ELECTROCHEMICAL ANALYSIS OF HEAVY METALS (Cd AND Pb) IN CONTAMINATED SOIL

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Received December 15, 2008    Accepted March 01, 2009

ABSTRACT

Heavy metal contaminated soil can be long term environmental concern. Hence, the assessment of heavy metal in contaminated soil has received much attention in present scenario. Electrochemical analysis is a reliable and cost effective method to evaluate toxicity of heavy metal in soil. In the present work the analysis was based on well planed sampling strategy appropriate selection and implementation of Electrochemical Sensor. For the determination of heavy metal the cadmium electrochemical sensor and lead electrochemical sensor were used.

The present study was carried out to observe the concentration and toxic effect of cadmium and lead in contaminated soil. Cadmium ion concentration was 1.2-1.3µg/g and lead ion concentration was 21-25 µg/g in the analyzed sample of contaminated soil by electrochemical sensors method.

Key Words: Ion selective electrode, Sensors, Heavy metals, Contaminated soil.

INTRODUCTION

It is a known fact that soil is getting contaminated with different type of pollutants. There are various types of pollutants with which the soil is getting contaminated. The main contaminates comes from pesticides and heavy metal discharge from Industries particularly metal and leather Industry. Heavy metal contaminated soils can be a long term environmental concern and a potential financial liability and concern. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Examples of heavy metal include mercury (Hg), cadmium (Cd) and chromium (Cr) and lead (Pb).

Heavy metals are natural component of the earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via, food, drinking water and air. Heavy metal poisoning could result, for instance, from drinking water contamination (e.g. lead pipes), high ambient air concentration near emission sources, or in take via the food chain. Heavy metals are dangerous because they lend to bioaccumulation. Bioaccumulation means an increase in the concentration of chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compound accumulate in living things any time they are taken up an stored faster then they are broken down (metabolized or excreted) Heavy metal enter a water supply by industrial and consumer waste, or even from acidic rain breaking
down soil and releasing heavy metals into streams, lakes, rivers and ground water.

For, environmental and health point of view, the three most pollutants heavy metal are lead, cadmium and Mercury. Effect of cadmium on the environment, It is biopersistent and, once absorbed by an organism, remain resident for many years although it is eventually excreted. In humans, long time exposure is associated with renal dysfunction. High exposure can lead to abstractive lung disease and has been linked to lung cancer. Cadmium may also produce bone defects in human and animals. The metal can be liked to increase blood pressure and effects on the rayo cardium in animals. The average daily intake for human is estimated as 0.15µg from air and 1µg from water. Cadmium is produced as an inevitable by product of zinc (or occasionally lead) refining, since these metals occur naturally with in raw ore however, once collected the cadmium is relatively easy to recycle. Cadmium found in fertilizer and sewage sludge (contaminating agricultural soil) cadmium is used for plating and corrosion treatment of iron and steel utilized in production of batteries, and in spray painting, and cutting cadmium and its area.

Lead exposures in environment through gasoline additives (organolead is contained in gasoline as an octane booster), lead based paint lead soldered cans and ceramic glazes. Occupational primary manufacture of lead, lead production from auto batteries and scrap metal. Production of batteries welding and cutting of lead alloys. For this purpose monitoring of these metals by different method deals by different workers8,9.

Effect of lead in health and environment. Inorganic lead-encephalopathy, seizures, decreased intellectual performance of children anemia and lead palsy in adults. Acute effects nephrotoxicity, Gastrointestinal upset anorexia, dysphasia, constipation renal dysfunction and lead seams in gingival. Organic lead sleepiness dizziness, fatigue insomnia and psychosis, High level of exposure may result in toxic biochemical effects in humans which cause problem in synthesis of hemoglobin, effects on the kidney joints and reproductive System, and acute or chrone damage to the nervous system.

Average daily lead intake for adults in U.K. is estimated at 1.6µg from air, 20µg from drinking water and 28µg from food. Most people receive the bulk of their lead from food water, in areas with lead pining and plumbo solvent water air near point of source emissions, soil, dust, point flakes in old houses or contaminated lead. Lead in the air contributes to lead levels in food through deposition of dust and rain containing the metal, on crop and the soil. Lead in environment arises from both natural and anthropogenic source.

From a above mentioned toxic effect of heavy metal in environment and human healthy the main concern of this work to develop the technique which is cost effective and real time analysis. For this concern electrochemical sensor have found very wide application in organic chemistry, environmental, geochemical, biochemistry biology, medicine, and equilibrium and stability constant studies. Several papers dealing with the application of ion selective electrode i.e. electrochemical sensor in study and analysis’s of soil industrial, organic and environmental sample10-13.

This paper presents a brief overview of preparation and function of electrochemical sensor for analysis of Cd and Pb. Electrochemical sensor find wide application in analysis of environment sample.
MATERIAL AND METHODS

Several different electrochemical sensors have already been developed to analyze Cd and Pb. In the present work membrane based Cd and Pb electrochemical sensor ion selective electrode were prepared. They consist of a membrane in which electro active materials are impregnated. For the preparation of Cd II and Pb II electrochemical sensor, specially prepared Cd II thiobarbutarate and Pb II salicyladoximate were used as electro active material. These membrane based ion selective electrode were employed successfully for preparation of heavy metal ion-selective electrode. These electrode shows nernstion response against the cadmium and lead in concentration change^{4,15,16}.

Cadmium and lead ISE pressed diameter of 8 mm and 2 mm showed in nernstion response from $10^{-5}$ to $10^{-1}$M of cadmium ion and lead ion concentration. Further more aiming to its application for analysis of contaminated soil. Electrochemical sensor is remarkable product of this approach. Electrochemical sensor responds selectively to the activity of ion species and often referred as ion selective electrodes. The membrane which forms an essential part of the construction of ion selective electrodes contains the electro active material. In barrel type ion-selective electrodes a suitable reference electrodes is inserted in the tube containing reference inner solution which is in contact with the membrane if an ion selective electrode is in contact with a sample solution containing the ion for which electrode is selective and a reference electrode is placed in the same sample solution, an electrochemical cell is formed. The EMF value measured will be equal to:

$$ E = E^0 + 2.303 \frac{RT}{ZF} \log [(aj + kij \ (aj)^{2\gamma})] $$

As long as the composition of the inner solution is kept unaltered and the potential difference at the reference electrode-sample solution, boundary remains virtually constant, $E^0$ is constant and the EMF of the cell will depend only on the composition of the sample solution. Two different membrane type cadmium II (thiobarbutarate) and lead II (salicyladoximate) were impregnated in an inert matrix. The electro active component is the most important constituent of an an ion-selective electrode system, salts of inorganic cat-ions furnish useful electro active material for the preparation of membrane which may be successfully employed in the fabrication of electrodes.

Preparation of ion selective electrode

In the present work the electro active material used where precipitates of Cadmium and lead obtained from Cd-Thiobarbutarate and lead salicyladoximate membrane precipitating reagents. The electro active materials which were used Thioburbutarate and Salicyladoximate.It may be emphasized that the choice of suitable material is not easy and large number of trial experiments have to be performed electrochemical sensor technique as an analytical tool for the analysis of heavy metal in sample. The characteristic of these two electrodes were studied in terms of (i) Electrode response (ii) response time (iii) effect of pH (iv) selectivity coefficient (v) application.

Electrode assembly

The structure of cadmium and lead ion-selective electrode fabricated is shown in Fig. 1, with different electro active membrane. The Cd thiobarbutarate membrane Is stuck in an epoxyresin (cipa Giegy)

This is electrode II electrode and has inner solution ($10^{-3}$M) cadmium chloride and Ag/AgCl inner electrode. The Pb
salicylaldoximate membrane is struck in an epoxy resin as interbinder. This electrode II and has inner solution ($10^{-3}$ M lead Acetate) and Ag/AgCl [inner electrode]. The performance of the electrode was examined by measuring the E.M.F. against model (Philips pH/mV meter Model PR 9405) and both electrodes; ISE as well as Ag-AgCl were dipped in the solution to record the potential of each solution). Characteristics of the Electrode were also studied.

Electrode Response and calibration curve

The Cd ion-selective electrode fabricated and reference electrode were placed in 200ml beaker. Sample of 100ml in a beaker was stirred during the measurement. The performance of the Cd$^{2+}$ ion-selective electrode was examined by measuring the E.M.F. of the following electrochemical cell.

$$\text{Ag} \mid \text{Cd Thiobarurate} \mid \text{Sample} \parallel 1 \text{M KNO}_3 \parallel 3 \text{M KCl} \parallel \text{Ag} \mid \text{AgCl}/\text{Ag}. \text{ Each electrode was immersed in } 10^0 - 10^{-1} \text{ M } \text{Cd}^{2+} \text{ solution of which the total ionic strength was adjusted with } 0.1 \text{ M KNO}_3 \text{ and calibration curves of each electrode were made. The electrode potential were recorded after their values had stabilized with in } \pm 0.1 \text{ mV min}^{-1}. \text{ The potential concentration curve were plotted as shown in Fig. 2a.}

The Pb$^{2+}$ ion-selective electrode fabrication and reference electrode were placed in 200ml beaker. Sample of 100ml in a beaker was stirred by magnet on a magnetic during the measurement. The performance of the Cd$^{2+}$ ion-selective electrode was examined by measuring the E.M.F. of the following electrochemical cell.

$$\text{Ag} \mid \text{Pb salicylaldoximate} \parallel \text{Sample} \parallel 1 \text{M KNO}_3 \parallel 3 \text{M KCl} \parallel \text{Ag} \parallel \text{AgCl}/\text{Ag}. \text{ Each electrode was immersed in } 10^{-6} - 10^{-1} \text{ M } \text{Pb}^{2+} \text{ standard solution of which the total ionic strength was adjusted with } 0.1 \text{ M KNO}_3 \text{ and calibration curve of each electrode after their values had stabilized with in } \pm 0.1 \text{ mV min}^{-1}. \text{ The potential concentration curve were plotted as shown in Fig. 2b.}

The electrode response of different solution of Cd II and PbII ions in concentration range of $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ to $5 \times 10^{-1} \text{ mol dm}^{-3}$ was recorded with the help of Cd membrane ion selective electrode indicator electrodes and saturated Ag/AgCl electrode as reference. The response was plotted on semi-log graph paper. Similar with Pb ion selective electrode in concentration range of $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ to $5.0 \times 10^{-4}$ was recorded with help of Pb ion selective electrode with help of ph ion selective electrode as indicator and saturated Ag/AgCl electrode as reference. A slope of Cd-Ion selective electrode was found to be 30 and slop of Pb salicylaldoximate ISE was found to be 29.
Table for the above curve is given below:

**Table 1 : Electrode Response of Cd (II) and Pb (II) Ion-Selective electrode**

<table>
<thead>
<tr>
<th>Concentration of Cd and Pb solution mol dm$^{-3}$</th>
<th>Measured electrode potential(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd II ion selective electrode</td>
</tr>
<tr>
<td>$1.0 \times 10^{-1}$</td>
<td>300</td>
</tr>
<tr>
<td>$5.0 \times 10^{-2}$</td>
<td>290</td>
</tr>
<tr>
<td>$1.0 \times 10^{-2}$</td>
<td>270</td>
</tr>
<tr>
<td>$5.0 \times 10^{-3}$</td>
<td>257</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>241</td>
</tr>
<tr>
<td>$5.0 \times 10^{-4}$</td>
<td>230</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>211</td>
</tr>
<tr>
<td>$5.0 \times 10^{-5}$</td>
<td>202</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>180</td>
</tr>
<tr>
<td>$5.0 \times 10^{-6}$</td>
<td>180</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>180</td>
</tr>
</tbody>
</table>

**Preparation of Buffer solution**

100 g of sodium acetate trihydrate, 100 g of disodium hydrogenphosphate 12 water, 100 g of potassium nitrate are dissolved in an adequate quantity of water. The solution dissolved 10 g of salicylaldoxime in 50 ml of ethyl alcohol is added to the previous solution and adjusted in 6.15 pH by adding acetic acid using a pH meter and the whole quantity is adjusted by water. When 1 vol % of this buffer was added to the contaminated soil sample, the pH of soil could be adjusted in about 6 pH.
Influence of pH

Each electrode was calibrated using standard solution that changed pH from 2 to 8. The pH was adjusted by adding small volume of HNO₃ or NaOH to the standard solution. The electrode potentials were recorded after their value stabilized and were plotted as a function of pH values and Cd²⁺ and lead ion concentration as shown in Fig 3a and Fig. 3b respectively.

![Fig. 3: pH range of cadmium and lead ion selective electrode. The potential difference on y-axis is 20mV.](Image)

For determining the working pH range of cadmium and lead ion selective electrode a set of solution of cadmium and lead were prepared in which Cd and Pb ion concentration was kept constant at 1.0 x 10⁻² mol/dm³, and the pH of these solutions were varied, the electrode response was noted and based on these data above graphs plotted between electrode potential and pH.

Selectivity

Selectivity coefficient were determined by the mixed solution method. For this the concentration of Cd ion was varied while the concentration of interfering ion was kept constant 1.0 X 10⁻³ mol dm⁻³. The potential for each solution were reported and plotted against Cd ion concentration. Similarly for Pb ion was varied while the concentration of interfering ion was kept constant at 1.0 X 10⁻³ mol dm⁻³. The potential for each were noted and plotted against Cd ion and lead ion concentration. The selectivity coefficient K_{Pot}^{*A,B} were calculated according to the relation K_{Pot}^{*A,B} = C_{A}/C_{B} where C_A and C_B are the total concentration of Cd²⁺ and that of an interfering ion obtained graphically in the sample solution, respectively Z_A and Z_B are the charges of Cd²⁺ and Pb⁺ the interfering ions, respectively.

Preparation of Sample Solution

In present work we adopted an acid digestion procedure (Environment protection Agency Method 3050) for total sorbed metals. In this method gives a reliable measure of the amount of metal added to soil as nonsilicate from industrial source. Reagents used Nitric acid HNO₃ (Conc. BDH Anagrade and 1:1 dilution in demonized water 30% Hydrogen peroxide, Hydrochloric acid (BDH analgrad.)

RESULTS AND DISCUSSION

Detection Limit of calibration curve with Cd ISE and Pb ISE are shown in
Fig. 2(a) and Fig. 2(b). The slope of Cd II and lead II ISE potential variation is 30mV and 29 mV. Detection limits, which are the lowest point of Cd$^{2+}$ concentration and Pb$^{2+}$ concentration that their calibration curves showed mention response are $10^{-6}$, $10^{-5}$, and $10^{-4}$ M$^{-1}$ for Cd$^{2+}$ and $10^{-5}$, $10^{-6}$ and M$^{-1}$ for Pb$^{2+}$ respectively. The ion selective electrode potential becomes unstable when potential variation goes up to over 87mV, which Cd ion and Pb ion concentration becomes $10^{-3}$ of the initial concentration.

Effect of pH

From Fig. 3 it was found that electrode potential and pH of Cd$^{2+}$ ion selective electrode and Pb$^{2+}$ ISE electrode potential is mostly independent of pH from 2 to 8 it is slightly interfered for pH value down to 4 for extremely low Cd and Pb concentration (Under $10^{-6}$ M$^{-1}$). The detection limit comes to $10^{-6}$ M$^{-1}$ for pH 3 and $5 \times 10^{-7}$ M$^{-1}$ for pH 2. Calibration of ISE and sample measurement should be done at the same pH values.

Response Time

In order to find out the response time of the electrodes the electrode was first dipped in $1.0 \times 10^{-1}$ mol dm$^{-3}$ solution of Cd$^{2+}$ and Pb$^{2+}$ ion and then the electrode was suddenly removed from this solution and dipped in Cd$^{2+}$ and Pb$^{2+}$ ION solution having concentration $1.0 \times 10^{-2}$ mol dm$^{-3}$. The response of each solution was recorded at every 5 second interval. The potential are then plotted against time Fig. 4(a) and Fig. 4(b) and it was found that the response time for Cd$^{2+}$ ISE 30 second and Pb$^{2+}$ ISE 45 second.

Effect of interfering compounds and its masking

Mercury Hg$^{2+}$, Silver Ag$^{+}$, Cu$^{2+}$, ion Fe$^{3+}$ interfere with Cd$^{2+}$ ISE and Pb$^{2+}$ ISE potential. Although under co-existence of interfering ions the Cd$^{2+}$ and Pb$^{2+}$ ion-selective electrode potential is not stable and the selectivity coefficients could not be correctly measured, the interference of ions mentioned were show in Table 2. The approximate errors (S.D.) of the selectivity value were 50-200% in repeated measurement.

In the application for contaminate soil analysis; practical selectivity could be improve by using masking reagents of interfering ions. By the use of 10% of the buffer solution, practical selectivity
coefficients were obtained as shown in Table 2.

### Table 2: Practical selectivity coefficients using buffer solution

<table>
<thead>
<tr>
<th>Ions</th>
<th>Cd$^{2+}$ ion selective electrode</th>
<th>Pb$^{2+}$ ion selective electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in aqueous solution</td>
<td>in 1% buffer solution</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>103</td>
<td>0.2</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>102</td>
<td>10–3</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>10</td>
<td>10–3</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>1</td>
<td>10–3</td>
</tr>
</tbody>
</table>

**Direct determination of Cadmium and lead in contaminated soil**

In the present work we applied the Cd$^{2+}$ Thiobarbutrate ISE and Pb$^{2+}$ salicyladoximate ISE for determination of Cd$^{2+}$ and Pb$^{2+}$ ion in the contaminated soil.

The concentration of Cd and Pb ion was determined by direct potentiometry using Cd and Pb ISE. Since the electrode in cadmium and lead solution is found to be very stable in absence of cadmium and lead ion. The concentration of Cd and Pb ion determined by with this Cd and Pb ISE as per electrode selectively responds to change in cadmium and lead ion concentration. For this analysis the concentration of Cd and Pb, Standard solution of Cadmium chloride and lead acetate (1.0 x 10$^3$ moldm$^{-3}$) was prepared. Several set of Cd and Pb solutions in the concentration range 1.0 x 10$^{-1}$ to 1.0 x 10$^6$ moldm$^{-3}$ were prepared with standard solution, potential of each solution was measured using Cd II ISE and Pb II ISE. Calibration curve was constructed by plotting measured each electrode potential against the concentration of Cd$^{2+}$ and Pb$^{2+}$, and Fe$^{2+}$ ion concentrate in contaminated soil. 50ml of above prepared soil sample solution was taken in a beaker. The Cd ISE and Pb ISE was dipped in conjunction with external reference electrode in the above sample solution, the potential was measured. After that calibration curve was constructed by plotting measured each electrode potential against the concentration of Cd$^{2+}$ and Pb$^{2+}$, and Fe$^{2+}$ ion.

The concentration of Cd and Pb ion in contaminated soil were found to be 1.2-1.3 µg/g and 21-25µg/g by Cd$^{2+}$ ISE and Pb$^{2+}$ ISE and the result was compared with the fresh soil sample which was anlyzed by AAS method. By AAS method we were found that the concentration of Cd$^{2+}$ are 1.03-1.05µ g/g and Pb$^{2+}$ are 16.15-16.14 µg/g in fresh soil sample. The concentration obtained by Electrochemical sensor or ISE method analysis shows that in contaminated soil Cd and Pb concentration are very much high in comparison of fresh soil.

In the analysis of soil under coexistence of 20-100 fold of Cu$^{2+}$, Pb$^{2+}$ and Fe$^{2+}$ ions against Cd$^{2+}$ and Pb$^{2+}$ ion low concentration range 1.2-1.3µg-l$^{-1}$ Cd$^{2+}$ ion and 21-25 µg l$^{-1}$ Pb$^{2+}$ could be successfully measured. From these data, it is clear that present Cd(II)-Thio-barbutarate, PbII, salicyladoximate ISE
are useful for the simple and speedy control analysis of heavy metals like Cd\(^{2+}\) and Pb\(^{2+}\) ion in the contaminated soil with sufficient sensitivity compared with AAS.

CONCLUSION

In the present work the new cadmium electrochemical sensors and lead electrochemical sensors were used for the analysis of heavy metals in soil. Different highly sensitive Cd\(^{2+}\) and Pb\(^{2+}\) ion-selective electrode was developed by different precipitate method using Ag-AgCl as indicator electrode\(^{17-20}\). These Cd\(^{2+}\) Thiobarutarate and Pb\(^{2+}\) salicyladoximate electrochemical sensors (ISE) shows good nernstion response and can be used in direct potentiometry in the field of chemical analysis of ions. Electrochemical sensors are simple in design and construction, have reasonable selectivity, Fast response time, real time analysis and applicability to colored and turbid solutions. Further ion-selective electrodes possess wide dynamic range and relatively low in cost. There characteristics have, therefore, led to the development of sensor for a member of ionic species for the analysis of various organic, inorganic and biologically important substance.

REFERENCES

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