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Chapter

Electrochemical Techniques for the Detection of Heavy Metals

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Abstract

The present chapter emphases on the approach of electrochemical sensor of metallic oxide nanocomposites to sense/detect heavy metal ions. Several methods have been incorporated with modified electrode for the sensing/detection of heavy metal ions. Among these methods square wave anodic stripping voltammetry method and differential normal pulse voltammetry method have been tested and being recommended for the individual analysis as well as simultaneous analysis of heavy metal ions by various researchers. We also endorse the said methods as the best choice for sensing of heavy metal ions however the material phase (plane) is also of specific importance in this regard. We suggest that these methods may be practiced by chemical industries the main sources of heavy metal ions waste. Furthermore, the statistical approach for the detection limit (3σ method) has been illustrated in the last paragraph of this unit.

Keywords: electrochemical sensing, rGO/MOx, heavy metal ions, material phase (plane), statistical approach for the detection limit

1. Introduction

1.1 Research background

As we know that the heavy metals in solution in the form of heavy metal ions (HMIs) contaminating water in a little quantity not only be risky to public health, but also may disturb aquatic life, i.e. the lowest level of heavy metal ions (HMIs) and its compounds are very toxic, dangerous for liver, brain, heart muscle, kidneys, human nervous system, blood circulation system and can damage skeletal system resulting in skeletal disease. In response to the needs of modern society and rapid industrial development, it is necessary to design high-efficiency, environmentally friendly, and low-cost electrochemical sensor. Nevertheless, major issues are associated with these sources, such as rapidly increasing prices, environmental consequences, and global climate change. These serious problems have necessitated the development of alternative energy sources.

In the past several decades, heavy metal ions (HMIs) have been of great attention, as they are enormously injurious in the biosphere and even their minute aggregate possesses an unfavorable threat to human health [1–3].

1.2 Methods used for the detection of heavy metal ions

The sensing and quantification of heavy metal ions (HMIs) are important in many applications, including waste management, environmental monitoring, developmental biology, and clinical toxicology. Several techniques/methods have been incorporated over the years for heavy metal ion (HMIs) such as atomic absorption spectroscopy (AAS), [4] inductively coupled plasma-mass spectrometry (ICP-MS), [5] inductively coupled plasma atomic emission spectrometry (ICP-AES) [6] X-ray fluorescence (XRF) spectrometry, [7] and so on. As these spectroscopic practices are time-consuming, their instruments are expensive and complicated in operation. Furthermore, the individual as well as simultaneous sensing/detection of heavy metal ions (HMIs) of great sensitivity and selectivity is the need of today. In this favor, electrochemical techniques/methods especially anodic stripping voltammetric (ASV) has been reflected to be a powerful, most sensitive, extremely rapid, and cost-effective method [8–12].

1.3 Electrochemical methods in sensing/detection of heavy metal ions

So many electrochemical techniques have been practiced for sensing chemical biomolecules and contaminants [13–15]. Normally, voltammetric methods for instance cyclic voltammetry (CV), linear sweep voltammetry (LSV), square wave voltammetry (SWV), differential pulse voltammetry (DPV) etc., potentiometric techniques and electrochemical impedance (EIS) techniques are employed in the sensing/detecting of analytes. In this regard, electrochemical behavior for the detecting of analytes are extremely applicable in micro fluidics and wider field of separation/partition science for the purposes of detection, valving and pumping. Few of the microscopic techniques are joined with electrochemical principles, such as scanning electrochemical microscopy (SECM) and chemically selective scanning tunneling microscopy (CSSTM), which are actually spatially resolved electrochemical sensors, even though they are classified as microscopic techniques [16]. An electrochemical sensor comprises of two constituents: (i) a recognition/perception element also called target receptor may be chemical or biological; and (ii) a material transducer/sensor usually a modified electrode that convert the sensing signals to an electronic signal. Collaborations between the detecting/sensing element of the substrate (HMIs) and the analytes are calculated through the quick reply, sensitivity, discrimination, and flexibility of the modified sensors (electrode) [17]. Durable contacts/interactions are usually linked with greater sensitivity and selectivity; however exemplary adjustability needs weak interactions. The serious factors like sensitivity, selectivity, response time, detection limit, signal-to-noise ratio, linearity, and stability are responsible for the performance of electrochemical sensors [18].

Among these methods square wave anodic stripping voltammetry method and differential normal pulse voltammetry method have been tested and are recommended for the individual analysis as well as simultaneous analysis of heavy metal ions (HMIs) by various researchers. We also endorse the said methods as the best choice for sensing of heavy metal ions however the material phase (plane) is also of specific importance in this regard.

The facet-dependent electrochemical behavior of Co_3O_4 nanoplates and nanocubes based on their adsorption/sensing behaviors toward heavy metal ions (HMIs) has been practiced. The Co_3O_4 nanoplates with plane (111) were better in electrochemical sensing than Co_3O_4 nanocubes with plane (001). Both adsorption quantities and density-functional theory (DFT) calculations were in accordance with the concept that the variance in electrochemical properties was due to the sensing of heavy metal ions (HMIs) [19]. It is prominent from the study that sensing interface modified electrodes play a key role in the sensing/detection of heavy metal ions (HMIs).

The graphene-analogue carbon nitride (GA-C_3N_4) has been recommended as suitable sensor for Cu^{2+} purpose. So far graphene base nanocomposites are considered promising candidate for heavy metal ions (HMIs) determination in water environment [20].

The electrochemical system for the sensing/detection of heavy metals in soil has also been reported. The electrochemical sensor with screen-sprinted electrode (SPE) adapted by ionic liquid (IL) n-octylpyridinum hexafluorophosphate (OPFP) and graphene (GR) was tested for sensing/detection of Cd (II) in soil [21]. The system was further tested for sensitive detection of trace cadmium ions by square wave anodic stripping voltammetry (SWASV).

We are trying to describe the electrochemical stand by combing the reduced graphene oxides/metallic oxides (rGO/MOx) nanocomposites for the analysis of heavy metal ions (HMIs) in solution by electrochemical methods. The detection simultaneous limit (3σ method) used for HMIs of the rGO/MOx nanocomposite modified electrode can be calculated for electrochemical methods on individual analysis as well as simultaneous analysis.

For electrochemical sensing Electrochemical Workstation (Potentiostat/ Galvanostat) with three electrode system or multiple channel system may be used as shown in **Figure 1(a)**. The pH of the solution may be maintained from (5–12) for different metal ions. The electrode composition also plays important role in the sensing/detection of HMIs as illustrated in **Figure 1(b)** larger surface area greater will be adsorption etc. **Figure 1(c, d)** describe the active planes playing important roles in sensing/detection. The Co_3O_4 nanoplates with plane (111) were better in electrochemical sensing than Co_3O_4 nanocubes with plane (001) as described in introduction. So far we experienced the reduced graphene oxide/Metallic oxides (rGO/MOx) nanocomposites are the best choice for the sensing/detection of HMIs of boilers (high temperature). Where reduced graphene oxide (rGO) act as a base and prevent metallic oxides (MOx) from aggregation. The reduced Graphene oxide/ Metallic oxides (rGO/MOx) nanocomposites facets (planes) also have influence on the sensing mechanism **Figure 1(d)**. **Figure 1(e, f)** illustrate the sensing/detection through square wave anodic stripping voltammetry (SWV) method and differential normal pulse voltammetry (DNPV) voltammetric peaks of reduced graphene oxides/ metallic oxides (rGO/MOx) nanocomposites modified electrode for the analysis of heavy metal ions (HMIs) or if someone may practice will get similar peaks at different potential specified for each ion. On the other hand, reduced graphene oxide/Metallic oxides with conducting polymers may be practiced with cold water solution system as conducting polymers are not stable at high temperature. Simply in **Figure 1(a–f)** we are try to explain that the sensing/detection of HMIs by nanocomposites are influenced by composition, active planes of the nanocomposites, the Co_3O_4 nanoribbons keep chemical sensitivity than Co_3O_4 nanoparticles with active (110), (220) planes and play key role to adsorb heavy metal ions than the latter [22].
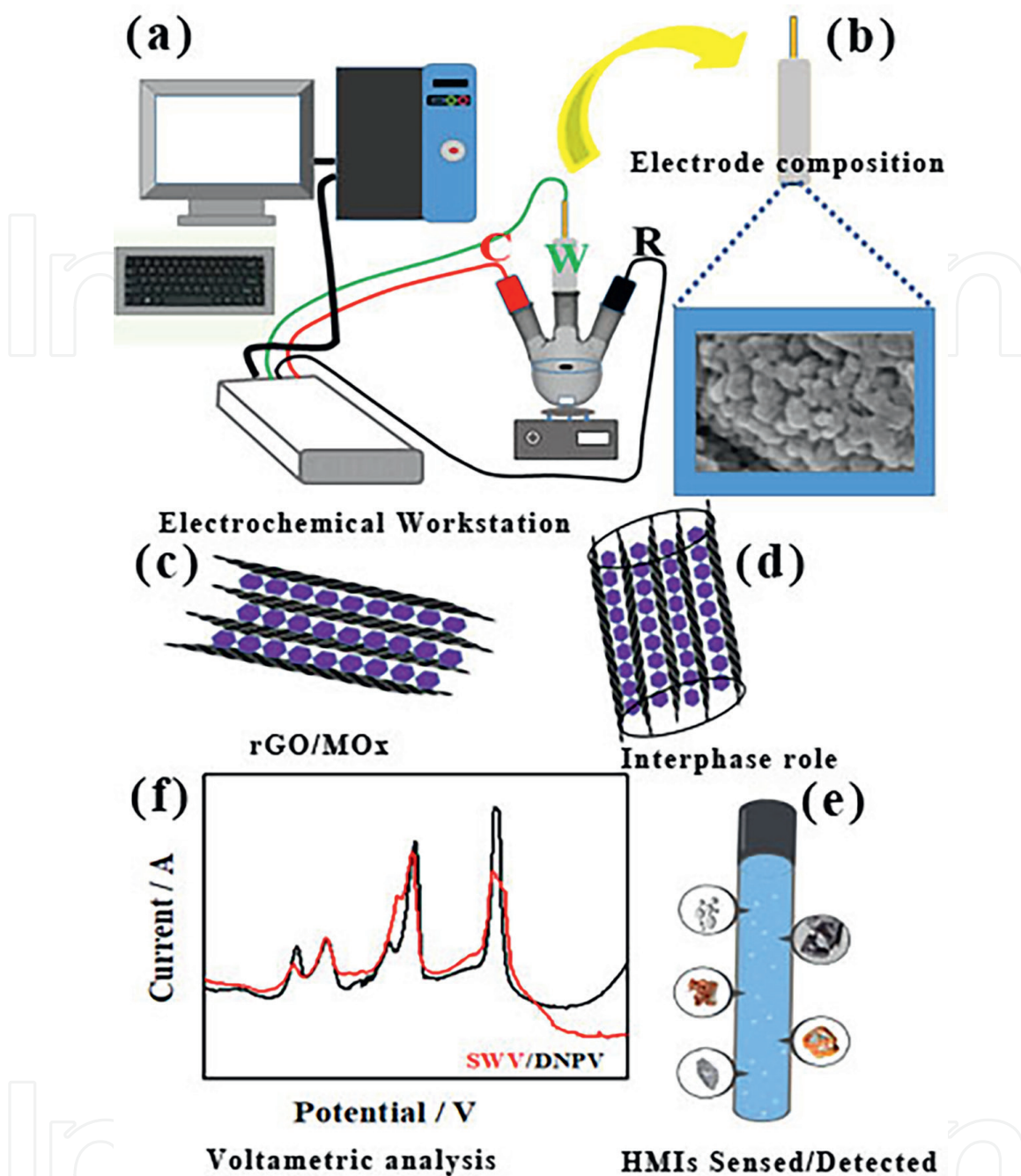
Figure 1.
Electrochemical workstation, (a) nanocomposite modified electrode, (b) reduced graphene oxide/metallic oxide phase (plane), (c, d) sensing mechanism (e) Voltammetric signals of square wave anodic stripping voltammetry (SWASV) and differential normal pulse voltammetry response of rGO/MOx modified electrode for the simultaneous analysis of heavy metal ions (HMIs) over a specified concentration range (1-10 μM) in acetate buffer (pH 5–12) (f).

2. Synthesis, modification and electrochemical use of rGO/MOx modified electrode

The reduced graphene oxide/metallic oxide (rGO/MOx) nanocomposites may be synthesized by the hydrothermal method or by chemical vapor deposition (CVD) method.

Electrochemical experiments may be performed at Electrochemical Analyzer/ Workstation (Potentiostat/Galvanostat) with a conventional three or multi-electrode

system. The working electrode may be glassy carbon (coated with reduced graphene oxide/Metallic oxides nanocomposites electrode. The silver/silver chloride (Ag/AgCl) or Calomel (Hg/Hg_2Cl_2) electrode and a platinum electrode may be tested as the reference and the auxiliary electrode, respectively.

2.1 Modified electrode preparation

The carbon electrode (CE) as a working electrode may be practiced after sonication in alcohol and soaking in deionsed water. The suspension of rGO/MOx nanocomposites after dispersing with ultrasonic agitation into alcohol may be coated on the electrode. So the nanocomposites film modified electrodes will sense/detect heavy metal ions.

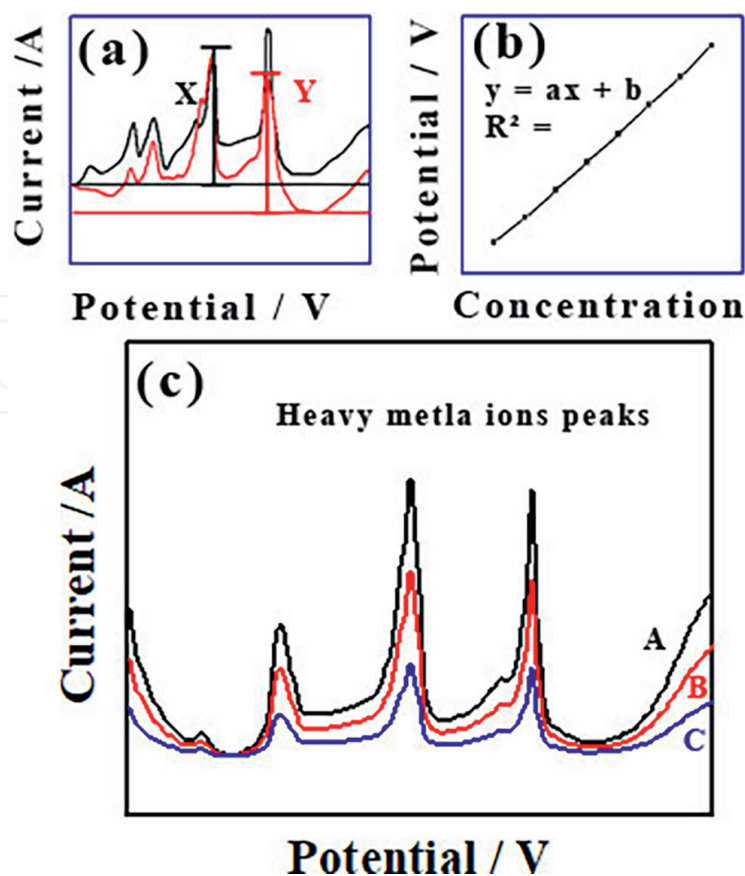## 2.2 Heavy metal ions detection

Among the voltammetry methods Square wave anodic stripping voltammetry (SWASV) and differential normal pulse voltammetry (DNPV) method if practiced for the individual analysis as well as simultaneous analysis of heavy metal ions will give better results. The heavy metals may be sensed at the definite potential range (V), frequency (Hz), amplitude (V), increment potential (mV) for the simultaneous and selective detection of heavy metal ions.

2.3 Square wave anodic stripping voltammetry (SWASV)

Among electroanalytical techniques stripping voltammetry (SV) is considered to be the most sensitive and extensively used method for the sensing/detection of heavy metal ions (HMIs). This type of analytical investigation comprises a two-step practice: pre-concentration buildup and voltammetry sensing/detection. In the initial stage, the working electrode is plunged in metal ions solution of desired concentration. The metal ions after assortment on the surface of working electrode are reduced with voltage optimization. In the final stage, the potential is drifted to positive value to re-oxidize the metal into metal ions and voltammogram means peak current and peak potential (i-E) are recorded. Each peak of voltammogram indicate the metal and the height of peak indicate the concentration metal ion. Various factors such as synthesis method, working of electrode, practical method etc. may affect the detection limit and the sensitivity of heavy metal sensors.

Wither square wave voltammetry (SWV) or differential normal pulse voltammetry (DNPV) electrochemical analysis are practiced to detect heavy metal ions (HMIs) of various concentration (μM) solution with increased potential of millivolt (mV) for SWV and DNPV at (pH 5–12) various peaks will appear. For the stripping analysis of HMIs using both SWV and DNPV the obtained results in the form of voltammetric peaks are shown in **Figure 2** with rGO/MOx nanocomposites when experienced for the simultaneous analysis of HMIs.

The different peaks at different value (−1.0 to +0.8 V) are assigned for of potential (V) and may be attributed to HMIs on SWV and DNPV respectively. **Figure 2(a)** shows SWV with red line and DNPV with black line. Where X and Y represent the potential of various metal ions, similarly, some other peaks may arise when concentration is increased due to metallic interaction [23]. **Figure 2(b)** Linearization equations, Adj. R^2 response may be developed for rGO/MOx nanocomposites and then at the last voltammetry analysis while changing concentration (A, B and C)

Figure 2.
The respective calibration curves of simultaneous detection of heavy metal ions (HMIs) with current intensity (X, Y) (a) linearization equations, Adj. R^2 response of rGO/MOx nanocomposites modified glassy carbon electrode. (b) Stripping voltammetry intensity peaks of various concentration (A, B & C) (c).

(i.e. 1-10 μM) in acetate buffer (pH 5–12) of the selected metal ions and are recorded as **Figure 2(c)**. The elongated peaks in **Figure 2(c)** show the different metal ions sensed/detected.

2.4 Individual as well as stripping behavior toward HMIs using SWV and DNPV

The square wave voltammetry (SWV) or differential normal pulse voltammetry (DNPV) response of rGO/MOx modified electrode or any modified electrode for the individual voltammetry investigation or simultaneous detection of heavy metal ions (HMIs) can be measured in (μM), their linearization equations and calibration curves and the limit of detection (LOD) can be easily calculated (**Tables 1** and **2**).

2.5 Sensitivity, limit of detection (LOD) and limit of quantitation (LOQ) calculation for the rGO/MOx nanocomposite

As shown in **Figure 2(a)** the corresponding calibration curves (−1.0 to +0.8 V) potential range for heavy metal ions (HMIs) simultaneous analysis are recorded for various concentration (1-10 μM). Similarly, the inset of **Figure 2(b)** and **Tables 1** and **2** represent the linearization equations and the corresponding correlation coefficients for rGO/MOx for both individual as well as simultaneous analysis on square wave voltammetry (SWV) or differential normal pulse voltammetry (DNPV).

S. No.	Concentration	Potential (V)
1	A	X
2	B	Y
3	C	Z
SE of Intercept		
SD of Intercept = SE of Intercept * $\sqrt{N}$		
LOD = 3.3*(SD of Intercept/Slope)		
LOQ = 10*(SD of Intercept/Slope)		
Slope		
$\sqrt{N}$		

Table 1.
Demonstrate the statistical calculation table of limit of detection (LOD) and limit of quantitation (LOQ) for simultaneous sensing/detection of heavy metal ions (HMIs) using SWV and DNPV voltammetry technique.

Metal ions	y = ax+b	Correlation coefficient (R^2)	Linearization eq. (I/μA)	LOD (M)	LOQ (M)
M^+	y =?	R^2 =?	I = (μM/mM) etc.	3.3*(SD of Intercept/Slope)	10*(SD of Intercept/Slope)
M^+	y =?	R^2 =?	I = (μM/mM) etc.	3.3*(SD of Intercept/Slope)	10*(SD of Intercept/Slope)
M^+	y =?	R^2 =?	I = (μM/mM) etc.	3.3*(SD of Intercept/Slope)	10*(SD of Intercept/Slope)

Table 2.
Statistical calculation of nanocomposites (rGO/MOx) for individual as well as simultaneous analysis of heavy metal ions (HMIs).

The limit of detection (LOD) and limit of quantitation (LOQ) for individual as well as simultaneous detection of heavy metal ions (HMIs) via rGO/MOx modified electrodes may be calculated/measured respectively.

The Sensitivity (μA/μM) for individual as well as simultaneous analysis may be calculated. The results gained by the use of rGO/MOx for limit of detection (LOD) and limit of quantitation (LOQ) both on DNPV and SWV voltammetry analysis may be compared with the World Health Organization (WHO) data for different heavy metal ions (HMIs).

The limit of detection (LOD) and limit of quantitation (LOQ) of the nanocomposites can be calculated using calibration standards. The limit of detection (LOD) and limit of quantitation (LOQ) may be determined by 3.3σ/S and 10σ/S respectively, where S is the slope of the calibration curve and σ is the standard deviation of reaction.

The slope can be assessed from the calibration curve of the selection. The estimate of σ is typically the root mean squared error (RMSE) or standard deviation of the residuals taken from the regression line. The slope is used to convert the variation in the response back to the scale of the theoretical concentration.

3. Electrochemical methods industrial application

As we know that Electrochemical methods have a wide spread application so can be practiced for the treatment of community, industrial waters and wastewaters. The requirement for the practice of electrochemical methods is to eliminate large particles from water. The electrochemical methods can take out pollutants (organic and inorganic), ions and microorganisms acquire for clean water of distilled water quality. The electrochemical reduction intended for metals salvage and conversion of determined organic compounds to a reduced amount of toxic forms.

Recently, special attention has been given to the treatment of industrial wastewater by using advanced treatment technologies, among all methodologies, electrochemical methods appears to be one of the most promising methods for treatment organic pollutant-containing wastewater. The profits of electrochemical technology include durability, low cost, easy operation, energy efficiency, automation, fast response, high sensitivity and environmental compatibility [24–26].

Furthermore, from the above discussion it can be illustrated that rGO/MOx nanocomposites modified electrode may be helpful to practice on industrial scale
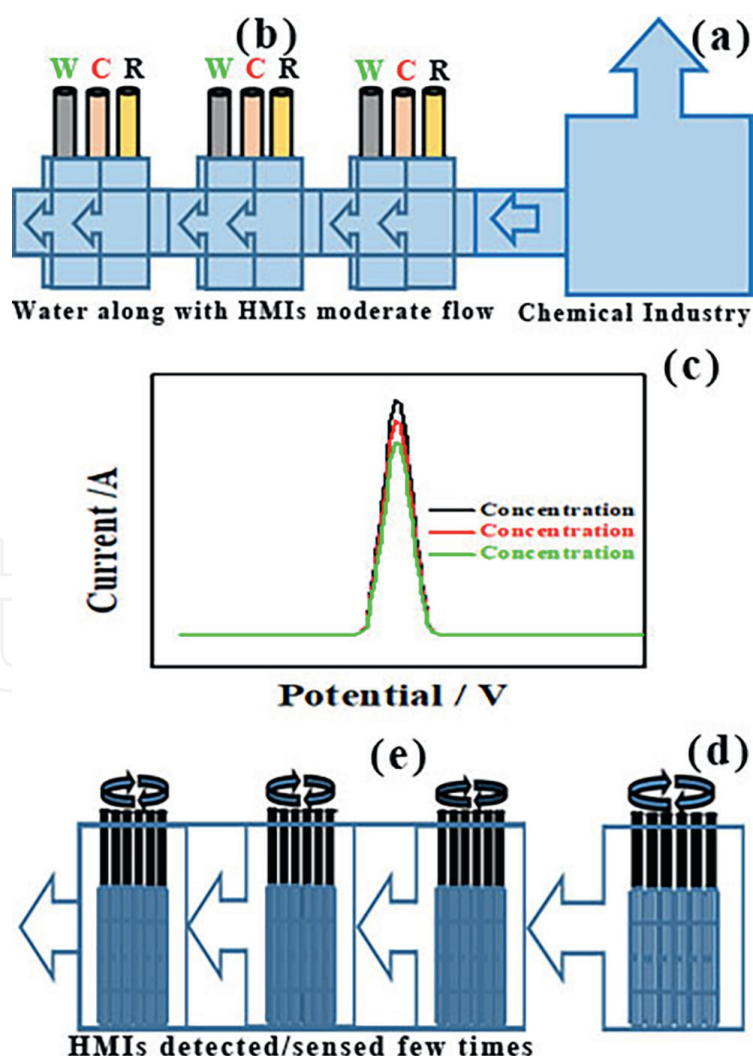
Figure 3.
Chemical industry contaminating water and detection of heavy metal ions (a, b), stripping voltammetry approach of rGO/MOx modified electrodes for the individual analysis (c) HMIs sensed few time in a flow from a chemical industry.

as well as in laboratory. Here in the last paragraph we have schemed to illustrate a chemical industry **Figure 3(a)** continuously contaminating the water (environmental and underground) along with HMIs. As has been reported by various researchers that nanocomposites modified electrode have the capacity to sense/absorb HMIs. If system of three or multiple electrode with modified nanocomposite is incorporated, then some amount of heavy metal ions can be sensed/detected **Figure 3(b)**. Therefore, we suggest that if from various concentration (1-10 µM) few amount of HMIs is sensed/detected by rGO/MOx modified electrode **Figure 3(c)**, in this way by using multiple nanocomposites modified electrodes when practiced may sense/detect few amount of heavy metal ions **Figure 3(d)**.

Therefore, if a plant having multiple modified electrodes **Figure 3(e)** connected together then HMIs sensed few times may decrease the concentration of HMIs from the waste water of the chemical industry. We suggest that in this regard rGO/MOx nanocomposites will be a best choice for the sensing/detection of heavy metal ions (HMIs) coming out from chemical industries contaminating drinking water.

4. Brief summary

In this unit, we have emphases on the reduced graphene Oxide/metallic oxide (rGO/MOx) nanocomposites for both individual and simultaneous detection of heavy metal ions (HMIs) in solution with the help of analysis on square wave voltammetry (SWV) or differential normal pulse voltammetry (DNPV). The nanocomposite may be synthesized by hydrothermal or chemical vapor deposition (CVD) method. The expandable graphite (EG) was reduced to graphene oxide GO during hydrothermal treatment and reduced graphene oxide during chemical vapor deposition (CVD) method to enhance the flow of electron on modified electrode. Furthermore, the MOx nanoparticles dispersed on graphene sheets will tend to accumulate the HMIs on the electrode surface. The Sensitivity (µA/µM) for individual as well as simultaneous analysis, limit of detection (LOD) and limit of quantitation (LOQ) both on DNPV and SWV voltammetry analysis and can recorded and calculated (**Tables 1** and **2**). That why Electrochemical techniques have the advantages of low cost, easy operation, fast response, high sensitivity and specificity, which are suitable for ion sensing.

5. Conclusion

In this Unit, we are trying to describe the electrochemical stand by combing the reduced graphene oxide/metallic oxides (rGO/MOx) nanocomposites for the analysis of heavy metal ions (HMIs) in solution by electrochemical methods. The detection simultaneous limit (3σ method) used for HMIs of the rGO/MOx nanocomposite modified electrode can be calculated for electrochemical methods on individual analysis as well as simultaneous analysis.

The enhanced electrochemical performance can be ascribed to three factors (1) rGO could be used to prevent the aggregation of MOx nanocomposites, resulting in fast migration of electrons; the MOx nanocomposite with active planes recollect chemical sensitivity and adsorb heavy metal ions.

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