuric acid and is readily attacked by nitric acid. Fused alkali hydroxides do not attack nickel. Several nickel salts, such as the acetate, chloride, nitrate, and sulfate, are soluble in water, whereas carbonates and hydroxides are far less soluble and sulfides, disulfides, subsulfides and oxides are practically insoluble in water [2, 3].

The primary source of nickel in drinking-water is leaching from metals in contact with drinking-water, such as pipes and fittings. However, nickel may also be present in some groundwater as a consequence of dissolution from nickel ore-bearing rocks. Nickel is used principally in its metallic form combined with other metals and nonmetals as alloys. Nickel alloys are characterized by their hardness, strength, and resistance to corrosion and heat. Nickel is used mainly in the production of stainless steels, non-ferrous alloys, and super alloys. Other uses of nickel and nickel salts are in electroplating, as catalysts, in nickel–cadmium batteries, in coins, in welding products, and in certain pigments and electronic products [4]. Nickel occurs predominantly as the ion Ni(H₂O)₆²⁺.
in natural waters at pH 5–9. Complexes with ligands, such as OH\(^-\), \(\text{SO}_4^{2-}\), \(\text{HCO}_3^-\), \(\text{Cl}^-\), and \(\text{NH}_3\), are formed to a minor degree in this pH range. Nickel concentrations in bottled mineral water will depend on the source and any treatment applied. Levels of nickel in a selection of bottled mineral waters were below the detection limit of 25 \(\mu\text{g/litre}\) [5].

A number of studies on the carcinogenicity of nickel compounds in experimental animals are available [6]. Generally, tumors are induced at the site of administration of the nickel compound. For instance, several nickel compounds induce injection-site sarcomas [7]. A marked variation in the incidence of injection-site sarcomas between different strains of mice has been reported [8]. There are only a limited number of studies on carcinogenic effects after oral exposure to nickel compounds [9]. As well, no difference in tumor incidence was observed in a lifetime study in rats exposed to 5, 50, or 125 mg of nickel per kg of body weight per day in the feed compared with controls. Owing to the high death rate and lack of information on cause of death, this study is of minor value in evaluating carcinogenicity after oral exposure to nickel. A similar 2 year study in dogs also revealed no increase in tumors [10].

The detection and assessment of the heavy metal ions in water supplies or effluent streams or in specific processes are important tasks in environmental protection and human health. Currently, although there are several methods commonly employed in metal ions analysis, e.g., atomic adsorption spectroscopy [10], electrochemical separation techniques [12], high-performance liquid chromatography [13], and capillary electrophoresis [14], while atomic adsorption method is offer good analytical performance in terms of precision and accuracy, nevertheless expensive from the viewpoint of reagent consumption and instrumentation capital cost. Accordingly, there is considerable interest in developing simple, rapid and economically viable methods that will afford facile analyses of heavy metal ions. The carbon paste electrode based sensor-based analysis is an alternative method which can provide real-time analysis, low cost in instrumentation.

Although electroanalytical methods in general and stripping techniques in particular provide very sensitive routes to the quantitation of many trace metals, widespread utilization of this family of techniques for the solution of practical analysis problems has been extremely limited. This situation is primarily explained by the
availability of alternate spectrometric and neutron activation methods for trace-metal determination that are considerably more selective than stripping procedures. Further, because of problems ranging from inordinately negative reduction potentials and slow electron transfer kinetics to the formation of intermetallic compounds upon electrodeposition, numerous metal ions of analytical interest simply are not accessible to the stripping approach as it is conventionally carried out. However, in view of the high sensitivity afforded by analyte accumulation prior to measurement, the development of electroanalytical techniques analogous to the stripping approach but possessing more selective analyte collection mechanisms represents an extremely enticing goal[15]. Recently, a number of investigators have demonstrated a new variation of electrochemical trace-metal analysis in which analyte preconcentration was carried out at chemically modified electrodes (CMEs), with surfaces specifically designed for the ability to react with and bind the target solute (16-23).

In this work, carbon paste electrode was used for the electrochemical studies of Ni (II) ions present in nickel sulphate and nickel chloride by using cyclic voltammetric (CV) technique and the adopted method is very simple.

6.9. Experimental
6.9.1 Apparatus and procedure

Electrochemical measurements were carried out with a CHI model 660c. Electrochemical workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The carbon paste electrode was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

6.9.2 Reagents

Nickel sulphate, nickel chloride and silicone oil were purchased from Himedia chemicals. The graphite powder, potassium ferricyanide, potassium chloride and potassium hydroxide procured from Merk chemical and all aqueous solution were prepared with double distilled water.
6.9.3 Preparation of carbon paste electrode

The carbon paste electrode was prepared by mixing 70% graphite powder and 30% silicone oil in an agate mortar for 30 min. The mixture was then packed into a homemade Teflon cavity and polished using smooth paper.

6.10. Results and discussion

6.10.1 Electrochemical response of Ni (II) ions presents in nickel sulphate and nickel chloride at carbon paste electrode

The electrochemical behaviour of Ni (II) ion present in nickel sulphate and nickel chloride at carbon paste electrode was studied by using CV technique. Fig. 1 represent the cyclic voltammograms for 1mM Nickel sulphate (curve b) and for blank solution (curve a) at carbon paste electrode in 0.1M KOH at sweep rate 100mV/s. In the Fig. 2 shows the cyclic voltammetric response for 1mM nickel chloride (dashed line) and for blank solution (solid line) at carbon paste electrode in 0.1M KOH at sweep rate 100mV/s. The well defined redox peaks were observed for both nickel sulphate and nickel chloride compounds oxidation of Ni (II) to Ni (III). For both Nickel sulphate and Nickel chloride the Ni (II) ions oxidised to Ni (III) at potential of 454mV and reduction of Ni (III) ion at potential of 366mV respectively. The redox peak potential difference ($\Delta E_p$) was 88mV. The carbon paste electrode shows conductivity during oxidation of Ni (II) to Ni(III) by one electron transfer.

6.10.2 Electrochemical behavior Ni(II) ion present in nickel sulphate and nickel chloride at carbon paste electrode in 1M KCl solution

The electrochemical behaviour of Ni (II) ion present in the nickel sulphate and nickel chloride at carbon paste electrode was recorded in 1M KCl solution at sweep rate 50mV/s. Fig. 3 shows the cyclic voltammetric response for 1mM nickel sulphate in the presence of 1mM potassium ferricyanide (curve b) and for 1mM nickel sulphate in the absence of 1 mM Potassium ferricyanide (curve a) at scan rate 50 mV s$^{-1}$ in 1M KCl solution. The Fig. 4 shows the cyclic voltammetric response for the nickel chloride in presence of 1mM potassium ferricyanide (curve b) and for 1mM nickel
chloride in presence of 1 mM potassium ferricyanide (curve a) in 1M KCl solution at scan rate 50 mV/s. In the absence of potassium ferricyanide nickel containing compounds does not reveal any peaks at potential window between 200mV to 1000mV at carbon paste electrode. In presence of potassium ferricyanide shows good redox peaks for nickel. It shows the Nickel bearing compounds exhibit excellent electrochemical properties in an alkaline medium due to the reversible one-electron redox process of the couple Ni (III)/Ni (II) [24]. But in the neutral pH it required mediator for showing conductivity in KCl solution. In the presence potassium ferricyanide the carbon paste electrode shows good conductivity and electrocatalytic property of nickel (II) ions.

6.10.3 Effect of scan rate on the peak current

Fig. 5a and Fig. 6a shows the cyclic voltammograms of 1 mM nickel sulphate and 1mM nickel chloride at CPE in 0.1M KOH solution at different scan rates. This was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport or not. The observation shows that with the increased scan rate, the redox peak current also increased gradually (Fig. 5a, Fig. 6a). The graph of anodic peak current (Ipa) vs. square root of scan rate (v^{1/2}) was plotted (Fig. 5b, Fig. 6b). The graph obtained was good linearity between the square root of scan rate (v^{1/2}) and Ipa. In the range from 100 to 500 mV s^{-1} the redox peak currents were proportional to the square root of scan rate (v^{1/2}) and the obtained correlation coefficient was 0.9960 and 0.9994 for nickel sulphate and nickel chloride respectively, which indicates that the electron transfer reaction was diffusion controlled[25].

6.10.4 Effect of concentration of Nickel

As the concentration of nickel sulphate and nickel chloride was varied from 0.1 to 0.5 mM and cyclic voltammograms were recorded (Fig.7a, Fig. 8a) in 0.1 M KOH solution at scan rate 100mV/s. The anodic peak current increases linearly with increase in concentration of nickel compounds and the obtained correlation
coefficient were found to be 0.9932 and 0.9985 for nickel sulphate and nickel chloride respectively (Fig. 7b, Fig. 8b).

6.11. Conclusion

In this work, nickel (II) ions were investigated in the compounds like nickel chloride and nickel sulfate at carbon paste electrode by using cyclic voltammetric technique. The well defined redox peaks were observed for both nickel chloride and nickel sulfate compounds in 0.1 M KOH solution as supporting electrolyte at scan rate of 100 mV/s. The effect of scan rate and concentration was studied, which indicates that the electron transfer reaction was diffusion controlled. The electrochemical behaviour of nickel ion can be studied in neutral pH and the CPE shows well defined redox peaks in presence of potassium ferricyanide as a mediator in 1M KCl solution. The method is very simple to identify the characteristics of Ni (II) ions.
Fig. 1. Cyclic voltammogram for 1mM Nickel sulphate (curve b) and for blank solution (curve a) at carbon paste electrode in 0.1M KOH at sweep rate 100 mVs$^{-1}$.

Fig. 2. Cyclic voltammogram for 1mM nickel chloride (dashed line) and for blank solution (solid line) at carbon paste electrode in 0.1M KOH at sweep rate 100 mVs$^{-1}$. 
Fig. 3. Cyclic voltammogram for 1mM nickel sulphate in the presence of 1mM Potassium ferricyanide (curve b) and for 1mM nickel sulphate in the absence of 1mM Potassium ferricyanide (curve a) at scan rate 50 mV s$^{-1}$ in 1M KCl solution.

Fig. 4. Cyclic voltammogram response for 1mM nickel chloride in the presence of 1mM Potassium ferricyanide (curve b) and for 1mM nickel sulphate in the absence of 1mM Potassium ferricyanide (curve a) at scan rate 50 mV s$^{-1}$ in 1M KCl solution.
Fig. 5a. Cyclic voltammogram of 1 mM nickel sulphate at CPE in 0.1mM KOH solution at different scan rates (0.1V/s - 0.4V/s).

Fig. 5b. Graph of anodic peak current vs scan rate.
Fig. 6a. Cyclic voltammogram of 1 mM nickel chloride at CPE in 0.1mM KOH solution at different scan rates (0.1V/s -0.4V/s).

Fig. 6b. Graph of anodic peak current vs scan rate.
Fig. 7a. Cyclic voltammogram for different concentration of nickel sulphate (0.1mM-0.5mM) at CPE in 0.1M KOH solution with scan rate 100 mVs$^{-1}$.

Fig. 7b. Graph of $I_{pa}$ vs. concentration of nickel sulphate

$R^2=0.9915, \ n=5$
Fig. 8a. Cyclic voltammogram for different concentration of nickel chloride (0.1mM-0.5mM) at CPE in 0.1M KOH solution with scan rate 100 mVs\(^{-1}\).

Fig. 8b. Graph of Ip\(a\) vs. concentration of nickel chloride


