Review on Detection of Phenol in Water

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Received: 29 April 2019, Revised: 12 June 2019 and Accepted: 13 June 2019

DOI: 10.5185/amlett.2019.0036
www.vbripress.com/aml

Abstract

Phenol gives a toxic response in the natural water and leads to show harsh effects on human being, plants, and animals. At low concentration, the phenol gives a pungent taste as well as odour to the consumption of water. It is because of such reason that phenol is contained in the environmental legislation, and it needs to be analysed for providing better results. Therefore it should be eliminated before discharging or reusing the waste flow to the environment. The current review is mainly focused on the growth related to the detection of phenol in the water. In the review the state, advantages, disadvantages of different techniques are discussed in brief. The methods mainly involve the electrodes which hold the interest for using new material in the form of binders and also to advance the other types of electrodes. It is observed that for the electrochemist, the electrochemistry of electrodes is considered as the most commanding approach. The significant merits of using electrodes are an enhancement of the selectivity for the electroanalytical approach. The preparation methods for the electrodes are simple, secure, versatile, and most commonly, it has many controllable variables which enables it best material used in the starting of various applications. There are different aspects of applications such as industrial technology transfers purposes; it affects the electroanalytical chemistry and diverse other fields as well, namely energy conversion, catalysis, storage, etc. Copyright © VBRI Press.

Keywords: Phenol, health, sensor, instrumentation, electrode.

Introduction

Water is recognised as a basic agent to evaluate civilisation of human being. With the increase in population, the growth will generally rise to about 9 billion by the year 2050. The lack of safe drinking water is the major ubiquitous problems influencing human health in several ways. Around 70% of the earth is covered with water, but yet only 0.14% of pure water is available to human bring for consumption. The increase in population has led to a harsh impact on the supply of safe drinking water. It has being postulated that about 1/3 poplulation is target to face the problem related to scarcity of water tll the year 2030 in whold word. It has also been noticed that situation is exaggerating since last year few years because of the water pollution caused by agricultural waste, industrial effluents and also from domestic sewage. Water pollution is a common threat to all living creatures. In the few decades, it was observed that vast extent of chemical contamination has occurred due to the source from industries, drought, agriculture etc. The phenol entirely pollutes the ground and surface water.

Background of phenol

It was clarified that phenol was firstly isolated the crude form in the 18th century. Pure form of phenol was confined by the year 1834, and the structure was formulated in the year 1842. Phenol was produced firstly in the 1860s for the purpose to be used as an antiseptic. The resins were then approached in near about 1872. Then the use of the industrial fields has been started from the 19th century. The production of aspirin dyes and explosive was first moved towards the industrial sector.

Source of phenol

The compounds of phenol are generated naturally from various sources such as waste of paper manufacturing industries, agriculture, dye industries, municipal effluents etc. Because of their toxic nature and persistence towards the environment, it is recognised as the primary pollutant.

Naturally occurring phenol

Phenols are the compound with a hydroxyl group that is linked directly to the benzene ring. Therefore, phenol is generally a specific name of hydroxyl benzene and the generic name of the family of the compound that is derived from hydroxyl benzene. The phenol structure is represented in **Fig. 1**.

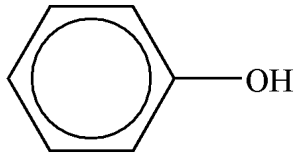

Fig. 1. Structure of phenol.

Physical properties of phenols

Phenol is said to be considered as chief molecule for the organic chemistry and it is even the origin molecule for various precursor products. The substituted phenol, a renounced category holds the phenol in the form of underlying structure [**1**]. It has a particular aromatic smell and is extremely toxic. The derivatives of phenol are weak acids because of the binding in the phenolic hydroxyl group leading to the efficient oxidisation in the environment [**2**]. It is easily present in the natural environment. The existence of hydroxyl groups with the phenolic compound clarifies that it is just like the alcohol as it forms the high strong intermolecular hydrogen bonds. It leads the phenol to get associated and enables it to have a high boiling point in comparison to the hydrocarbons with the same molecular weight. The capability of phenol to form strong hydrogen bonds with the water reveals that phenol is the most highly soluble substance in water.

Strength of phenols as acids

The phenol structure is the same as alcohol, but yet it is the most active acids. The pKa value of phenol is 9.89, while the pka value of alcohol is 18. Pka values of phenols are < 11. It is a weak acid in comparison to the carboxylic acid, namely acetic acid, whose pKa value is 4.75.

Resonance

The results of experiments and theories exhibit the phenol's higher acidic nature to engage itself for electric charge distribution leading to the negative charge on –OH group, hence the proton are strongly held. In response to it, the benzene ring of phenol shows that it is an electron-withdrawing group in comparison to the cyclohexane ring of cyclohexanol.

The effect of resonance shows that the carbon atoms bearing the hydroxyl group in phenol are sp^2 hybridisation whereas cyclohexane is sp^3 hybridised. The sp^2 hybridised carbon atoms are *s* character than the sp^3 hybridised carbon atoms which is shown in **Fig. 2**.

There is a factor responsible for influencing the electron distribution, and that is the accessibility for all the phenol resonance hybrid composed on the structure **2-4**. Due to which, the electron departs from a hydroxyl group and also make oxygen as the positive one.

Contrarily, it is observed that the acidic nature of phenol in comparison to cyclohexanol is more dependent on few resonance structures of the phenoxide ion. The charge separation is not involved in the **2-4** resonance structures for the phenoxide ion. Based on resonance theory, **2-4** structure stabilises phenoxide ion more than phenol. Since the phenoxide ion is highly stabilised, it shows acid-strengthening effect.

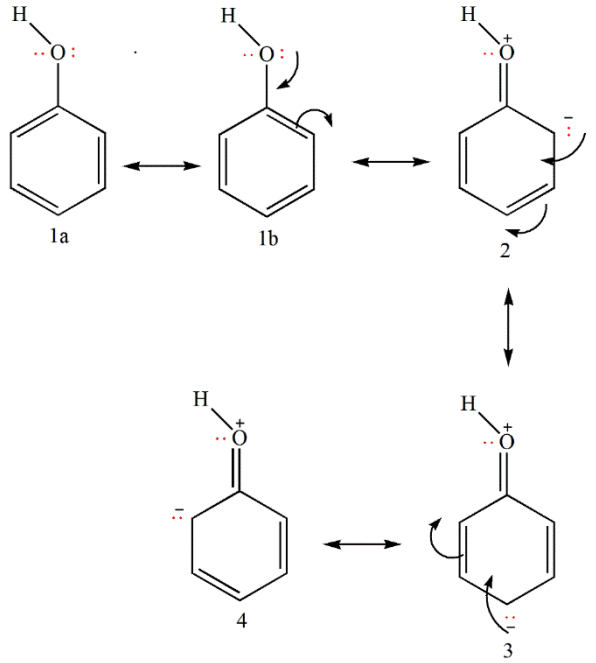

Fig. 2. Resonance structures for phenol.

Due to –I effect of hydroxyl group; the ring gets deactivated to some extent, and due to the +R effect of the hydroxyl group, the ring deactivation is eliminated. Hence, it is found that the final results of the hydroxyl group as –I and +R effects show activation of the ring. It exhibits a dipole moment 1.70 D, the negative close of the dipole factor far away from the ring maturing is the existence of *n* es on O atom, as shown in **Fig. 3**.

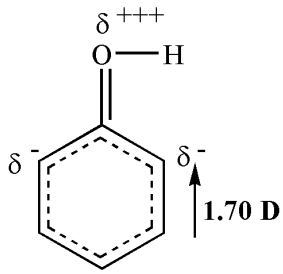

Fig. 3. Dipole moment in phenol.

There are few double bond character in the O—C bond where 'O' atom delivers a tiny amount of positive charge. The two *o*- and the *p*- carbons provide a small amount of negative charge. Since 'O' atom is positively charged, it partially draws out electrons from O—H bond which enables 'H' atom to deliver the adequate quantity of positive charge. Phenol does not show keto-enol tautomerism as ketone conversion is not suitable for tautomerism. The mechanism is shown in **Fig. 4**.

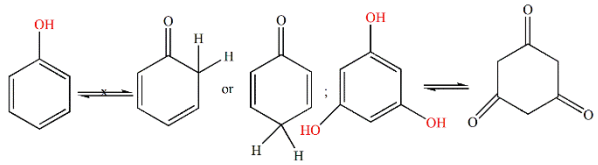

Fig. 4. Structure of keto-enol tautomerism.

As indicated, it is revealed that phenol does not exhibit the properties of the ketone. The ring of the phenolic compound is activated, so it goes through the aromatic electrophilic substitution reaction more easily than benzene, whereas it is less facile. The ring gets ruptured in the presence of oxidising agents as well. The rings get deactivated due to the presence of nitro, carboxyl at *o*- and *p*- positions. Therefore, in spite of nucleophilic substitution, the electrophilic substitution will be favoured since rings get resistant for oxidation. The electrophilic substitution takes place at *o*- and *p*- positions because they are negatively charged partially.

The 'O' and 'H' atoms of OH group releases positive charge partially, hence 'H' atoms possess an ability to reflects the properties of compound involving active hydrogen. The mechanism is exhibited in **Fig. 5**. It does not show the features in term of the base for +R.

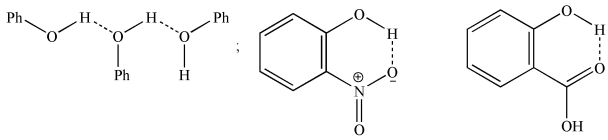

Fig. 5. Role of H-atoms in phenol.

The molecules of phenol get amalgamated to each other with the help of H-bonding because the 'H' atom is positively charged, thus partially enabling the b.p.s and m.p.s to become high in corresponding to the arenes. The phenol possesses properties of moderately soluble in water and high solubility in organic solvent due to the formation of H-bonding. The *o*-nitrophenol and *o*-hydroxybenzoic acid have intra-molecular H-bonding whose b.p.s, m.p.s, and solubility is very less in comparison to *m*- and *p*- isomers. Hence, phenol is found to possess a carbolic smell and shows a corrosive effect on the skin.

The acid character of phenol

The phenol tends to cease the proton attached with 'O' atom to eliminate the positive charge. The mechanism is quite common in an aqueous medium where it gives out phenolate ion as a conjugate base. The complete process of the acidic character of phenol is shown in **Fig. 6**.

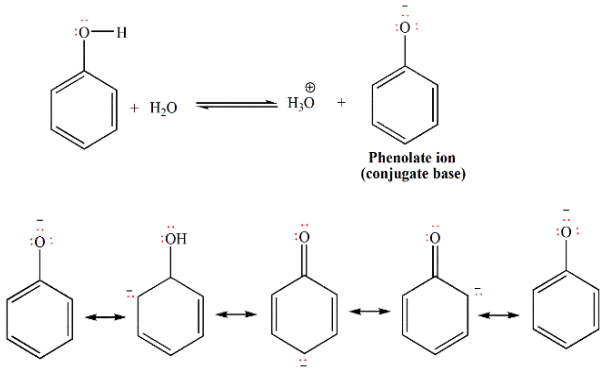

Fig. 6. Acid character of phenol.

Mostly, the structure in resonance hybrid has iso-valent hybridisation where it does not allow a positive charge on 'O' atom. The lone-pair of electrons on the 'O' atom is delocalised in no small extent. So, the ion acts to be stable, and it does not donate an electron. Thus, it is a weak base where the acid is substantial in comparison to the conjugate base.

Isomers

The phenolic compound has three isomers possessing the same properties as well as the structure and is applied in various application such as dyes, food, industrial production of pharmaceuticals, antioxidant, cosmetics etc. The structure of isomer is shown in **Fig. 7**. The isomers are scattered in soil and aquatic sources leading to the problematic degradation because of its highly toxic nature and highly stable behaviour in the environment [**3**].

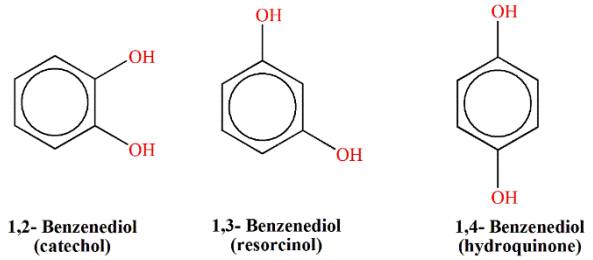

Fig. 7. Structure of isomers of phenol.

p-benzoquinone is the compound produced from the oxidation of hydroquinone. The oxidation process is carried out with the help of mild oxidising agents whereas the complete oxidation process is carried out for removing a pair of the electron ($2e^-$) and two protons ($2p^+$) from the hydroquinone. The reaction is reversible. The reduction of *p-benzoquinone* through the mild reducing agent into hydroquinone is exhibited in **Fig. 8**.

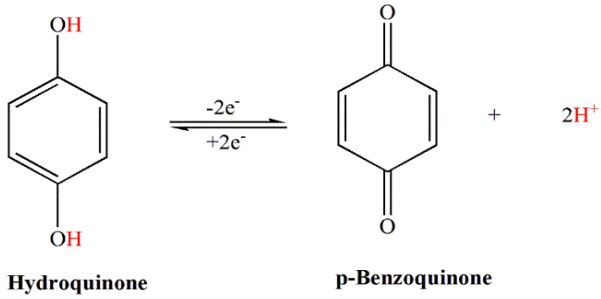

Fig. 8. Oxidation of hydroquinone.

Health effect

Phenols are the organic pollutants that are toxic or resistant to some of the microorganisms since the effluents cannot be treated by any biological activity. Inhalation and dermal exposure of phenol in a human being are irritating for eyes, skin, and mucous membrane. Oral exposure to phenol is also toxic to a human being. Ingestion of even 1 g of phenol is dangerous, which may lead to severe health problems

such as convulsions, loss of coordination, tremors, respiratory arrest and muscle weakness. It shows high affinity towards the nervous system, leading to severe injuries of it. Therefore, owing to the various threat, most of the phenol is engaged in environmental legislation [**4**].

Foreign agencies

To overcome the toxic effect of phenol on health, US EPA has regulated the limitation of phenol higher than 40 ppb in air and greater than 10 ppm in water [**5**]. The EPA has stated various compounds as the primary pollutants based on different aspects such as toxicity, persistence and bioaccumulation. The compounds with concentration level > 0.5 µg L^{-1} are present in the environment because of the industrial effluents [**6**], and 0.1 µg L^{-1} is current for drinking water. The permissible limit for phenol in the natural water is 0.001 ppm [**7**]. WHO has prescribed the allowable limit of phenol in water as 1 mg/L.

In many countries, specific laws have fixed the concentration limit of phenol in pure water. The upper limit for phenol in drinking water is 0.5 µg/L by EU-Directive 80/778, 50 µg/L for bathing water by 76/160/CEE and 1-100 µg/L for surface water by 75/440/CEE.

Hence, by the concentration of phenol and complex matrix, the appropriate cleaning methods and instrumental analysis are required for the betterment of the society.

Indian agencies

The BIS has given the permissible limit for phenol concentration in drinking water to be 1 mg/L, whereas MOEF India has prescribed the limit as 1 mg/L in the industrial waste for inland water surface and 5 mg/L for public sewers as well as marine coastal region.

Existing technologies

Phenol is considered a harmful substance in term of the health of human being and aquatic ecosystem mainly because of its highly toxic and bioaccumulative nature. Therefore, for reducing environmental pollution and for preventing the degradation of different water resources, the accurate estimation of the concentration of phenol is needed. Detection as well as determination of phenol concentration can be carried out by various method such as colorimetry [**8**], gas chromatography (GC) [**9**], gas chromatography-mass spectroscopy (GC-MS) [**10**], high-pressure liquid chromatography (HPLC) [**11**], spectrophotometry [**12**], biosensor-based methods like amperometric [**13**], enzymatic [**14**], optical [**15**], and whole cell biosensor [**16**], and so on.

Varities of preconcentration methods are adopted for determination namely, solid-phase extraction (SPE) [**17**], liquid-phase microextraction (LPME) [**18**], dispersive liquid-liquid microextraction (DLLME) [**19**], ultrasound-assisted emulsification-microextraction (USAEME) [**20**], and solidification of floating organic droplets (UAEM-SFO) [**21**], solid-phase microextraction [**22**]. However, seeking new methods is still essential for the analysis of phenols in water samples. Various types of detection are shown in **Fig. 9**.

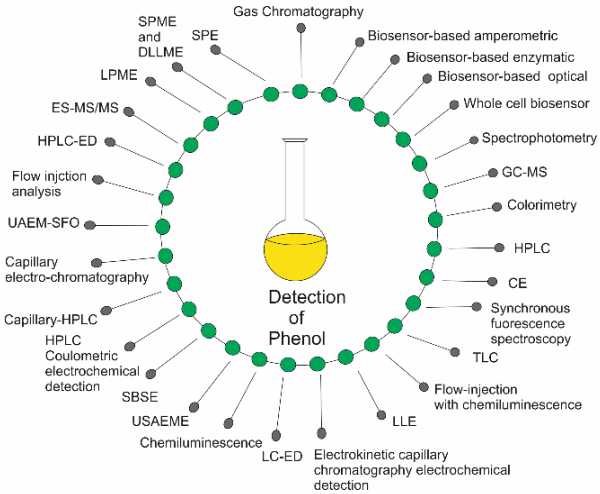

Fig. 9. Different type of detection.

Colorimetry

Colorimetry is the technique introduced by Clerk Maxwell and Hermann von Helmholtz. The principle behind Colorimetry is the measurement of the colour intensity by comparing the known standard colour intensity. It is the technique which is designed for measuring the concentration of a substance by analysis of its colour intensity. When the light falls on any material, the light will get absorbed, reflected, refracted and transmitted through which intensity can be measured.

There are three main parts of the colorimeter, such as the source of light, the sample containing cuvette and the detector. The light beam is passed through the cuvette providing standard and then through the sample. The concentration of the sample gives the result of absorbance and transmittance. The absorbed light is detected with the help of the detector showing the result. The values obtained are plotted on the graph, and the comparison will help to determine the concentration of the unknown sample.

There are two fundamental laws of Colorimetry: (a) Beer's law, and (b) Lamberts Law

a) Beer's Law: This states that when the beam of monochromatic light passes through a solution having a concentration in increasing order, the intensity of monochromatic light decreases.
b) Lambert's Law: This law deals with the relation between the thickness of absorbing solution and intensity of monochromatic light through a transparent medium. It also states that intensity of monochromatic light decreases with the increase in the depth of absorbing medium.

Alkasir *et al*. [**23**] did the detection of phenol and its derivatives in 2012. It was done by a colorimetric paper-based bioassay. This detection was concentration

dependent and showed a change in colour. It was also done through the naked eyes. It was a natural detection process and served as an inexpensive method.

Advantages

1. It gives a fast and accurate measurement.
2. It can give intensity results in a high range.
3. It is carried out by one chemical species at a time.
4. It can control itself against the non-chemical substance.
5. It is a cheap technique.

Disadvantages

1. Absorption can be done only for reasonably dilute solutions.
2. It is necessary to maintain the colour of a solution; otherwise, change in result will be observed.
3. It cannot measure intensity if the solution contains slight impurity.
4. It is essential to maintain fluctuations in electricity.
5. Error in the result can be seen due to the same colour of the interfering substances.

Gas chromatography (GC)

Martin and James introduced gas chromatography in the year 1952 [**24**]. The commercial gas chromatography was firstly developed in 1954 by Griffin and George. Later, other companies developed the device of gas chromatography.

When two phases are there with a partition consisting of one mobile phase and one stationary phase, then the separation of a component of the mobile phase requires a technique called Chromatography. Gas chromatography is the one in which stationary phase consists of large proportion as solid while mobile phase as gas. In this technique, separation is done by the vaporisation process. The sample used to analyse gets vaporised and moves with the help of mobile phase, i.e. gas so that solid stationary phase comes in equilibrium with the solutes of sample and separation can be done. It can be used for the analysis of solids, liquids and gases. Then the volatile solution used for the solutes gets dissolved.

It involves a broad range of molecular weight of about 2 Daltons to 1000 Daltons. Distillation is the separation method, but chromatography has replaced distillation as gas chromatography deals with the chemical nature of the stationary phase. This significant variable makes chromatography a powerful technique.

The endocrine disrupting properties of phenols and other pharmaceutical products affected the environment, and Lee *et al*. [**25**] determined it in 2005. There is a various method for identification and determination, but they were time-consuming. This technique gave multiple parameters. For extraction, phenol and acid eluted were done, which produced the separate group extraction. This process is more beneficial for the sewage mixture. The product can be converted into different derivatives, and selective and sensitive analysis can be done.

Advantages

1. It can separate both organic and inorganic materials.
2. It gives highly accurate and precise results.
3. It is an inexpensive technique.
4. It is simple to use and is reliable.
5. As compared to other technique, it shows high-resolution power.

Disadvantages

1. The sample should be thermally stable. Otherwise, it will thermally degrade.
2. Appropriate care is needed while injecting the gaseous sample.
3. This technique can separate only the volatile specimen.
4. It is complicated to analyse a significant amount of sample.
5. It is challenging to operate a conventional GC.

Gas chromatography-mass spectroscopy (GC-MS)

This method was developed and used in the mid-1950's. The scientist Gohlke and Mclafferty have developed the GC-MS technique [**26**]. When the technique was developed, it took too much time to analyse, but after 1996, the development was made, and the analysis took just 90 seconds for analysis. The technology involves the detection of the effluent of many compounds. It is a combination of gas chromatography and mass spectroscopy. Because gas chromatography helps in the separation of substance, but it does not give any information about the isolated compounds while mass spectroscopy can provide the details about the compounds. The basis for the gas chromatography technique is the resolution involving separation of components. On the other hand, the mass spectroscopy requires mass resolution, i.e. it analyses and separates on mass to charge ratio.

This GC-MS technique consists of two significant steps: firstly, in gas chromatography, the separation of compounds in the pure form is done with the volatility concept. Secondly, the separated compounds move out through the column and go towards the mass spectrophotometer and detect the compound to give the detail of mass and charge. The column inlet is provided for the introduction of the sample. For volatilisation, there is a heated chamber present. The carrier gas always moves in two directions in the inlet of the column so that the sample moves with a carrier gas. In the splitless system, the sample can be introduced in a large quantity. GC-MS prefer the analysis of volatile compounds instead of considering non-volatile and high molecular weight compound. It can be useful in environmental analysis, detection of drugs, and for unknown sample identification.

Phenol constituents were separated by using this technique of gas chromatography. This method uses gas chromatography and mass spectroscopy. The phenol complex mixture was studied, isolated and then identified. This was mainly analysed for the phenols in coal liquefaction. The carbonisation and gasification of

coal have phenol constituents, and this serves the most reliable method for characterisation and separation [**27**].

Advantages

1. Separating highly concentrated samples is easy.
2. It can be handled easily. Hence every lab prefers this technique.
3. It involves chemical ionization and also electron impact ionization.
4. It can be used for fingerprint identification.
5. It is suitable to analyse the gas sample directly.

Disadvantages

1. Derivitization is needed.
2. It deals with selected ion monitoring.
3. It faces challenges in term of atmospheric gases.
4. Extracts are evaluated from non-biodegradable substance plastics.
5. Additional preparation is needed for the non-volatile matrices.

High-pressure liquid chromatography (HPLC)

Chromatography was first introduced by the Russian botanist Mikhail Tswett in the twentieth century. HPLC is a technique used for the separation of components mixed in the liquid medium with the help of another liquid medium in the chromatographic column. For this separation, two phases are there, such as the stationary phase and mobile phase.

(a) Stationary phase: Liquid medium or solvent is placed into the column with the packing material and remains for a long time in a stationary phase.

(b) Mobile phase: Other medium is poured continuously through the column so that it gets mixed with the stationary phase and carries the analytes from the solvent.

The interactions between the molecules of the solvents and packing material may be the cause of separation of the mixed compound. Later on, with the help of spectrophotometer via colour intensity, the compound can be identified. This technique has a principle similar to that of liquid chromatography, but it is more superior in case of sensitivity, speed, and efficiency. This is also called "High-Performance Liquid Chromatography". It is mostly used in the field of Pharmaceuticals, biological compound, toxic compounds, etc.

Phenol extracted from olive oil with solid phase extraction technique and then HPLC was used for the analysis. Mateos *et al*. [**28**] showed this method for phenol identification and analysis. This technique gave a quantitative estimation of phenol. It was used with UV detection and served as a suitable and precise method for phenol.

Advantages

1. It gives a highly accurate and reliable analysis.
2. It is a highly sensitive technique.
3. It performs fastly.
4. It works with high resolution.
5. It is an automotive technician.

Disadvantages

1. Instrument cost is high.
2. Sometimes sensitive to specific compounds.
3. It faces complexity in the term of operation and working.
4. Increased path length leads to increased absorbance.
5. It requires expensive solvents and columns.

Spectrophotometry

Spectrophotometry is the technique which measures the absorption of a beam of light. It quantitatively measures the properties of reflection and transmission of material, solutions or transparent solids sources of the light intensity. The spectrophotometer directly detects the spectra of absorbed light. A spectrophotometer also detects the photon absorbed by the sample solution. It can identify the reflection and transmission with the help of the wavelength of light. From the year 1941, the spectrophotometry was used in the biological field. It was first used in 1990 for proteins [**29**].

A monochromatic film is used to transfer the light source in a single beam. The aperture is provided before the cuvette containing the sample. The beam is then passed through the sample which is present in the cuvette. After that, the beam is moved to the photodetector where the concentration is detected and converted into a digital value which is in a readable form. This is the case for single beam spectrophotometer. In double beam spectrophotometry, the difference is just between the splitting of light; so that at the same time, the light can pass through the sample and reference. The cuvette is made up of plastics or glass where the visible light is used. In case of UV light, the cuvette should be of quartz.

There are different types of spectrophotometer such as,

(a) *Single beam spectrophotometer*

It involves multiple beams of light, which pass through the sample for detection of the intensity of light. The sample allows the passage of all the light. The process is simple but time-consuming.

(b) *Double beam spectrophotometer*

In this, there is a separator to split the light so that the sample and reference can be detected simultaneously.

(c) *Visible light spectrophotometer*

It is used to detect the light precisely in the visible region. The different source can be utilised such as halogen or LED etc.

(d) *Ultraviolet spectrophotometer*

It is used to detect the light in the ultraviolet region. The samples are used in the solid and liquid form. And one important aspect is that the cuvette must be made from quartz.

(e) *Infrared spectrometer*

In this type, the light in the infrared region is detected.

In the lignin preparation, the phenolic hydroxyl group was determined by Goldshmid in1954 [**30**]. This was a rapid and straightforward method. The phenol absorption in the alkaline solution is the basis for this technique. The resulting curve difference and absorptivity gave the phenol determination. The content of phenol in the sample was calculated by using the two given parameters.

Advantages

1. It is a simple technique
2. It is non-destructive to samples
3. Unknown concentration can be determined.
4. It is a highly sensitive technique.
5. It can be useful for the detection of a chemical property.

Disadvantages

1. It only detects the visible and near-visible portion of light.
2. Calibration is required in case of the UV-visible spectrophotometer.
3. The performance of the device slows down when it comes in contact with the dust and grim coats mirrors.
4. Using faulty designed instruments, the stray light is obtained.
5. Noise may be caused by the sample, which may lead to a reduction in the accuracy of the measurement and sensitivity.

Biosensor-based amperometric

For the biological processes management and controls, the environmental regulation and requirements of the environment, maintenance of food and water quality are the fundamental requirements from the safety point of view. The advanced technology has to be safe for human and animal health, and so the needs for technology development must be taken into consideration. The newly formed technique should be efficient with time, accurate, quick result building, and most significantly, it should be economical.

Hence, sensors should be developed in a new manner like biosensors. As from the word biosensor, we can understand that there is something related to biological, electrical or electrochemical aspects. Application of biosensors is smooth, efficient and cheap.

When biological substances are operated with physiochemical detectors, the instrument is called as biosensors. It works on the principle of interaction between biological activity, optical signals and electrical signal, known as bio-matrix where biosensors convert the properties. Amperometry is the process which uses electric current or variation in electric current for ion identification by making the use of biosensor. The amperometric biosensor is the device used to monitor electron transfer like bio ocular electronic devices. These are the most modern, familiar, and commercialised device. These devices are the leading cause for the development of analytical biotechnology, which is a newly arising field. Product concentration and the current are directly related to amperometric biosensors. The first amperometric biosensor was designed as an amperometric enzyme electrode in 1962 by Lyon and Clark [**31**]. It was developed for glucose identification

There are three types of amperometric biosensors as (a) direct transfer, (b) mediated, and (c) unmediated. The commercially used amperometric biosensors are the mediated one.

Kulys and Vidziunaite [**32**] did the phenol determination by this biosensor based amperometry. For this, they developed biosensor by using graphite electrode and recombinant fungal laccase polpyorous pinsitus. This biosensor senses the phenol, 1-naphthol, guaiacol and other related compounds of phenol. Enzyme immobilisation with bovine serum albumin was also done.

Advantages

1. It is selective to substances.
2. It is simple to work.
3. It is simple to handle.
4. It can detect benzene, trimethylamine gas, alcohol and herbicides.
5. It is a cost-effective and long-lasting method.

Disadvantages

1. Working time of amperometric biosensor is short.
2. It responses late as compared to biosensors.
3. Accuracy is not up to the mark.
4. Redox element is required for the enhanced current production.
5. Surrounding environment may cause hindrance.

Biosensor-based enzymatic

The biosensor is the device which can be used to connect the transducing part to the element which is biologically active for converting the information obtained in the form of signals. Transduction of signals means response vibrations should give the concentration of the precise element [**33**].

There are different types of biosensors, depending on the specific receptor and transduction.

Depending on receptor

(a) Enzymatic biosensors
(b) Immunological biosensors/ Immunosensors
(c) Gaseous biosensors

Depending on transduction

(a) Optical biosensors
(b) Thermal biosensors
(c) Electrochemical biosensors

The enzymatic biosensor is the biosensors in which the isolated enzymes are used to facilitate the biochemical reactions. These enzymatic biosensors derived by the biological interaction can be used to give quantitative or semi-quantitative information after analysis. The enzyme required should be versatile and

functional, which can also be a biomolecule. Enzymatic biosensors serve efficiently to detect pollutant. For the preparation of enzymatic biosensors, the mobilisation of the enzyme is necessary as biochemical reactions should control the activity of the enzymes.

Clark and Lyons [**34**] discovered the enzymatic biosensors in 1962. They observed the relationship between glucose oxidation by enzymes and the coreactant consumption.

Rodriguez-delgado *et al.* [**35**] in 2015 used laccase as a biosensor for showing the detecting ability and quantification of compounds derived from phenol. Laccase biosensors exhibit rapid approach to monitor on-line as well as *in situ* phenol compounds along with the features representing high sensitive nature and reproducibility that can be set to the standard limit of food, pharmaceutical industries and environment.

Advantages

1. It is the best alternative to other techniques.
2. It gives a fast response.
3. It shows high sensitivity.
4. It has high selectivity.
5. It is favourable for an oxidation-reduction reaction.

Disadvantages

1. It is an inhibitor-sensitive method.
2. Production of biosensors is costly.
3. It shows irreversible thermal deactivation
4. It shows a high-temperature coefficient.
5. In contact with immobilisation, they can lose their activeness.

Biosensor-based optical

The control model for getting the information and analysed data to develop the biological model, enhancing the detection of a compound can be said as a biosensor.

The optical biosensors involve the interaction of the substrate and biomolecules, which helps in releasing photons for light emission. The detector is provided to the system so that the sensor could detect the emitted light. It involves the optical signals for the detection hence called as optical biosensors.

The biosensors are merely the analytical device provided by the biological sensing element. The assembly had a physical transducer. Optical biosensors denote the electrical signals, which are translated from the interaction between target and recognition element [**36**].

These types of biosensors are enormously used in the biotechnological, clinical, and medical fields. The optical fibres have the advantage in the detection of the hazardous pollutant; hence, it is mostly applicable in the biosensors for designing optical biosensors. As the detection is direct and rapid, the use of it is increasing day by day [**37**]. The fundamental thing about this biosensor is that the sample can be utilised without pre-treatment.

The biosensors are developed to reduce the previous complication that has aroused due to available techniques. Therefore, increasing the use of such an optical biosensor is applied for accuracy and precision. Abdullah *et al.* [**38**] suggested about the immobilisation of MBTH in the adequate Nafion/ sol-gel silicate film. The biosensor showed features such as right sensitiveness, stabilisation, and reproducible behaviour.

Advantages

1. It is a powerful technique.
2. It is the best alternative to other technique.
3. It shows high sensitivity
4. It rapidly detects the compound.
5. It is a simple operation and reproducible.

Disadvantages

1. Equipment cost is high.
2. It shows sensitivity towards the surrounding area.
3. It faces the challenge in term of surface modification.
4. It requires significant optical devices.
5. There is no availability of femtometer.

Whole cell biosensor

This type of biosensors was developed to detect environmental pollution. Different types of biosensors are available; among such type whole cell biosensor is the one who works with the transducer and represents itself as “Bio-reporters”, by involving the use of cells from protozoa, fungi, plant cells, algae, and bacteria. It can be applied to the full range of pollutants present in pesticides, biological oxygen demand, heavy metals, etc. The property of flexibility enables it to be used as a primary technique for the detection of contaminants. Quantitative analysis can be done using the biological cells.

It differs from the other analytical techniques as it doesn’t require probe for further processing. There is no effect due to the use of this technology, and hence, it is the most suitable one and used in the living immobilised cells for giving practical information.

Different types of biosensors are classified based on the following factors [**39**],

(a) Recognition elements available
(b) Signals transduced

The waste coming out from different industries is harmful. Whole cell biosensors do pollutant detection. The whole cell biosensor is coupled with the optical biosensors for the detection of pollutants. This makes the detection of the pollutant smooth and accurate. Zeng *et al.* [**40**] in 2015 synthesised the whole cell method to detect phenol by making the use of wild-type *Bacillus amyloliquefuciens* endospores. The phenol concentration was estimated by the detection of absorption signals at 510 nm.

Advantages

1. It gives information about the total availability pollutant rather than its free form present along with other recognised compounds.
2. Continuous monitoring is possible.
3. It is cheap in maintenance.
4. It is used for quantitative and qualitative measurement.
5. Estimation is rapid and easy.

Disadvantages

1. Longlasting cells are required.
2. Handling is tricky.
3. It mostly requires knowledge of microbiology and cell culture.
4. It requires knowledge of hazardous and toxic compounds.
5. Knowledge of biochemistry is limited.

Capillary electrophoretic method (CE)

This method is based on the principle that according to the physical characteristics, the small charged particles separate by moving towards the opposite pole on the combination of electrophoresis and chromatography. And this performance makes the technique superior over other analytical methods like HPLC. It works by the electroosmotic flow. The capillary action does not pull the solvent, but there is a supply of electrical potential, which helps in the movement of the buffer solution. This technique was first developed by Guttman and Coulter in the year 1989 [**41**]. Later, they formed the Beckman Instruments.

It applies to different molecular weights materials involving the biopolymers and inorganic ions. Small particles, as well as macromolecules, can be separated by capillary electrophoresis [**42**]. The separation of biopolymers includes materials like proteins, DNA, etc. Hence, this technique can be applied in the pharmaceutical field, such as for phenol detection [**43**]. Capillary electrophoresis did the detection of eleven priority phenols. Capillary of internal diameter 20 µm and electrophoretic buffer with 1mM fluorescence was used. Just within 14 minutes of the period, 14 compounds are separated and detected by this technique. Industrial phenols are also detected and separated by using this method [**44**].

Advantages

1. Operation cost is low.
2. It is an efficient technique than other ones like capillary gas chromatography.
3. Detection is easier when analyte becomes active.
4. It is simple to handle.
5. It consumes less time.

Disadvantages

1. It cannot be performed at high voltage.
2. Micro-electrode fabrication and placing them in the small space of capillaries will be trying one.
3. Detecting portion of the tube needs to be naked.
4. Sensitive as well as the limited resolution, may cause hindrance.
5. Products get degraded if stored improperly.

Synchronous fluorescence spectroscopy

The Fluorescence spectroscopy method is applied to investigate the fluorescent compounds when the concentration is low, which yields the knowledge of preparation, structure and stability.

When studying the complex mixture of the samples, this method could be the suitable one helping to reduce scattering of light and simplifies the spectra. The available two-dimensional techniques have been the reason to develop this technology. This process is mainly concerned with a single range for various fluorescent compounds.

It now becomes a real-time monitoring technique. Mostly, this method is helpful in the field, like cell culture, involving animal cell culture. Almost all the areas of science-namely the chemistry, clinical, physics, biochemistry, material engineering, and chemical engineering, this technique are applied as it is used for quantitative analysis.

Synchronous fluorescence spectroscopy was well used by the team of scientists for the study of the liquors. The test, colour, quality are the critical factors in the making of liquors, which makes them different from each other. Hence, the difference between liquors should be maintained. The distinction between brandies and wine distillates was obtained by using synchronous fluorescence microscopy. The difference between the wavelength during the excited and emitted state was constant, and spectra were recorded from 220 to 700 nm. There was about 99.5% accuracy in the result [**45**].

Advantages

1. It is a relatively cost-effective technique.
2. It is easy to operate.
3. It is a non-destructive technique.
4. It is non-invasive.
5. It can give various properties without preparation of time-consuming samples.

Disadvantages

1. It cannot be applied for identification.
2. All compounds do not show fluorescence.
3. Contamination may result in a reduction of the fluorescence.
4. The signal becomes sensitive towards pH.
5. The signal becomes sensitive to temperature as well.

Flow injection analysis

It consists of the continuous flow of the liquid stream in which a fixed amount of sample is injected into the constant flow of moving liquid. The reaction between the sample and liquid take some time. Due to the entry of the sample into the continuous stream, some changes may occur which are responsible for forming a zone of mixing. At the exit of the liquid medium, the detector is

provided so that it detects the changes in the different parameters continuously. If the sample and liquid are adequately mixed, the identified amount of compound could be produced. Thus, there are three fundamental points in the principle of flow injection technique such as an injection of the sample into the fluid flow; the injection should be controllable and reproducible and finally the monitoring time and analysis of the injection. This technique is widely used in the study because of its full applications and versatility like the speed of analysis, automatic injection analysis, etc. The concept of flow injection analysis was developed by James and Martin in 1952 [**46**]. From this study, the injection of the sample into a flowing stream was used. This was prepared in case of gas chromatography.

A minimal amount of sample creates approximately 1 ml of waste; hence, a large number of analysis produces massive waste. About a hundred sample can be run in one hour in this method. For a single study, the minute sample is used; therefore, it is said to be a micro-chemical method. For the determination of the phenolic compounds, flow injection analysis was used with spectrophotometry. Phenol was detected by two different reactions in this technique. First one is the reaction between amino antipyrine and phenol while in other reaction, the coupling of phenol with 2-methyl-3-benzothazolinehydrazone takes place. The detection limit for phenol was 12-30µg/ L [**47**].

Advantages

1. It performs with a high sampling rate.
2. This technique is flexible when a modification is required.
3. It is economical in construction and working.
4. It is straightforward and easy to handle.
5. This technique is selected for analysis in comparison to the other conventional methods.

Disadvantages

1. Short reaction time is responsible for less sensitivity.
2. It is applicable for handling a few samples.
3. Constant supervision is required during industrial processes.
4. Consumption of reagents and sample is high.
5. Repetition is high.

Capillary-HPLC

The instrument of capillary HPLC consist of the solvent delivery system, Hewlett packed model with flow rate maintained at 200 to 400 µl/ min. The flow processor is provided for the solvent delivery system. There is a filter present in the processor and solvent delivery system. The sample can be loaded manually with the injector. Columns are directly connected to the injector. At the endpoint, the UV absorbance detector is provided for the detection. The absorbance can be done at 241 nm. Capillary HPLC is a developed form of HPLC, in which the reduction of column diameter to the capillary size about 100- 500 µm is used for the separation and detection. The column size reduction is reduced to increase the separation efficiency of the column. To obtain excellent efficiency, the rate of flow should be low. The flow rate can be achieved with the help of such capillary, which is near about 0.4- 100 µL/ min. Excellent results can be obtained by increasing the ionisation of molecules, and the capillary HPLC can achieve it. If the diameter is higher than the average size, then the poor separation and resolution are seen. The separation column is required to separate biomolecules, and further detection is carried out by using the mass spectrophotometer.

Chung investigated about the complete detection through the capillary-HPLC [**48**]. The standard deviation for the recovery was observed to be 20% on the total phenol detection. Out of 11, ten phenols were separated by applying 40% (v/v) MeCN at 5.0 pH value in the mobile phase.

Advantages

1. Small diameter columns have reduced the cost.
2. It is a highly efficient technique.
3. It is a highly sensitive method.
4. It deals with high resolution.
5. Small quantity is enough for the analysis.

Disadvantages

1. A significant amount of sample is not required.
2. Handling is quite tough.
3. It is not benefitted for most of the chemicals.
4. Retention time is required.
5. It involves the behaviour of nature.

Capillary electrochromatography

Capillary electrochromatography is the technique based on the principle of separation with the help of an electric field instead of applying pressure. The chromatographic column is used to separate two phases in which the buffer and mobile sample phase are passed through the chromatographic column. It works in the same way for sensitivity and selectivity as that of capillary HPLC. The flow required in this technique is the electro-osmotic flow. The flow is coupled with the high separation power between stationary and mobile phase like in HPLC technique. The capillary possesses both mobile phase and the stationary phase, but the partition separates them. The separation is done between the capillaries of 50 to 100 µm.

It is a combination of two techniques, hence can be called a hybrid method. As it is the advanced technology over all the chromatographic techniques, it can be applied to a large extent.

Capillary electro-chromatography determined the analysis of phenol and their derivatives in the tobacco smoke [**49**]. In the tobacco industries, the production of tobacco has an essential factor for a smoke. Phenol, hydroquinone, resorcinol, etc. was determined by this method. The determination of the side stream and mainstream of smoke was done very accurately.

Advantages

1. Analysis can be done rapidly.
2. The limited sample is required for analysis.
3. It requires a short time.
4. It is a highly efficient technique.
5. Sensitivity is greater.

Disadvantages

1. The temperature should be controlled.
2. It shows limited analysing reaction with the buffer solution.
3. Voltage should be controlled to reduce the formation of bubbles.
4. It is highly exposed to methodological variables.
5. The mechanism of separation is not deducted in most of the cases.

Thin-layer chromatography

The principle of thin layer chromatographic technique is used to separate and detect the molecule or compound from the given mixture of the solution. It involves two phases: solid phase and a liquid phase. Solid is used as a stationary phase which may be adsorbent and liquid is used as a mobile which is solvent or mixture of different solvents. Thin layer chromatography can separate various types of organic compounds.

Analysis involves:

(a) Types of compound present
(b) Amount of compound
(c) The purity of the compound
(d) The reaction progress
(e) The chromatographic conditions

It is sensitive up to 0.00001g of the compound. This technique helps detect the identity of the unknown compound in comparison with the known compound by running both the mixtures at the same time, and it requires the R_f value. "R_f" is the ratio of distances travelled on the plate by a substance and a solvent.

The analysis of phenol substances was determined quantitatively by thin layer chromatography where the phenolic groups are not substituted. The thin layer of silica gel or cellulose was applied to the chromatographic plate. The sample was made to run through the specific reagent, and the determination of phenol was done. This was considered as the most suitable and comfortable method [**50**].

Advantages

1. It is pure and quickly performed the technique.
2. This technique is highly sensitive.
3. A minute amount of sample is required for analysis.
4. This is a cost-effective technique.
5. It performs with less number of equipment.

Disadvantages

1. The length of the plate is limited for running the sample mixture.
2. The open system technique may cause changes.
3. Temperature and humidity have an impact on results.
4. Compounds should be non-volatile.
5. Resolution capability is limited.

Flow-injection with chemiluminescence

When the molecule or atom is excited and come to the ground level again, the process is carried out electronically where some energy is released in the form of radiations with the help of photons, this process is known as Chemiluminescence.

As it deals with luminescence and productive activity, this property makes it a better technique of detection over other analytical methods. The presence of ions in natural water is an important parameter to understand the features of the water. The biogeochemical nature can be identified by using flow injection with Chemiluminescence.

The reaction between the alkaline solution of poly-hydroxy phenol and luminol was enhanced for the poly-hydroxy-phenol determination. The phenol detection limit was 0.03 µg/ L. The use of ferricyanide and ferrocyanide was considered to be necessary for the method involving Chemiluminescence [**51**].

Advantages

1. It is a simple technique.
2. It performs analysis rapidly
3. This technique is cost-effective.
4. Detection is excellent.
5. It is used for the detection of a broad diversity of species.

Disadvantages

1. It is less sensitive.
2. Dispersion leads to low accuracy.
3. Dilution may take place due to excess time interval.
4. It is in the time-consuming process.
5. Seperate detection step causes automatic disruption.

Liquid chromatography-electrochemical detection (LC-ED)

The principle of liquid chromatography-electrochemical detection is the separation of the compound using the chromatographic column but in the presence of an electric field. The compound undergoing the reactions may be a reduction or oxidation reaction. There is a requirement of the electrode for the mobile phase to experience a chemical reaction. Therefore, the measurement is further carried out in the form of current.

The pharmaceutical field involves the extensive use of the LC-ED technique because the method performs selectively and with accurate detection. As compared to the other detection like fluorescence and ultraviolet detection; this is more superior technology since it doesn't require Derivitization, which is an essential aspect of this technique. Hence, it can apply to different fields like pharmaceutical, biological, environmental, monitoring in clinical activities, etc.

For the reducible compounds, the sensitivity decreases significantly as compared to the oxidative compounds.

Knutsson *et al.* [**52**] detected the chlorinated phenol in water. In their study, the membrane extraction system of liquid was joined to the LC-ED. The organic solvent was used so that selective extraction could occur. In just 30 minutes, the phenol extraction was done. Approximately five chlorinated phenols were identified by this method.

Advantages

1. Detectors are very selective.
2. It is easy to operate.
3. Routine sample analysis can be done quickly.
4. Electrode surface activity can be monitored easily.
5. The detectors can deal with the solute, which can undergo the reduction and oxidation reactions.

Disadvantages

1. It can be applied to the electrically active compound.
2. Detectors are destructive.
3. The mobile phase should be pure, oxygen free and should lack metal ions.
4. The response of the detector is prolonged.
5. Response time is less in comparison to other methods.

Chemiluminescence

The concept of Chemiluminescence has been derived from naturally occurring luminescent animals. Radziszewski was the first person to create the artificial luminescence and observed that the reaction in which oxygen is dispersed in the bubbled form in the ethanolic chemical solution produces emission of the yellow colour [**53**]. After that, different luminescence was developed from various sources and solutions.

The light is produced in the cold form with the help of the chemical reaction of two different chemicals. It provides light in a different way such as visible, ultraviolet and infrared. Analytical chemistry employs the application of chemiluminescence in various fields like chromatography, including HPLC [**54**], thin layer chromatography [**55**], flow injection analysis [**56**], etc.

Vdovenko *et al.* [**57**] suggested the simple Chemiluminescence method to determine phenol. They have illustrated two patterns for phenol assay dependent on the interrupting influence on the chemiluminescence generated with the help of oxidation of luminol. But the test of the respective water effluents did not affect as the recovery value was noted as 92-96%.

Advantages

1. It is a highly sensitive technique.
2. It produces light at high speed.
3. It is helpful in the medical field like DNA probe assay, immunoassay, etc.
4. Instrumentation is straightforward.
5. No requirement of any other equipment or machine.

Disadvantages

1. Sometimes due to fast detection, the result may not be correct.
2. Luminol can destroy DNA.
3. Light is produced for a short duration.
4. Expensive reagents are required.
5. It requires quantification of a microwell plate.

HPLC-ED (Electrochemical detection)

The technique is based on the principle that the HPLC get involved during the separation of the compound but is combined with the electrochemical cell which creates the electrochemical reactions so that the electron transfer helps in the detection of the separated compound through the connection electrode. In this process, the chromatographic column possessing the substance is activated electronically for the transfer of electron. The essential aspect is that it deals with electrochemical detection and chromatography.

It is essential to detect the minute amount of compound present in the mixture during the chromatographic technique, and HPLC-ED serves the best way to separate and identify the compound sensitively and rapidly. Due to the use of electrochemical detectors, they flexibly increase the detection. The detectors can give a more rapid response at a low concentration also. The electrode used can be of different materials such as carbon, gold, mercury, platinum, etc. among which mercury is the most suitable one. In this, the signals are dependent on the flow rate of the mobile phase. Since it is not a stationary technique for the measurement, therefore it is responsible for providing selectivity and sensitivity, and it is also helpful for the complex mixture sample.

Bartosova *et al.* [**58**] used the best method HPLC-ED to determine BPs dependent on amperometric detection. The technique was used for the analysing bromophenols in running water and plastic products.

Advantages

1. It is a highly sensitive technique.
2. Graph of detection can be plotted in a few seconds after filling readings.
3. Electrode shows a quick response to the detection.
4. It is a highly precise and accurate method.
5. It measures signals with stability.

Disadvantages

1. The mobile phase complex must be electrically active.
2. There is a limitation in the detection range.
3. Electrode suffers poorly.
4. Electrode gets drifted in response to time.
5. It lacks high sensitivity.

Electrokinetic capillary chromatography-electrochemical detection

This technique is merely the advanced modification of capillary electrophoresis. In this process, the ionic and non-ionic compounds are the primary target, in which the stationary phase of the electrolyte is separated easily. In this, the electric field is applied for the separation. Separation can be done through the electro-osmotic flow and sometimes has an impact on the components of the separated compounds.

It works for capillary chromatography. Therefore, it can carry a small volume of sample. It is mainly for pharmaceutical analysis or detection of amino acids, vitamins etc.

The extensive use of cosmetics requires the aspect for the detection of chemicals added in the cosmetics. The determination was done by Wang *et al.* [**59**] for eight different phenolic additives. The analysis was done with sodium dodecyl sulphate within 30 minutes. The limits of detection for all the analytes were 1.1×10^{-7} to 1.2×10^{-6} g/L.

Advantages

1. It can separate tiny molecules.
2. It efficiently isolates the molecule in short retention time.
3. It is applied for both ionic and non-ionic compounds.
4. It is highly efficient for separation.
5. A moderate amount of sample is required.

Disadvantages

1. It has low sensitivity for low concentration.
2. Detectors have some limitations.
3. It has poor reproducibility.
4. It needs to improve sensitivity.
5. Volume capacity is limited up to 1.8 µL.

HPLC coulometric electrochemical detection

The new development done in the HPLC technique is the coulometric electrochemical detection after the electrochemical detection. It is operated by electrochemical detection simultaneously with the redox reactions.

Coulometric detection involves the current measurement of time. Charge or electron transfer is required for the detection of the electrochemical reaction. It can detect in a small range of about 0.5 fmol/ mL to 50 fmol/ mL, and the lowest limit is 2pmpol/mL. It is mainly used to determine the biological analysis of the reduced compounds. The highest sensitive determination of the acetic acid solution was observed.

The material possessing affinity towards electric current could be only detected, but the electrode could not be identified.

Determination of phenolic compounds with the HPLC coulometric method was done by Aaby *et al.* [**60**] in 2004. Three cinnamic acid derivatives and flavonoids behaviour were detected by using ferric reducing activity power (FRAP) and oxygen radical absorbance activity.

Advantages

1. It possesses the highest sensitivity to detect.
2. It is highly reliable.
3. It is a particular technique.
4. It is easy to operate.
5. It is a highly precise and accurate method.

Disadvantages

1. Consumption of solvent is high.
2. Technology needs maintenance.
3. It has poor reproducibility.
4. There is a time taking process.
5. Response time is less.

Electrospray-tandem mass spectrometry (ES-MS/MS)

This technique has application in the medical field like biochemical genetics, clinical, new-born assay, etc. Mass spectroscopy helps in the identification of inborn errors of the different components like fatty acids metabolism, organic acids, etc. The pre-treated sample is required for this technique of identification. Therefore capillary gas chromatography is the best method to prepare a sample for identification so that the spectrometer can detect the distinctive spectrum of the compound. This technique was developed twenty years back, where biochemical genetics was used for the first time.

The characterisation and degradation of phenols by this technique was determined by FCC Moura *et al.* [**61**]. Fenton system did the oxidation of phenols with the use of composites. Fenton reaction was used due to the organic pollutants present in water, which is the best method for oxidation. In the Fenton system, Fe^0/ Fe_3O_4 and H_2O_2 were used.

Martin *et al.* [**62**] suggested the use of ES-MS/MS method for detecting the alcohols and phenols in the essential oils that are joined with the precursor ion. The particular purpose is mostly employed for quick screening of oils that are critical to select the alcohol and phenols for the quality control processor for the fast calculation of extracts produced an abundant amount.

Advantages

1. It analyses the sample in less time.
2. It can detect and give a quantitative estimation of different metabolites.
3. The output is high.
4. Results can be reproduced
5. Handling is easy.

Disadvantages

1. Equipment cost is high.
2. It is limited to laboratory sample preparation.
3. The attachment of quadrupole to another analyser is overwhelmed.
4. It consumes a lot of time.
5. Selectivity is less.

Solid-phase extraction (SPE)

The principle of solid phase extraction involves the separation of a component or analyte using two phases; solid phase and liquid phase. The materials present on the surface of the liquid are removed by holding with the solid phase followed by further retrieval process. It is carried out in four simple steps as,

(a) Conditioning of the sample so that it can be quickly reacted with the sorbent.
(b) Loading the sample and retaining it.
(c) I am washing the extractants.
(d) Elution, where the different chemicals or solutions are added for natural removal of the extracted compound.

The pre-treatment to the mixture is required. There are fewer chances of using this technique without pre-treatment like maintaining pH of mixture and dilution of the mixture so that the contact time with the solid sorbent will be superior.

Solid phase extraction is a simple method for phenol detection. Mateos *et al.* [**63**] were the group that suggested the accurate analytical method for determining phenol containing compounds and flavones in olive oil both qualitatively and quantitatively. The phenol from olive oil from (amino acid cartridge) diol cartridges was isolated. Then extracted compound was analysed by HPLC.

Advantages

1. It economically operates.
2. There are no problems related to the emulsion.
3. It is a highly accurate technique.
4. It requires fewer amounts of reagents and solvent.
5. It deals with high recovery and reproducibility.

Disadvantages

1. Many tough choices are there for this technique with better results.
2. It takes a long duration to produce the output.
3. Dilution of the mixture is necessary.
4. It is a time-consuming process.
5. The removal of interference is not adequate.

Liquid-phase micro-extraction (LPME)

It is the same as the liquid phase extraction technique used for the sample preparation for the analytical process. But this one is more superior technology for extraction. To reduce the generation of waste after the procedure, minimising the consumption of sample and reagents is done and the technology is developed as LPME. Usually, the aim behind the development of the microextraction method is to obtain the sample in a short time with high enrichment, which is used for direct analysis. The condition required for the process is that it should use a limited amount of equipment, chemicals, and solvent.

It can be handy in restoring the solvents since the microliter of solvent is required. It is used in field sampling. It deals with the separation of the water miscible compound to give the immiscible water compound. This technique is of different type depending on the way of performance as,

(a) Dispersive liquid-liquid microextraction (DLLME): The liquid extraction sample is used with the dispersive sample for fast extraction by producing cloudy mixture when mixed into the solution to give an extract.
(b) Single drop microextraction (SDME): The organic solvent can be added dropwise into the aqueous sample for the extraction.
(c) Hollow fibre micro-extraction (HFME): It is a process of transferring a substance from an aqueous phase to an organic phase that is immobilised within the pores of the wall of a hollow fibre.

This technique was used by Zhao *et al.* [**64**] for the extraction of phenol from water. As phenols and phenolic compounds have toxic nature, they have to be removed from the water samples. In this paper, the explanation related to the extraction of the phenols is done. Within 35 minutes, phenol was extracted, i.e. for more than 100 folds, the enrichment factor was obtained.

Advantages

1. It is a simple technique.
2. It performs at a faster rate.
3. It is simple in operation.
4. It is inexpensive in case of equipmentation and exploitation.
5. Extraction is fast in short duration.

Disadvantages

1. In the case of static LPME, the time required is more.
2. When operated with a single drop, direct immersion process, it is unstable.
3. The separated operation for injection and extraction of the product is necessary.
4. Needles gets bent continuously, which causes an increase in expense.
5. The coating forms the strips.

Dispersive liquid-liquid microextraction (DLLME)

The principle of this technique involves the extraction of the material by dispersing the organic solvents into the water-miscible liquid, which leads to the formation of droplets into the solution which can be extracted. Like other available techniques for sample preparation, this method is also required a bright and clean sample. But the difference is that it produces highly enriched sample by using very less amount of water. This is the reason why it applies to a variety of analytical techniques.

For the LLME technique, there are certain drawbacks associated. For the proper extraction, it requires a significant period. Thus, Rezaee *et al.* [**65**] developed the method of DLLME in 2006.

To determine the disrupting endocrine phenol, DLLME and DDME were used by Darias *et al.* [**66**]. The detection of phenols from sea water was done with the help of HPLC. The average recovery of 98% was obtained. It served as the best method because the analyte and solvents were reacted at the contact surface was very high.

Advantages

1. It is simple and precise technique.
2. Extraction occurs rapidly.
3. Less extraction time is required than LLE.
4. It is easy to operate.
5. The minimum organic solvent is required.

Disadvantages

1. It is selective to solvents as it requires denser solvents than water.
2. More toxic solvents are used than less toxic. Solvents.

3. The extraction efficiency is low.
4. Extracts are not environmental friendly.
5. It is difficult to take out the small amount of suspended droplet from the solution (<5L).

Ultrasound-assisted emulsification-micro-extraction (USAEME)

The reaction between the two immiscible phases such as water and an organic solvent which are mixed by simply dispersing the small amount of the organic solvent into the water and allow it to react for extraction of a compound in less time. Ultrasonic emulsification removes the compound. EME assisted the basic principle by Ultrasound. The ultra-sonication process does emulsification. The radiations were responsible for accelerating the emulsification. The analytical technique uses the layer of the sample, which gets separated [**67**].

The pre-treatment of a sample is done before passing towards any analytical technique like chromatography. Correctly, due to the high purity of the sample, it is used for HPLC.

Due to its high efficiency towards obtaining the best pure analyte, it has become the best alternative technique for various methods like solid phase extraction, liquid phase extraction, etc. for water treatment including all type of water such as municipal water, tap water, sewage water and river.

The USAEME was employed for the analysis of phenol and its derivatives in the water like parabens and triclosan. The Derivitization of the specific compound was acetylated by using reagent, which is inexpensive. The recovery of about 85% was obtained [**68**].

Advantages

1. It is easy to operate.
2. It is a fast technique.
3. High recovery is a critical point.
4. It is an economical technique.
5. It is environmentally friendly.

Disadvantages

1. Temperature control is necessary. Otherwise, the poor quality of extract is obtained.
2. It is time –consuming process.
3. The density of the solvent leads to change in extraction time.
4. Air bubbles are formed due to rapid stirring.
5. Since the process is performed for an extended duration, the equilibrium is not achieved.

Ultrasound-assisted emulsification microextraction and solidification of floating organic droplets (UAEM-SFO)

The floating DLLE technique. There are two liquid phases for which organic solvent are used. One acts as a removing solvent and another act as the disperser. As the solvent is dispersed into the sample, the sample appears in the cloudy form and leads to the solidification of the separated materials. This is operated with agitation either manually or mechanically. The droplet formed has to be removed quickly with the help of a specific technique. Centrifugation is the best way for emulsion and extraction.

"The organic solvents used for the process should be light as compared to water so that the extracts get separated easily as they will float on the surface. For obtaining the solidified droplets, the freezing point of the solvent should be between 10°C to 25°C. The ice bath is used to solidify the droplets, which are floating. The solidified droplets can be easily collected from the sample. This is the concept of solidification".

Various factors are necessary to form the droplets because if the formation of droplets is not in proper condition, the separation will not be possible. The extraction process is affected by different parameters such as salt formation, stirring speed, disperser, solvent, temperature, pH, etc. The extracting solvent is further used for the analytical technique, but it should not hamper the analysis.

Wang *et al*. [**69**] reported about the detection of five derivates of phenol in the wine and blood of human being making the use of the unique, sensible, novel technique of UAEM-SFO linked with HPCE. The enhancement dependent factor of the analytes was observed to be ranging between 114-172, and the extraction recovery was noticed as 69-86%.

Advantages

1. The extraction process is fast.
2. Use of an organic solvent is less.
3. The process is simple.
4. The enriched component is high.
5. The mechanism is fast.

Disadvantages

1. Extraction is hamper by temperature, pH, etc.
2. Instruments used are costly.
3. The recovery process is weak.
4. The solvent used for the extraction needs to be suitable.
5. Formation of droplets needs to be favourable.

Solid-phase microextraction (SPME)

The principle of solid phase microextraction is based on the fact that separation is done without the use of the preparation of sample but using the exact amount of extracting phase which is supported by a solid material rather than sample medium. This technique was invented by Pawliszyn and his co-workers [**70**] in 1989 and then introduced in 1990 [**71**]. The sample is required to prepare for analysis. It does not require a solvent for sample preparation, so the method is superior.

The central aspect of this method is that it does not deal with exhaustive extraction. Another fundamental point is that this technique can be used on both laboratories as well as large scale. This method is the innovation in the chromatographic processes. It works with a blunt instrument, not in a very elaborative form. The device requires two main designs, tube design and fibre design. The configuration of the apparatus in case

of tube design is the same as that needed for the solid phase extraction, where extracting step is the only difference. This technique involves selective and sensitive performance. Therefore, it is mainly used in mass spectroscopy.

The use of sorbent coated silica filters was involved in the determination of phenols. After the extraction of fibre, it was transferred to the gas chromatograph. In the last step, the analytes get separated, and the quantity is determined. This technique is rapid and straightforward [**72**].

In the food industries, the flavour of the product is significant, which depends on quality. Scientists have used SPME technique for the analysis of fruits, food, wine, a cereal made products and even the pharmaceutical, and agricultural products for deriving the personal care products and pesticides etc. They have explained the micro-extraction technique based on the partitioning of the extracting phase. Fused silica gel is used for the partitioning so that coating is provided to the products. All the processes are done for analysis in SPME technique, i.e. sampling, isolation and concentration [**73**].

Advantages

1. The SPME has straightforward construction and operation.
2. The cost of maintenance is small.
3. It has a rapid sampling speed.
4. It does not require solvent consumption.
5. It produces the bright and clean extract.

Disadvantages

1. Drops can get wasted.
2. Selectivity is low.
3. The stationary phase is available in a limited number.
4. Polar matrix has some defects.
5. The requirement for temperature is not highly recommended.

Liquid-liquid extraction (LLE)

Liquid-liquid extraction is the technique used to extract the required component from the liquid by using another immiscible liquid which can be water or any other liquid or solvent. Instead of batch reactors, it can be efficient for continuous batch reactors on a large scale. The main objective is the total recovery of the solute, where solute present should be concentrated.

The LLE is done when the third liquid is added to the mixture of two liquids. The third one is not miscible, but it can separate the components and create new phase. The newly formed phase is the desired one, and it is transferred to extract.

Liquid extraction was carried out in the past decades, like in making of coffee and tea. Humans made different brewing from plants to create an extract by this method. Extraction works with the difference in solubility to separate organic solutions. It is possible to separate the compound needed even when the liquid layers are not miscible. It can also be said as solvent extraction instead of liquid extraction. It is mostly used in substantial scale for product recovery in oil industries, petroleum industries, etc. Liquid-liquid separation is very much suitable for the biological products in the mining industries. As it is used for large scale operations, more safety must be levied to prevent any harm to workers.

Rudakov *et al*. [**74**] used the LLE method for phenol detection. They also applied acetonitrile as the modifying substance. During the experimentation, the dynamics of the formation for the different phases on mixing the composition, along with the water, are observed.

Advantages

1. It can handle temperature sensitive material.
2. Heat sensitive materials can be treated at a moderate temperature.
3. The highly transparent material is obtained.
4. It leads to form azeotrope mixtures.
5. Minimum energy is required for separation.

Disadvantages

1. It is costly as equipment, and operating cost is high.
2. It produces toxic solvents and faces the problem of disposal.
3. It can generate a mist of solvents.
4. There is a chance to static electricity generation.
5. It needs a high flash point solvent.

Stir bar sorption extraction (SBSE)

Stir bar sorptive extraction is the pre-treatment technique to obtain a transparent sample for the process. It is based on the principle of rapid mixing of the mixture with the help of a magnetic rod to get the extractor analyte. Different analytical techniques require some pre-treatment for further processes like GC, LC, which is provided with detectors where the pre-treatment process requires substantial time than the actual analysis.

Baltussen *et al*. [**75**] introduced the concept of SBSE technique in 1999. Nowadays, technology is developed to obtain the samples almost for all the analytical processes to treat organic compounds, pollutants from pharmaceutical products, biological fluids, food products, environmental products, water treatment, wastewater treatment, soil, etc. This is mainly because they are simple and has wide-range spectrum and able to prepare a highly concentrated sample. Sometimes temperature may serve as an essential factor to affect the stir bar extraction process but not always because heat helps to achieve the equilibrium condition in the process, which is required.

The phenols present in water samples in the trace amounts were determined with the help of SBSE method, and it was done by Kawaguchi *et al*. [**76**]. The phenol derivatives and phenolic compounds like 2,4-dichlorophenols, bisphenol and pentachlorophenol etc. were determined during the process.

Advantages

1. It is a beneficial technique to obtain a sample.
2. Extraction can be done from gaseous non-volatile mixtures.
3. It can deal with shallow concentrated solutions.
4. Faster extraction of a sample can be obtained.
5. Stir bars can be reused.

Disadvantages

1. Non-polar and semi-polar compounds are main target of extraction.
2. Reproducibility can be decreased with variations in the preparation.
3. The quantity of sample is affected by adsorption and desorption.
4. It requires control conditions for maintenance.
5. After extraction, desorption is required.

It is found that most of the methods mentioned above are associated with laboratory work requiring the complicated instrumentation and tools as well. Due to such circumstances, uses of these techniques are restricted, and it cannot be accessed in an individual's house for assuring the purity of the water used for consumption.

The EIS is not applied randomly for sensing the chemical, but yet it is capable of providing more accurate data in comparison to other techniques, namely voltammetry etc. For any of the Transducer or sensor, it is necessary that the electrode modifying material is capable enough to ensure the sensitivity. Therefore, the EIS has gathered interest due to various parameters such as simplicity, short analysis time, easy-to-handle, fast response, automation, high sensitivity, convenience, reproducibility, low cost, responsiveness, and possible miniaturisation. It is a demanding method for monitoring phenol in real condition, and it is quite promising for evaluating the public risk of exposure towards such compound. Another benefit of employing this method is that it can be carried out in opaque media enabling it to be more advantages compared to spectrophotometric methods.

Electrochemical techniques

Various types of electrochemical techniques are mentioned below:

Voltammetry

According to the history of science, the voltammetry is derived from electrochemistry, which was originated in 1922 by the invention of polarography. It was invented by Czech chemist Jaroslav Heyrovsky who received Nobel Prize for chemistry in 1959 for his discovery and growth of polarography. It is the calculation of current resulting in the application of potential. The voltammetric measurement employs electrochemical cells of three electrodes, such as working, auxiliary, and reference. The application of three electrodes by the potentiostat instrument permits the use of potential function and estimation of current.

Various voltammetric methods are used and are distinct from one another through potential function employed for electrode during the reaction, which is explained in detail.

Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry includes the application of potential linear sweep for the working of the electrode at the time of randomly monitoring the flow of current in the circuit. The signal generator evolves the voltage sweep corresponding to E_f from E_i which enables the potentiostat to regulate such potential wave for the electrode which has been put for further studies. The direction of scan is not limited, rather it may be positive or negative, and in regulating the principle, the rate of sweep may have any constant value.

$$sweep\ rate = \frac{dE}{dt} \tag{1}$$

The present approach of analysing is mostly used for polarography. But, at well-organised state, the limiting current mainly derived from redox reaction in the LSV are employed for determining the concentration of electroactive species quantitatively.

Square Wave Voltammetry (SWV)

The technique of square wave voltammetry invented by Ramaley and Krause and is developed by Osteryoungs *et al*. [**77**]. It serves to be a versatile technique when compared with other methods. It is the approach where potential waveform made up of square wave formed symmetrically with constant amplitude is covered on the potential of base staircase potential [**78**]. It shows the plot with the difference in measured current in the forward (i_f) and reverses (i_r) cycle against the average potential of the waveform cycle, respectively. Here in this method, due to the current function being symmetrical, the potential leads to the occurrence of peak potential at $E_{½}$ of redox couple [**79**]. SWV has significant advantages of excellent peak separation and highly sensitive nature.

Anodic Stripping Voltammetry (ASV)

It is an electrolytic technique where mercury electrode is placed at the negative potential for reducing the metal ions in the solution, which in turn leads in the formation of amalgam with an electrode. The solution is continuously stirred as it is responsible for carrying most of the analytic metal of electrode to maintain concentration in the amalgam. The analytes, when reduced and accumulated for some duration, tends to increase the potential of electrodes into oxidising it and liberate the current signal. The current so obtained with the help of anodic stripping depending on the particular mercury electrode, which is directly proportional to the concentration of the analyte.

Normal Pulse Polarography (NPP)

It is the type of voltammetric measurement that is the alternative of polarographic size aspiring to decrease the capacitive contribution of current at the back area with the elimination of consecutive potential ramp that varies and also changing into a set of potential steps. It is generally found that in the average pulse polarographic, the particular level starts with the same value where faradaic electrochemistry does not take place. It is also observed that the amplitude of appropriate consecutive steps increases with little increments. For preparing the potential benefit to initial one for the new step, the mercury drop is dislocated from the capillary. A graph called polarogram is plotted for measured current against the potential where the steps take place, resulting in a condition that current does not follow the mercury drop growth. The polarogram of the regular pulse is sigmoid in shape. It is noticed that just after the initial step, the capacitive current tends to decay arithmetically, but the faradaic current decays in the form of the square root of time. Just before the dislocation of the drop, the diffusion current occurs and it is measured that permits for exclusive differentiation for the capacitive current in the back area.

Differential Pulse Polarography/Voltammetry (DPP/DPV)

This method of differential pulse polarography was suggested by Barker and Gardner [**80**]. The DPV was captive enough to generate highly sensitive nature; it shows high energetic resolution and leads to separation of varieties of species. The DPP is different from NPP technique as here the particular pulse has fixed amplitude between 0.01 to 0.1. The current is calculated before the use of pulse at the two adjacent points from particular pulse. The variation of the current measured at a particular point of particular pulse is calculated, and it is then plotted in contrast to the potential of the base. The current extends to the maximum value at the potential near the redox potential. It is then reduced to zero when current times are in diffused control state. Hence, a symmetric peak is formed on the current response.

Fast Scan Cyclic Voltammetry (FSCV)

It is a linear sweep voltammetry method where background subtracted voltammogram is responsible for providing detailed knowledge for the species that are electrolytes. The current effect for different potential are calculated, thus enables it to be a suitable method for detecting an additional current response from different electroactive species. It is a rapid method possessing a particular scan recorded for 100 ms. The quick scan rates tend to reduce the signal towards the noise ratio.

Cyclic Voltammetry (CV)

Cyclic voltammetry is the technique to evaluate the electrochemical nature of a system. It was briefly illustrated by Randles for the first time in 1938 [**81**]. It is the most applied method to attain the qualitative knowledge for electrochemical reaction. The influence of CV is generated from the capability that enables to yield considerable knowledge and understanding for electron-transfer reactions, kinetics, and thermodynamics of redox process, and the coupled chemical reactions etc. It is noted that CV is the first approach put into practice experimentally for electroanalytical study. Such condition is because it deals fast location potential of species, and it can easily estimate the effect of media in the particular redox process [**82**].

The solvent

Various physicochemical features are noted for selecting a solvent needed to perform electrochemical work [**83**]. The solvent should be liquid at the ambient temperature, should have efficient solubility for an anionic substance to generate the conducting electrolyte. It should pose an ability to dissolve the desired electroactive species. It should have a sizeable potential area or field to study the redox process needed for the method where the solvent should not go through oxidation or reduction within the region. It should have capable acid-base features. Lastly, it should have the essential parameter in the form of dielectric constant.

Water is the cheapest solvent with different physicochemical features. It can dissolve the ionic compound and leads to the formation of extremely conducting solutions. Most of the compound desired for electrochemical process gets dissolved in it. It fulfils the features of acid-base, which is noted. The water is reduced or oxidises the oxygen and hydrogen very efficiently. Therefore, it is capable of possessing an area of 2.0 V for further study related to other methods. Water freely leads to the formation of oxide films on the solid electrodes influencing the reproducibility and reactivity. Some of the reactants are least soluble in water as well serving as defects that are overcome by making the use of solvent mixed with alcohol or by alcohol stock solution.

Acetonitrile

Acetonitrile is the solvent exhibiting the inert electrochemical features. The limits at the anode are + 3.0 V and at the cathode is – 3.0 V. The limits are established through the supported electrolytic oxidation and by the water reduction. In the absence of impurities, the chemistry of radical ion is studied pleasingly. Hence, it is found that acetonitrile shows inadequate solubility response towards ionic species. The salts with organic ions, namely the tetra-alkyl ammonium salts, should be used.

Dimethylformamide (DMF)

Dimethylformamide is the aprotic solvents capable of diffusing ionic species. For the anion radical, the cathodic limit of DMF is – 0.3 V. Therefore, it is considered as the best solvent for the study related to

anion radical or the di-anions. The solvent gets decomposed at the positive potential area of + 1.0 V. It is noticed that cation radicals are least stable in this respective medium.

Dimethyl sulphoxide (DMSO)

In the cathode region, the DMF and DMSO show the same electrochemical features. It also has cathodic potential limits better than the DMF. As it is not essential, the cation radicals are found to be a bit stable in the DMSO medium.

Methylene chloride

The methylene chloride is the needed solvent to study about organic oxidation. It is stable till + 3.0 V the same as that of acetonitrile. The di-cations and cation radicals are stable in methylene chloride medium. The large molecules of electrolytes and polymer dissolved quickly in this medium in comparison to the acetonitrile. But yet, solvents get decomposed at the negative potentials of -1.0V. The anionic species are least stable in methylene chloride medium.

The complete non-polar solvents namely benzene or various hydrocarbons are employed for studying solution phase [**84**] and surface processes [**85**]. Some brief explanation for the solvent applied in the electrochemistry is presented [**86**]. Different solvents possessing purity level for voltammetric studies are discussed, and it is available in large extent.

The deionised water continuously distilled off with the alkaline $KMnO_4$. The water is recognised as a pure one whose purity is investigated through the conductivity measurement. But yet, it is estimated that the respective solvent (water) may have a few volatile impurities also [**87**]. Such impurities can be removed by passing distilled water vapour from the column consisting of Pt catalyst at 800 °C where the oxygen is given accordingly. Through this procedure, all the organic impurities are oxidised.

Water is the essential form of impurity in the non-aqueous solvents. It can be removed by refluxing with various compounds such as anhydrous $CuSO_4$, $AlCl_3$, P_2O_5 etc. and then drill them many times to collect the exact fraction. The process of distillation is operated at the eliminated pressure to avoid decomposition of solvents. Few aprotic solvents are capable enough to absorb moisture; therefore, vacuum lines are used at the time of purification, storage and then they are put into use of voltammetric work [**88**]. The most suitable and easy steps include the method of dehydrating agents, anhydrous alumina, in the form of internal additive [**89**]. But for all such procedure, it is foremost to get assurance that such material has no interference in voltammetric behaviour by any means.

Supporting Electrolytes (SE)

Supporting electrolytes are the ionic salts or the ionisable compound present in the solvents. It can enhance the electrochemical processes in different ways. It reports the conductivity to solvents leading to the continuous flow of current within the solution. There are various essential features that SE should possess. It should be in the state of electroactive in the area required for the potential region. It should have a high concentration. It should be in such an order that no space charge is formed around the surface. Therefore, there is no effect of space charge potential on the kinetics of charge transfer. It should not be adsorbed on the surface. Another necessary feature for SE is that it should not form ion pairs with the anion or any complexes or the products during the electrode process.

The compound such as H_2SO_4, $HClO_4$ and HCl are used to carry out the study in acidic media whereas NaOH or KOH is used for research in the alkaline solution. Generally, in the neutral area, where buffering is significant, then acetate, citrate, pyrophosphate and phosphate buffers are applied.

The critical factor required for selecting the supporting electrolyte for an aprotic solvent is the solubility. Various tetra-ethyl ammonium (TEA) are found to exhibits excellent solubility response in the aprotic solution. The most common form of TEA, namely tetra-n-butyl ammonium (TBA) salts, are used for good solubility response since they are regularly present as halides. The fluoroborates and perchlorates can be formed due to the double decomposition of such salts with the sodium salts. The precipitate form of $TAABF_4$ or $TAACIO_4$ is recrystallised for two to three times [**89**]. The hygroscopic electrolytes are dehydrated in an oven, and then it is stored in the desiccators. Appropriate precaution should be taken to handle the explosive salts $NaClO_4$. They should not be heated more, or it should not be grounded in the mortar with any type of force.

Electrodes

The approach of new electrochemistry had led to the demand for enhanced electrodes and its setups. The arrangement of the electrochemical cell showing three different electrodes is recognised nowadays. They are working electrode, reference electrode, and the counter electrode.

Working electrodes

The working electrode should be made of such a material which could provide the high signal to noise ratio. Therefore, the electrode can be selected by mainly two factors, as

(a) Target analytic behaviour
(b) The requirement of the current for the measurement of the potential.

Various types of working electrodes are shown in **Fig. 10**.

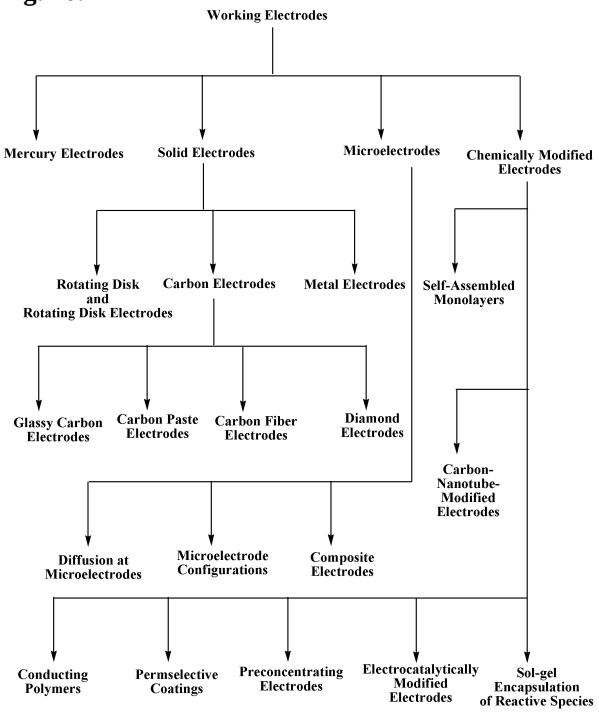

Fig. 10. Various types of working electrodes.

Also, there are other factors on a minor basis, including mechanical properties, conductivity, toxicity, cost, reproducibility of the surface and availability. Mainly, the electrode is composed of carbon, mercury and of metals like gold and platinum. These electrodes can be explained as,

Mercury electrodes

The choice of the material for making electrode should be based on the properties in favour of easy and quick result and mercury electrode possesses a smooth surface with reproducibility. The advantageous feature of mercury electrode is that it maintains high overvoltage for hydrogen, which is helpful to extend potential on the cathode. Mercury is toxic and quickly gets oxidised; this may restrict the use of the mercury electrode.

Again mercury electrode consists of several types which are commonly used, as

(a) Hanging Mercury Drop Electrode (HMDE)
(b) Dropping Mercury Electrode (DME)
(c) Mercury Film Electrode (MFE)

The toxicity of mercury is the point of concern. For this, the development of a solid amalgam electrode was done. Electrocapillary and polarography studies involve the use of dropping mercury electrode (DME). Electrocapillary consists of mercury reservoir in which electrical power is inserted. The movement of mercury is done by gravity through the capillary. The height of the mercury column can be adjusted for continuous drop time. For the proper working of DME, the capillary should be maintained, and it can be applicable in pulse polarography.

In cyclic voltammetry and analysis of stripping, the electrode like HMDE can be used. In the mercury reservoir with the vertical capillary, the drop of mercury can be displaced.

For flow amperometry and stripping analysis, MFE is used. It involves the thin layer of mercury covered by the conducting support. In MFE, the main component is a substrate which consists of metal surface which is coated with a film of adherent oxide so that the there is an interaction of the metal surface with the coating. The support is required for the formation of mercury film on the glassy surface. As the mercury surface requires assistance, it doesn't have the pure composition. Hence it possesses lower overvoltage and current with a higher rate. There is another substrate which can be used in the mercury frame electrode, and that is iridium. The material should possess low solubility and best adherence to the film.

Solid electrodes

The range of anodic potential is limited for the mercury electrode when the oxidizable compounds need to be monitored. Thus, the solid electrodes are provided for the anodic potential with an extendable limit. Most commonly, the material like gold, carbon, and platinum can be used as a working electrode. In some cases, other materials like copper, silver, and nickel can be used. To understand the electrochemistry of the solid electrode, the monograph is essential. Also, the response of the surface of the electrode is dependent on the behaviour of the material. Such electrodes need a pre-treatment for the expected results and these pre-treatment processes dependent on the nature of a material. The processes like chemical, electrochemical, mechanical, thermal and potential cycling required for the electrodes should be of good behaviour. Electrochemical activity is suitable for solid electrodes which are not in case of mercury electrodes. A tube is fitted in the insulating material, and in that tube, the electrode is embedded. On wall jet detector acts as a thin layer detector for the flow analysis. This type of electrode can be used in the form of a disc. Nowadays, the electrodes are a mainly thin film of silicon-based, printed strips or micro-fabricated screen and also ultra-microelectrodes.

Rotating disc electrode/rotating ring disc electrode

This electrode is designed in such a way that the electrode should be vertical in the shaft which is connected to a motor operated with an angular velocity at a constant rate about an axis; this axis should be perpendicular to the surface of a rotating disc. Such a movement of the disc are responsible for forming the layer of fluid and displaces for the centre of the disc. The fluid spreads uniformly on the surface of the disc, and as the angular velocity increases, the diffusion layer thickness reduces.

Carbon electrode

Carbon is low-cost material, suitable for sensing, have great potential, active in surface chemistry and also have less background current. This is the reason why solid electrode can be made by using carbon. In spite of having such properties, it shows the low transfer of electrons as compared to the metal body. This is because the manufacturing of carbon electrode surface and their origin influences the electron transfer. All types of carbon materials are the same in structure, and their relationship of reactivity and structure can be observed by the study of the carbon electrode. In terms of adsorption and reactivity, carbon-carbon surface edges are more than graphite plane. To increase the reactivity of the surface, the pre-treatment should be done. This pre-treatment and type of electrode influence the performance of the electrode. Different types of a carbon electrode in various forms are available like carbon paste, carbon films, glassy carbon, carbon strips with screen printed and also some composites of carbon.

Glassy carbon electrode

Glassy can also be considered as vitric, and it has outstanding properties. It has significant potential and possesses excellent electrical and mechanical properties. The polymeric resin in the pre-modelled state is heated, and the material can be prepared; this overall process should be carried out in the inert atmosphere. For the removal of hydrogen, oxygen and nitrogen, the carbonisation process is carried out at a temperature between 300° and 1200°C. Glassy carbon electrode consists of a structure showing a thin layer sheet of graphite, which is cross-linked by twisted ribbons. Such structures show small pore size and have high density due to which there is no requirement of processes like saturation. For improving the analytical performance, it is necessary to treat the carbon electrode to make it more active. Polishing of small particles of alumina is the way for pre-treatment. Before use, every time the electrode should be cleaned. For cleaning of the electrode, deionised water is required. For the activation of the material, the processes like laser treatment, chemical, electrochemical, and heat treatment are carried out. As the efficiency of the electrode increases, the contaminants present on the surface can also be removed. This happens due to the presence of highly dense oxygen group on the surface of the electrode and the explored edges of the electrode.

The GCE has frequently used electrode for working purpose due to its highly stable nature, and it can detect excellently. There are various factors which can be advantageous for electrochemical analysis, such as minimum background current, large potential window, minimum economic cost, high surface chemistry, suitability for different sensing and detection capability. But it is noticed that the electron transfer rate in GCE is slow in comparison to the other electrode of noble metal [**90**]. In accordance to it, the electrochemical activity on the respective electrodes tends to increase for the analytes as soon as the surface is forwarded for anodic oxidation after which the advanced oxidised functional group are developed [**91**]. There are certain demerits of GCE in term of low sensitivity which restricts its use for working purposes. For enhancing the electrochemical response, lots of efforts are comprehended on GCE where a practical step was imposed in the form of treatment regarding the modification. The GCE coated with specific materials show more sensitive nature towards phenol by which the current was improved, and the detection mechanism was inherited [**92**]. It was observed that the modified electrode exhibited some demerits. Firstly, the manufacturing of modified electrode is challenging, inconvenient, or it is even complicated. Secondly, the dressing substance leads to flaking off, and the electrode is folded easily, lowering the ability of reproducibility during the detection process.

Carbon paste electrode

Carbon paste electrode includes the mixture of graphite powder and some binders which forms the exact binding material. Such a surface is renewable and offers negligible background current [**93**]. There is a vast choice available for making the material called as pasting liquids. The liquids like paraffin, bromonaphthalene, mineral oil (Nujol), and silicon grease can be used. The electron transfer rate is faster with the less thickness of the paste on the surface of the electrode otherwise the reactivity of the electrode is affected by the composition, width and also background current [**94**]. If the pasting material is not proper or it is not present, then the electron transfer will not be at a higher rate. Sometimes there is an infusion of the pasting material with the electrically active species. This pasting material has to mix with the graphite material. The technology used for the two-dimensional electrode is screen-printing technology.

Carbon fibre electrode

In Electroanalysis carbon fibres can be used, but nowadays, ultra-microelectrodes are showing the recent growing interest. The materials are produced during preparation of the composites with the high strength, with pyrolysis or with vapour deposition by catalysis of chemicals. These carbon fibre materials are classified into three types as low, medium, and high.

The material is also most famous for electrochemical studies as it is highly porous [**95**]. Like another pre-treatment process of the electrode, carbon fibre electrode are processed by heat treatment and activated electrochemically [**96**]. The fibres are the main component of electrochemical reaction, and the fibres should be of 5-20 μm. The glass capillary is used to mount the fibres on it. Care should be taken that carbon should not get contaminated with epoxy as the capillary is with epoxy adhesive. It is advantageous to use it because of its small size, which increases its applications in microenvironments. In medical biology, the release of neurotransmitter can be detected.

Diamond fibre

It is also called as an insulator because it can act as semiconductor due to its semi-metallic behaviour. In electrochemical measurement, diamond fibre is of most valuable. The boron doped diamond film electrodes fabrication is done by vapour deposition [**97**].

The properties of the electrode are helpful for a sizeable potential window with stable current. It doesn't adsorb compound, i.e. fouling of the compound is zero or less, the characteristics of the signals possess low sensitivity for oxygen which is in dissolved form, robust and also electrochemically active. The main advantage is that it works well without pre-treatment. New areas are opened due to the diamond electrode even though they have high potential and extreme condition. It possesses all the explained properties, which makes it suitable for application in electrochemistry and chloro-phenols flow detection etc. [**98**].

Metal electrode

For designing the metal electrode, the novel metal of choice is gold and platinum. These are commonly used metals for the metal electrode. The requirement of a suitable electrode is fulfilled by such electrode which can provide full anodic potential, and the transfer of electrons is appropriate. But there is a problem with the hydrogen overvoltage which is low and affects the cathodic potential.

In comparison between gold and platinum, gold is the most efficient metal, and it is inert. Different materials like nickel, copper or silver can be used for electrode formation, e.g. for the detection of materials like carbohydrates and amino acids in alkaline medium, the electrode made from nickel and copper are suitable. And in case of sulphur and cyanide compounds silver electrode is most appropriate. Gold and platinum electrode doesn't show a stable response, whereas the above electrode shows a durable response even though there is the formation of oxy-hydroxide with high valence and these behaves as mediators [**99**]. To replace mercury electrode, bismuth film electrode is a good option [**100**]. There is another option also like alloy electrode. A particular function is that it can perform like bio-functional catalysis. It can have application in full cell [**101**].

Platinum electrode

Platinum is the exclusively employed material to construct the working electrodes in spite of being a precious metal. Platinum can be quickly processed, and it is an electrochemically inert metal. It is considered as the best suitable metal for a working electrode with the positive potential, whereas there is intervention occurring through the reduction of hydronium ion at the negative potential. It is the rare metal for the working electrode for the rigorous anhydrous organic system because of its high potential capability in positive as well as negative direction.

Platinum microelectrode of large diameter is constructed by welding a concrete disk of platinum at the end point of the brass rod. Later, the brass rod and platinum disk are concentric placed to a Teflon shroud surrounding the whole assembly. The surface of platinum is changed to mirror quality by employing the polished paste containing the sub-micron alumina particles. The surface of the electrodes should be polished again and again to discard the contaminants attained at the experimental process.

The platinum disk electrodes and platinum microelectrodes of small diameter are made by covering the platinum wire of short length in the soft glass. It is noticed that the diameter of platinum disk formed and diameter of the wire used during the process are similar. The electrodes are generally polished due to the problematic nature of glass shroud by the paste containing sub-micron diamond particles.

The solid metal electrodes possess specular properties, durability, and extended lasting capability due to which it applies to an electrochemical system to a large extent. The solid metal electrodes have a limitation as it is restricted to the negative potential in the solutions.

Gold electrodes

The gold working electrodes are much similar to the platinum electrodes. Gold is generally cheaper than platinum but is not electrochemically inert in comparison to platinum. The gold electrode surface faced oxidation at a moderately positive potential. Hence, it enables the use in various aspects.

Microelectrodes

Nowadays, to reduce the size of any material, instrument or equipment is an advantageous and modern trend, and it is growing in every field [**102**]. Microelectrode should not be higher than 25 μ, and this dimension is a must. For monitoring of studies like a neurochemical event, nitric oxide detection, surface characterisation, and especially for detection of the single molecule, the nanoscopic electrode tips can be used [**103**].

There are some unique properties of microelectrode which increase the opportunities in biochemistry. These are given below:

(a) Minimal current makes it easy to be used in the solution of high resistivity.
(b) It creates a significant pressure drop.
(c) The capacitance of the microelectrode can be reduced.
(d) The mass transfer rate of electro-active species can be increased. For the different kinetic study, electron transfer rate should be limited [**104**].

Composite electrode

Such composite electrode shows the same advantages as single micro-electrode systems [**105**]. There is an advantage of the availability of large surface which creates higher currents. The problem about single micro-electrode is that the handling of the instrument is quite

tricky because of its minimal size. When the insulating matrix is continuous, an exposure of the surface of the electrode is random or uniform. It can have the application in nanotechnology.

Microelectrode configurations

The electrodes of various substance are reduced in the geometrical shape, and its dimension should be minimal in comparison to the diffusion layer, mainly at the surface of the electrode. The frequently applied used shape is the circular shape conductor which is embedded in the form of an insulating plane. Other geometrical shapes involve microband, microcylinder, microhemisphere, microring etc. The microband and microcylinder electrode are long having a dimension in terms of millimetres providing excess currents and they also maintain enriched diffusional flux.

Diffusion at microelectrodes

The total diffusion-limited current is mainly the diffusion of planar flux and radial flux

$$i_{total} = i_{planar} + i_{radial} \quad (2)$$

The common expression for the radial component in the form of a disk, hemisphere or spherical shapes are given below:

$$i_{radial} = arnFDC \quad (3)$$

where r is represented as electrode radius and a as a function of the electrode geometry. The value of a is 4, 2π, 4π for disk, hemisphere, and spherical geometrical shapes respectively. The radial diffusion obtained by the expression yields higher flux at the perimeter, which clarifies the non-uniform current density.

Chemically modified electrode

Instead of the traditional types of the electrode, a chemically modified electrode serves as the modern type. The surface of the electrode is modified in such a way that the electrode should response the reagent or chemical into which it is dipped. It is more helpful in the problems of electrochemical analysis, thereby increases the applications in the sensing devices and electrochemical field. The applications involve the synthesis of material through electrochemical reactions, for energy conversions and also in the devices such as microelectronic. The applications increase by membrane permeation process, accumulation and by the rate of electron transfer. Such applications and information on the chemically modified electrode are reviewed [**106**]. It also has applications in the medical fields like in the drug delivery for controlling their release, in the devices for electrochromic display, protection from corrosion, in a fuel cell, synthesis and for designing surfaces of the electrode. The surface efficiency can be enhanced by coating the polymer film. The polymers can be applied on the electrode surface by a casting method. In this method, the solvent is mixed in the polymer, and the solution is placed in the form of a droplet on the electrode or electrode dipped in the solution after which the solvent is allowed to evaporate. The whole process happens with a monomer through the electro-polymerisation method. The thickness should be proper on the electrode or sensor so that the response will be appropriate. In such a type of electrode, the modifier like DuPont Nafion perfluorinated sulfonated cation exchanger is employed. The mixture of polymers can be advantageous in the application. The chemical modification, sol-gel encapsulation, composite making, adsorption method and chemo-sorption are the ways of adjustment in the typical electrode making.

Self-assembled monolayer

The layer is formed on the gold surface for maintaining the reactivity of the sulphur and gold. The layer is of ethanolic solution which contains alkane-thiols [$X(CH_2)nSH$, with $n>10$. The monolayer is self-assembled and has various applications from the 1980s [**107**]. Due to the monolayer surface formation, it has applications lithography, bio-sensors, sensors and a device for information storage.

Carbon nano-tubes modified electrodes

Carbon nanotubes show the best electronic, geometric, chemical, and mechanical properties [**108**]. As we know, there are two types of carbon nanotubes as single-walled carbon nano-tubes and multi-walled carbon nanotubes. A single-walled involves a graphite sheet which can be rolled whereas the multi-walled one shows the structure of tree trunk which appears as if they are arranged concentrically. They possess the property which is applicable for electrochemical detection reaction and modification of surfaces. Such electrode enhances the efficiency of analyte and reduces fouling [**109**]. These electrodes are provided with such a property or modified in such a way that it can be with the end caps having defects in edge planes [**110**].

Sol-gel encapsulation of reactive species

Sol-gel encapsulation is one of the ways to modify the electrode. Sol-gel films serve for the encapsulation of species with low temperature [**111**]. These films can be prepared with the help of polycondensation of a monomer of hydroxyl. It requires the precursor of alkoxide like $Si(OCH_3)_4$. This process forms the porous glass-like network, i.e. permeable to the analyte. Sol-gel encapsulation has different properties like mechanically rigid, physical characteristics, and thermally stable instead of the only entrapping modifier. The material like gold powder or carbon powder can be used to disperse in the sol-gel mixture [**112**]. The selective binding can be prepared by using molecular imprinting [**113**].

Electrocatalytically modified electrodes

It has been observed that the desired redox reaction at the naked electrode includes the slow transfer of electron kinetics. Hence, it takes place at a suitable rate of potentials more than the thermodynamic redox potential. The reaction is catalysed through the attachment at the

surface by appropriate electron transfer mediator [**114**]. The primary function of the mediator is for assisting the charge transfer mechanism between the analyte and the electrode. The mediated reaction of the process can be explained by the following equation:

$$M_{ox} + ne^{-} \rightarrow M_{red} \quad (4)$$

$$M_{red} + A_{ox} \rightarrow M_{ox} + A_{red} \quad (5)$$

where *M* is the mediator, and *A* is the analyte.

Preconcentrating electrodes

The Preconcentrating CMEs, along with the surfaces framed to react and binds the target analytes to possess many opportunities in the field of chemical sensing [**115**]. Such an idea corresponds to the stripping voltammetric schemes in which target analyte is separated from dilute material in the surface layer of the preconcentrating electrode, and it gets reduced or oxidised at the time of scanning.

Permselective coatings

The permselective coatings enhance the selectivity as well as the stability of the electrochemical devices. It can be achieved by the exclusion of the additional matrix component from the surface of the electrode. On the other hand, it permits the migration of target analyte.

Conducting polymers

The conducting polymers are the topic of interest due to its outstanding features, which include the ability to modify reversibly in between positive charged conductive state and the neutral one. In insulting form, it possesses a capacity for integrating and ejecting the anionic species at the time of reduction and oxidation [**116**]. The redox alteration is delocalised at various groups of conducting polymer [**117**]. A molecular orbital is developed by the conjugation of π-electron system that gets elongated near the chain of the polymer [**118**].

Reference electrodes

The working electrode potentials within voltammetry set up is mainly brought under control by a standard unit known as the reference electrode. It has been found in various literature that thermodynamic scale for half-reaction potential is measured in contrast to the "standard hydrogen" in the form of the reference electrode (SHE). But in general practice, standard hydrogen is highly active for the various application.

Standard hydrogen electrodes

It is an electrode with standard potential, which is used as a reference electrode for comparing or determining the potential of other electrodes. The most commonly used reference electrode is standard hydrogen electrode (SCE) whose potential is considered as zero at all temperature. It consists of two co-axial glass tubes. The inner tube contains an inert solid material like platinum, which is surrounded by a solution containing H^+ ion of unit activity at 1 atm pressure. Adsorption of hydrogen ions takes place an inert solid. The half-cell reaction for the standard hydrogen electrode is represented by:

$$2H^{-}(aq.) + 2e^{-} \rightarrow H_2(g)$$

The value of half-cell potential for SHE is taken as 0.00 V, But the conditions required for SCE is challenging to maintain. Hence the electrode potential deviates from 0.00 V and can be given by the following Nernst equation:

$$E_{Pt|H_2,H^+} = E^0_{Pt|H_2,H^+} + (RT/F)\ln\left(\alpha_H / \sqrt{P_{H_2}}\right)$$

$$P_{H_2} = P_{baroetric} - P_{H_2O} + \left(4.2\times10^{-5}\right)h$$

where h is the height of the delivery point for hydrogen supply to the solution (in mm), $P_{baroetric}$ is the barometric or atmospheric pressure (in atm), P_{H_2O} is the partial pressure of water vapour (in atm).

Application of SHE is limited as it needs pure hydrogen, and it is challenging to prepare and maintain it. It is also affected by the presence of AsH_3, CO, HCN, H_2S, SO_2 etc. in the electrolyte solution as they may cause the poisoning of the platinum electrode. Also, solution must be free of metals as the reduction of metals can occur at the electrode, which may affect its electrode potential. Due to these limitations, it cannot be used practically. Instead, another electrode having a known electrode potential can be used as a reference electrode. The most commonly used electrode is calomel and mercury/mercury chloride.

Standard calomel electrodes

It is also called as Mercury/mercury chloride electrode. It is a type of reversible electrode which was first introduced in 1890 by Ostwald. It is the most commonly used reference electrode. It consists of either a glass tube containing mercury covered with mercury chloride or a glass tube filled with a paste of Hg, Hg_2Cl_2 and KCl solution surrounded with a saturated KCl solution having constant activity. The saturated KCl solution used contains some potassium chloride crystals. To provide contact with an external circuit, the platinum wire is used. The purity of mercury and the technique of addition of Hg_2Cl_2 to mercury affects the performance as well as the potential of the electrode. The half-cell reaction for calomel electrode is given by:

$$Hg_2Cl_2(s) + 2e^{-} \leftrightarrow 2Hg(l) + 2Cl^{-}(sat.)$$

The standard electrode potential for calomel electrode is +0.268 V at 25˚C. But, the potential of the electrode is affected by the chloride concentration in the filling solution. So, it can be determined by the following equation:

$$E_{Hg|Hg_2Cl_2} = E^0_{Hg|Hg_2Cl_2} - (RT/F)\ln\alpha_{Cl^-}$$

SCE can be reproduced. It has a disadvantage that it can only be used at a temperature below 50˚C as Hg_2Cl_2 becomes unstable at a temperature above 50˚C. Also, the mercury used in this electrode has a health hazard. It has application in cyclic voltammetry and pH measurement.

Mercury/mercury (I) sulphate electrodes

It is the second most commonly used reference electrode after SCE. The construction of $Hg|Hg_2SO_4$ electrode is the same as that of SCE. The electrolyte solution used in this electrode either contains potassium sulphate of definite concentration of H_2SO_4. It is least sensitive to chlorine, unlike $Hg|Hg_2Cl_2$ electrode. The reaction taking place at the electrode is given by:

$$Hg_2SO_4 + 2e^- \leftrightarrow 2Hg + SO_4^{2-}$$

The electrode potential of Mercury/mercury (I) sulphate electrode is given by the Nernst Equation given below:

$$E_{Hg|Hg_2Cl_2} = E^0_{Hg|Hg_2Cl_2} - (RT/F)\ln\alpha_{SO_4^{2-}}$$

where, $E^o{}_{Hg|Hg2SO4}$ = 0.615 V vs NHE at 25˚C. This electrode is useful for the reference electrode in solutions which contains H_2SO_4.

Silver/silver chloride electrodes

It is used as a reference electrode. It is a widely used electrode due to its simple construction. Its construction is almost similar to the calomel electrode. It is composed of a silver wire coated with solid AgCl. Coating of silver wire is done either thermally or electrochemically. But, the films produced by the electrochemical method are thinner than the films produced by the thermal process. The wire is immersed in an electrolyte solution, which is saturated with KCl and AgCl. Sometimes, in place of KCl, NaCl or lithium chloride is also used in an electrolyte solution. The half-cell reaction is given by:

$$AgCl(s) + e^- \leftrightarrow Ag^+ + Cl^-$$

The electrode potential of Ag|AgCl electrode is given by the Nernst equation (1) which shows the dependency of electrode potential on chloride activity, which is contributed by both KCl and AgCl.

$$E_{Ag|AgCl} = E^0_{Ag|AgCl} - (RT/F)\ln\alpha_{Cl^-}$$

The value of E° is +0.222 V, while the actual electrode potential of Ag|AgCl electrode is +0.197V. It has an advantage over calomel electrode as it is easy to construct, inexpensive, non-toxic and stable, and it can be used at high temperature as well as varying pressure conditions. It is most commonly used in the seawater environment as a reference electrode for testing cathodic protection corrosion control system.

Mercury/mercuric (II) oxide electrode

It is used in the solution having high alkalinity. Many reference electrodes such as calomel, Ag|AgCl and $Ag|Ag_2SO_4$ are not compatible in alkaline solution as there is a possibility of diffusion of hydroxyl ions into the filling solution of the electrode which deviates its electrode potential. But Hg|HgO electrode is stable in alkaline solution as the oxide is highly stable in an alkaline environment. Its potential is not affected by electrolyte but depends on the activity of hydroxyl ions as well as water. The construction of calomel and Hg|HgO electrodes are the same. The half-cell reaction is given by:

$$HgO(s) + 2e^- + H_2O \leftrightarrow Hg(l) + 2OH^-$$

The electrode potential of this electrode is given by:

$$E_{Hg|HgO} = E^0_{Hg|HgO} - (RT/F)\ln\left(\alpha_{OH^-}/\sqrt{\alpha_{H_2O}}\right)$$

where, $E^0_{Hg|HgO}$ = 0.615 V vs. NHE at 25˚C. HgO has slight solubility in water and solubility constant 'K_s' is given by:

$$K_s = \alpha_{Hg^{2+}} + X\left(\alpha_{OH^-}\right)^2$$

This electrode can be used for several days and can be reproduced at ± 0.1 mV.

Copper/copper sulphate electrode

It is a type of reversible electrode which is used as a reference electrode. It is composed of a copper rod surrounded with saturated copper sulphate solution in a plastic tube. It involves a redox reaction in which copper metal and copper sulphate salt participate. The reaction is as follows:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

The electrode potential of $Cu|CuSO_4$ electrode depends on the activity of copper ions, which is represented Nernst equation as given below:

$$E_{Cu|CuSO_4} = E^0_{Cu|CuSO_4} + (RT/2F)\ln\alpha_{Cu^{2+}}$$

where, $E^0_{Cu|CuSO_4}$ = 0.337 V

It has rapid electrode kinetics and has the most common application in cathodic protection corrosion control system. It is also used as a half cell in Daniel-Jakobi galvanic cell.

Palladium hydrogen electrode

It is used as a reference electrode for high-temperature conditions. The characteristics of $Pd|H_2$ and hydrogen electrode are much similar. The difference between the SCE and the palladium-hydrogen electrode is the bubbling of hydrogen in the solution, which is absent in the palladium-hydrogen electrode. The significant feature of $Pd|H_2$ electrode is to absorb H_2. On absorption of molecular hydrogen, two-phase are formed in palladium: Alpha and Beta phase. Alpha phase forms when hydrogen concentration is less than 0.025 atoms per atom of Pd, while beta phase formation takes place when concentration of H_2 corresponds to the non-stoichiometric formula $PdH_{0.6}$.

The reaction taking place on hydrogen electrode is given by

$$H^+ + e^- \leftrightarrow 1/2\ H_2$$

The Nernst equation for the electrode potential is given by

$$E = E^0 + (RT/F)\ln\left(\alpha_{H^+}/\sqrt{P^{H_2}/P^0}\right)$$

Counter electrodes

In the classical electrode cells with the working and reference electrode, the current is pushed to flow generally by the reference electrode in term of measurement. As the adequate amount of current is allowed to flow via the reference electrode. The internal chemical composition tends to change, enabling the potential to shift from the expected standard value. Therefore, it is most essential to develop electrochemical measurement in the absence of current flow with the help of the reference electrode.

The counter electrode is made from any of the material by making the use of the specific geometrical electrode. Hence, the selection of pattern or the design depends on the material that is chemically inert for the respective test solution where the counter electrodes possess large surface area. It is found that coil of platinum wire is of great interest, whereas the copper, aluminium or stainless steel are capable of showing good response in the non-corrosive solutions in which metal cation interference are not favourable. It is noticed that for the electrochemical cell made of metal, the cell itself is used in the form of an auxiliary electrode.

Since the flow of current is at the auxiliary electrode, there itself the electrochemical processes will take place. It has been observed that if the working electrode is responsible for reducing any product, the products get oxidised by the auxiliary electrode. Hence, the product liberated by the electrode may lead to interference during the measurement. So, avoid such circumstances, the auxiliary electrode is kept the separate block with an electrolytic solution in ionic contact to the test solution by making the use of glass frit. In many of the experimental cases, the counter electrode is generally placed in the test solution in contact with the reference electrode as well as the working electrode.

Electrode fouling

Electrode fouling is the main issue for electrochemical phenol detection, which is the outcomes of polymerisation of phenol molecule [**119**]. There is a way to solve this problem that is by modifying the surface of the electrode with the proper manner or applying a nanoparticle which comes from composite material with the action of electrocatalytic [**120**]. But yet, fouling creates the problem for the electrode as it reduces the ability of sensitivity, reusability and diminishes the reproducibility. On applying a modified electrode for the detection of phenolic based compounds, the electrode should be polished, and further remodified for each new step. The steps include commonly two methods such as drop-dry and dip-coating, to enhance the analysis technique [**121**]. But yet, it is still a challenging issue to resolve the problems of fouling mechanism concerning scientific interpretation as well progression of a suitable technique to overcomes its drastic effects. The chemical reaction occurring at the anodic oxidation of the phenolic compound is shown in **Fig. 11** [**122**].

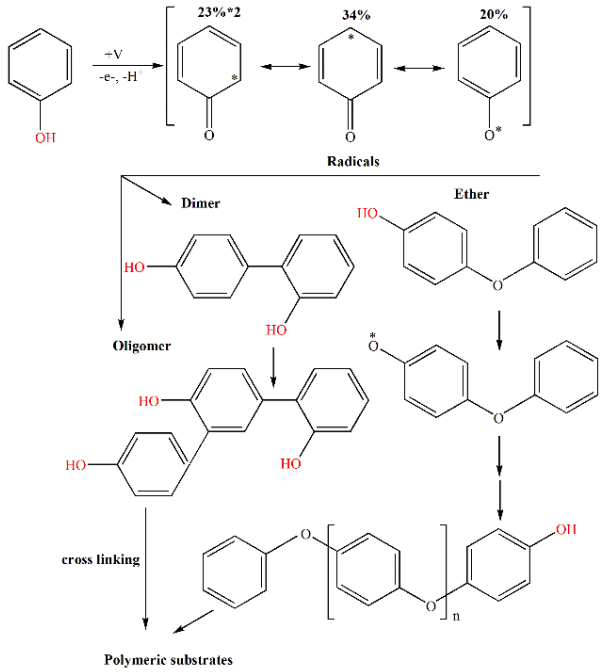

Fig. 11. Chemical reactions step during the phenol oxidation.

Phenol oxidation mechanism

Phenol detection could be possible by the oxidation process carried out on solid electrodes. **Fig. 12** shows the pathway of the reaction for the phenol detection indicated for further estimation. The process reaction between quinone and ether quinone are inert were the primary products are organics acids in the form of oxalic, maleic acid [**123**].

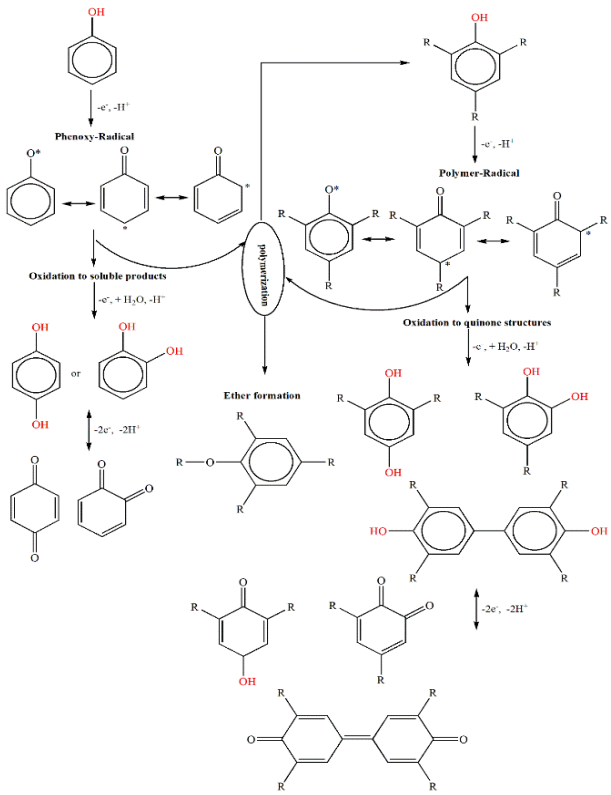

Fig. 12. Phenol oxidation and polymerisation pathways.

The phenol oxidation is performed on the surface of electrodes, leading the passivation of surface since there is a formation of the polymer. Therefore, to get rid of the disadvantages, the technique of polymerisation needs to be enforced. For phenol oxidation mechanism, various processes, namely adsorption or precipitation of unwanted species collateral relation due to modification of surface electrodes can be controlled [**124**]. The species recollects their particular features which are employed for modification of surface electrode and it endorses the enhanced of different methods like bioassays, preconcentration determination of distinct compounds [**125**].

Review in phenol

Sakthinathan *et al.* [**126**] developed a material for the sensor by molecular sieves. This material has excellent oxidation behaviour to detect the phenol molecule when compared to the bare SPCE. The electrochemical activation plays a significant role in the SPCE surface morphology. This sensor shows a sharp peak at 485 nm because of its fluorescence quenching, and a sharp peak of anodic nature is also observed at 0.866 V due to the oxidation. It indicates that only one electron and one proton takes part during the phenol oxidation.

Soriaga and his co-workers [**127-129**] suggested the oxidation of various type of aromatic compounds on the surface of the Pt electrode. Several aromatic compounds are adsorbed irreversibly directly at the surface of the electrode. Outer Helmholtz layer (OHL) reaction takes place by adsorbed layer with no reduction in kinetic parameters such as no apparent loss of reversibility. A hydroquinone redox reaction is an example of an OHL reaction where the compound has to be a significant part of the layer possessing the formation of carbon dioxide. In the inner Helmholtz layer (IHL) reaction, the degree of oxidation was entirely dependent on the adsorption site.

Gattrell and Kirk [**130**] reported the phenol oxidation on the surface of the platinum electrode. During the phenol oxidation reaction, the changes in the electrode and its surface oxide, as well as electrode passivation through the product reaction, was carried out by several electrochemical techniques like chronoamperometry and cyclic voltammetry. Phenol molecule reacted on both the layer of Pt electron, which is of two types such as inner and outer Helmholtz layer. When the phenol molecule reacts with IHL it was irreversible, and it shows conductive behaviour, but when it reacts with OHL, it provided simple oxidation with a minimum participation of quinone to form an organic structure such as ether. By XPS technique, the outcomes of the film at Pt and PtO is chemically the same but varies in thickness showing the passivation of the electrode is not just due to the thickness.

Sun *et al.* [**131**] developed the various anode electrode for phenol sensor. The curves of different electrode's material such as SnO_2-Sb, SnO_2-Sb-Ni and SnO_2-Sb-Ni-Nd show the electrochemical technique CV with or without the concentration of phenol pollutant. The amount of the current of three electrodes was significantly enhanced with phenol concentration while without phenol concentration, the value of current was little. In the case of LSV technique, the order of the anode electrode is SnO_2-Sb > SnO_2-Sb-Ni > SnO_2-Sb-Ni-Nd. The side reaction involved for oxygen evaluation shows that the doping of Ni-Nd has better performance regarding catalytic behaviour in phenol oxidation.

Patra and Munichandraiah [**132**] suggested the phenol oxidation of a polymer which is conducting in nature. Non-platinum metal thoroughly coats this polymer. During the phenol oxidation by PEDOT/SS electrode, two intermediate compounds occur, forming poloxyphenylene and benzoquinone in the solution. It is revealed that the surface of PEDOT does not show any effects either by the adsorption of the intermediate compound polyoxyphenylene or by oxidation of phenol. The particular mass of PEDOT plays a crucial role in the phenol oxidation. It further clarifies that increase in the specific weight of PEDOT tends to decrease the fouling.

Teofilo *et al.* [**133**] organised the model as QSPR to show the co-relating effect of molecular descriptors on the fouling by the action of phenol derived compound on the Pt and BDD against the PLS regression. The phenol oxidation into phenoxyl radicals tends to show higher reactivity of newly developed species. PLS model was responsible for enumerating the phenol electro passivation at Pt electrodes, which were further applied in different laboratory work. Since the PLS model is not so useful in presenting the statistic value, but yet it provides relevant information about the methods to apply in various purposes. The theoretical knowledge gives ideas about the particular molecular characteristic of phenol compound studies for fouling on Pt and BDD.

Montilla *et al.* [**134**] prescribed about the action of Pt in the process of electrocatalysis of Sb-doped TiO_2 electrodes for phenol oxidation. They made it clear that when Pt was instilled in the oxide layer, it tends to raise the service life of electrode to two orders of magnitude. The quantity of Pt present in the electrode was responsible for evaluating the electrocatalytic activity of electrodes corresponding to the oxidation of phenol. The voltammetric study reveals that phenol oxidation ability reduces concerning the quantity of Pt present in the oxide layer. It was found that the execution of phenol oxidation at 1.8 V was the same as that of studies made during the potential step.

Canizares *et al.* [**135**] performed the comparative study for electrodes to relate the behaviour of the activity where AISI 304 SS and BDD were found as oxidation of phenolic waste. The volumetric study made it clear that both the electrodes indicated remarkable changes in term of electrochemical behaviour. The AISI 304 SS electrodes surface possessed some changes when it was applied in the form of anode treatment of the waste in the area of electrolyte stabilisation as well which inculcated the facts that it could be useful in the treatment of waste.

Hagans *et al.* [**136**] illustrated the BDD electrode made with the help of the CVD process for the application in the phenol oxidation into carbon dioxide. The study was carried through CV where instead of multiple cycling activity, the electrode remained as electroactive. There is an interesting the fact that no fouling of the electrode was noticed which reveals that various mechanism process could be applied for phenol oxidation.

Ajeel *et al.* [**137**] suggested a new method to examine the passivation and adsorption of the phenolic-based compound on electron degradation by applying impedance method. 20 CBD electrode indicates that the anodic peak was observed at 1.25 V for the phenol molecule. It further reflects that increase in sweep rate leads to the rise in phenol oxidation peak and current peak, making it clear that the process of oxidation inferred here is irreversible. Therefore, the capacitive loop enhanced with potential till it reaches the maximum point of 1300 mV and further this value reduced with an increase in the potential.

Ajeel *et al.* [**138**] performed the activity at the various percentage of CB on the diamond electrode for phenol oxidation with the help of the electrochemical technique of CV. All three electrodes were undertaken to study at 1.25 V, which showed an anodic peak. At this CV, no cathodic peak was seen, which suggested that the irreversible process occurs during the phenol oxidation for all the three electrodes. There is an interesting note that the oxidation peak was not clear for 40 CBD electrode. It gives clear evidence that it is generally because of the low oxygen evolution present in the solution. Hence, it is obligatory to mention that after 10 h, the pH increases from 6 to 9 during the oxidation process.

Azevedo *et al.* [**139**] confirmed an exciting aspect that is no phenol oxidation occurring at BDND electrode by applying the technique of SWV. The electrode S1 and S2, the ΔEp were observed as 1100 and 800 mV. They found that electrode S1 shows the availability of sp^2 carbon oxidation, which is subjected to choking in the kinetic responses. Various aspects are to keep in mind for electrode S1 that bulk amount of boron atom needs to be available at the sites where it should not lead to a continuance of the electronic phase. The S1 electrode has no confined current profile for activation of phenol concentration, which is contrary to the voltammogram formed for S2 electrode. When the comparative study of S1 and S2 electrode was done, it was observed that S1 has least current density where the maximum potential starts for the oxidation of phenol was 1.20 V, whereas S2 electrode has an efficiency of 1.12 V. The results of oxidation displayed the least detection limit of 0.1 mg L^{-1} for the S2 electrode.

Beitollahi *et al.* [**140**] investigated a new and remarkable electrode as BE/IL/GPE for detecting phenol, where it was mainly applied to resolve the real samples in the laboratory. The voltammetric study exhibited a clear availability of anodic peak at 830 V potential, and the phenol sensitivity of the electrode was 0.077 μA/μM for phenol.

Duan *et al.* [**141**] suggested the process of phenol oxidation on PbO_2 electrode. They noticed that on adding phenol to the electrolyte anodic peak were formed at 0.98 V by the phenol oxidation. The above facts reveal that phenol gets oxidised directly to PbO_2. The CV study undergoing different scan rates, adsorption was the leading cause of controlling the phenol oxidation. On the PbO_2 electrode, the discontinuation in the concentration phenol showed integrated activity towards the current, which referred that it followed the pseudo-first-order reaction.

Hammani *et al.* [**142**] prepared a cost-effective sensor by Al_2O_3 embedded on carbon to detect the phenol. They investigated and later suggested that phenol contain an oxidation peak ranging between 0 to 1 V which clarified that the process is entirely irreversible. It also exhibited that the potential of the peak tends to decrease due to the availability of Al_2O_3. The outcomes state that phenol oxidation peak potential tends to a negative value as the pH increase making it clear that electrochemical phenol reaction includes the proton as an essential constituent. The enhanced mechanism is controlled with the help of adsorption so that it increases the quality of phenol on the surface of Al_2O_3/AC-CPE, which also increase. The value of The diffusion coefficient was noted as 1.58×10^{-6} cm^2s^{-1}.

Jovic-Jovicic *et al.* [**143**] carried out the activity to determine the behaviour of chitosan modified clay to detect phenol pollutant. The CV study exhibited that there is a formation of one peak at 0.92 V, which is assigned for the oxidation of the hydroxyl group. The potential range showed a tremendous effect on the shape or pattern of CV measured during the acidic medium. Hence, it was carried out in alkaline solution owing to the features such as low passivation rate and high electrode stability.

Liu *et al.* [**144**] developed a three-dimension graphene material that has a tendency of micropillar structure for detecting the phenol pollutant. The GO shows a two-dimension structure that further has to be multi-stacked on the surface of PDMS micropillars as a three dimension. This is later reduced as a three-dimension structure in the conduction form. The enzymes embedded on three-dimension graphene were improved in comparison to two-dimension graphene, which trends enhances the sensitiveness for the detection process.

Massa *et al.* [**145**] investigated the electrodeposition of MnO_x on Ti and TiO_2-NTs for detecting the phenol oxidation. Different oxidation states of MnO_x and Mn were formed. α-MnO_2 was the active phase, and it was also the stationary phase as well. The TiO_2-NTs regulates for increasing surface area as well as stability, whereas it minimises the potential of the working process. The interaction of substrate plays a significant part for the capacitance of MnO_2 films, which refers to various morphological aspect rendering the features of the electrode.

Mayorga-Martinez *et al.* [**146**] suggested the improvement of biosensor dependent on BiNP/Tyr electrode. The development was attained by BiNP/Tyr alliance on the electrode working for SPE by applying glutaraldehyde in the form of cross-linking agent. The biosensor reflected high sensitivity for detection of phenol enriching the lowest detection limit as 62 nM, but the linear response was noticed till 71 mM.

Oriero *et al.* [**147**] formulated the sensor as a silica-PVA-tyrosinase sensor to detect the pollutant of phenol. Mats with 10 μm thin structure showed various properties such as minimal electrode contamination by the use of surface adsorption. The study carried out through CV and chronoamperometry exhibited good behaviour towards sensitivity and response time. The performance was not enhanced by maximising the surface area of the electrode, which was due to an unknown pathway for charge transfer or species from a network of fibre towards the conducting electrode layer.

Quynh *et al.* [**148**] reported about the detection of phenol by non-enzymatic action on the NPG film. The two linear range detection was seen at a concentration ranging between 0.5-200 μM. The limit of detection was confirmed to 0.5 μM. It was observed that Bare Au electrodes showed a weak response. The response of current ready to steady condition at 100 s just after the addition of 20 μ, but it ultimately showed an unstable response after addition of 30 μM of phenol which made it clear that there was an occurrence of electrode deactivation in bulk amount.

Scavetta *et al.* [**149**] suggested about the comparative study of Ni/Al LDH film, which is generally thin to detect phenol. The activity of the device and coated adhesive was determined as they were considered to play a significant part to perform for a long duration. The detection of phenol was done with the help of amperometric technique. Since the detection of phenol was a complicated process due to different circumstances, the sensitiveness tends to showdown approximately 20% of the initial data just after a day of experimentation. But yet the response of reproducibility was excellent, and the electrode coated with LDH was considered as a disposable tool to analyse phenol.

Singh *et al.* [**150**] synthesised an E-rGO material to detect phenol. The material was tested, and it was found that it has a positive response for both the condition that is the standard solution and real samples. It was also observed that the E-rGO was pH dependent. When the pH was between 3 to 7, there was a reduction in the polarisation resistance. Whereas when the pH was between 7 to 11, then was an enhancement in the polarisation resistance. The value of impedance was dependent on the concentration of phenol between 1.0 μM to 40 μM. It was noticed from the Nyquist plot shows that the E-rGO did not affect the different sources of water.

Spataru and Spataru [**151**] suggested the study of Pt-Pty composite to detect phenol through the voltammetric method. It is mainly believed that the usage of highly expensive electrocatalyst cannot be the most influential drawback for the analytical application as such it can be reimbursed either by least Pt loading or by the large surface area of the matrix. The experimental results revealed that for the acidic medium, the observed oxidation peak current is employed for a fast and individual approach to determining phenol in the concentration ranging between 0.3 to 10 mM. The main benefits of using Pt-Pty composite for phenol detection is the existence of excellent resistance for fouling. Such features are essential as they provide a better platform for carrying out other experimental studies to develop novel composite material containing enhanced behaviour towards anodic oxidation of phenol.

Cevik *et al.* [**152**] reported about the study of Fe_3O_4-Si-(GMA-co-Vfc)-HRP to detect phenol. Various studies were carried out, such as reusability, storage stability, temperature, effects of pH. For phenol of estimation between 3.0-7.0 mM, the electrode response was attained, showing high sensitivity behaviour approximately more than 99.2% for compounds of phenol. From the electrocatalytic response, it was clear that it was linearly dependent on compound of phenol ranging between 0.5 to 17.0 mM.

Table 1 summarises the modified electrode along with its methods, linear range and detection limit for phenol in literature. It has been assumed that since electrochemical methods are employed for detecting phenol, the electrodes get modified because it ensures the low detection limits. But yet reports suggest that limits of detection in experimental form is calculated through concentration data in spite of the general limits of detection.

DPV	:	Differential pulse voltammetry
SWV	:	Square wave voltammetry
LSV	:	Linear sweep voltammogram
Tyr	:	Tyrosinase
HRP	:	Horseradish peroxidase
SiPGMA	:	Silane polyglycidyl methacrylate
Ppy	:	Poly(pyrrole)
CNT	:	Carbon nanotube
PVF	:	Polyvinyferrocene
MWCNT	:	Multi-walled carbon nanotubes
SPE	:	Screen-printed nanoparticles
BiNPs	:	Bismuth nanoparticles
AuNPs	:	Gold nanoparticles
DTDAB	:	Dimethylditetradecylammonium bromide
NCPE	:	Nafion-incorporated carbon paste electrode
PVA-SbQ	:	Poly(vinyl alcohol) bearing styrylpyridinium groups
MWCNT	:	Multi-walled carbon nanotube
GNP	:	Graphene nanosheet paste
SPE	:	Screen printed electrode
MCN	:	Mesoporous carbon nitride
SBM	:	Solid binding matrix
HPDB	:	N-(4-hydroxyphenyl)-3,5-dinitrobenzamide
CPE	:	Carbon paste electrode
BDD	:	Boron-doped diamond
PDPA	:	Poly diphenylamine
BSA	:	Bovine serum albumin
GA	:	Glutaraldehyde

Table 1. Modified electrode with methods, linear range and detection limit.

Modified electrode	Method	Linear range	Detection limit	Reference
Al_2O_3/AC-CPE	DPV	1.0×10^{-3} -1.0×10^{-4} (mol/L)	1.51×10^{-7}(mol/L)	[**142**]
Tyr/PO_4-Ppy/Pt	Amperometry	--	1.71×10^{-7}(mol/L)	[**153**]
S1 (with statics substrate-holder	SWV	(30-130) × 10^{-6}(mol/L)	1.0 mg/L	[**139**]
S2 (with spinning substrate-holder	SWV	(30-130)× 10^{-6}(mol/L)	0.1 mg/L	[**139**]
Graphene micropillar	Amperometry	(0- 2000) × 10^{-9}	50 × 10^{-9} (mol/L)	[**144**]
BiNp/Tyr	Amperometric	(3-71) × 10^{-6}(mol/L)	62 × 10^{-9} (mol/L)	[**146**]
ITO-silica-PVA-tyrosinase	Chronoamperometric	(10-150) × 10^{-6}(mol/L)	0.0042× 10^{-9} (mol/L)	[**147**]
Nanoporous gold	Amperometric	(20-200) × 10^{-6}(mol/L)	0.5 × 10^{-6} (mol/L)	[**148**]
Ni/Al LDH on Pt	Amperometric	(0.005-0.65) × 10^{-3}(mol/L)	0.005 × 10^{-3}(mol/L)	[**149**]
E-rGO	Impedance spectroscopy	(1-40) × 10^{-6}(mol/L)	0.2× 10^{-6}(mol/L)	[**150**]
platinum –polytyramine composite	CV	(0.3-10) × 10^{-3}(mol/L)	---	[**151**]
Ti/BDD	LSV	(0-20) × 10^{-3}(mol/L)	---	[**154**]
Si(GMA-co-Vfc)x-HRP	Amperometric	(0.5-17) × 10^{-3}(mol/L)	25× 10^{-6}(mol/L)	[**152**]
Fe_3O_4-SiPGMA-HRP	CV	(0.5-15) × 10^{-3}(mol/L)	0.5× 10^{-3}(mol/L)	[**155**]
Ppy/CNT-HRP	Amperometric	(1.6-8.0)× 10^{-3}(mol/L)	0.93× 10^{-3}(mol/L)	[**156**]
Ppy/PVF-HRP	Amperometric	(0.5-8.0)× 10^{-3}(mol/L)	0.22× 10^{-3}(mol/L)	[**157**]
Au-CPE-Tyr	Amperometric	(4×10^{-3}-48×10^{-3}) × 10^{-3}(mol/L)	---	[**158**]
$MgFe_2O_4$-SiO_2-Tyr	CV	(1×10^{-6}- 2.5×10^{-4}) (mol/L)	6.0×10^{-7}(mol/L)	[**159**]
Tyr-MWCNT/SPE	Amperometry	(2.5-75)× 10^{-6}(mol/L)	1.35× 10^{-6}(mol/L)	[**160**]
Tyr-AuNPs/SPE	Square wave voltammetry	47 ppb-15 ppm	47 ppm	[**161**]
MWCNT-DTDAB-Tyr/NCPE	Cyclic voltammetry	(1.5-2.0)× 10^{-6}(mol/L)	1.1× 10^{-6}(mol/L)	[**162**]
PVA-SbQ-Tyr/SPCE	Amperometry	< 30)× 10^{-6}(mol/L)	---	[**167**]
PVA-SbQ-Tyr-HRP/SPCE	Amperometry	(0.025-60)× 10^{-6}(mol/L)	---	[**167**]
Tyr-ZnO nanorods/Au	Amperometry	(0.6-20) × 10^{-6}(mol/L) (20-50) × 10^{-6}(mol/L)	0.6× 10^{-6}(mol/L)	[**164**]
Poly(zincon) electrode	Voltammetry	(21-292) × 10^{-6}(mol/L) (357-922) × 10^{-6}(mol/L)	9× 10^{-6}(mol/L)	[**165**]
Unmodified BDD	Cyclic voltammetry	(5×10^{-5}- 2×10^{-3}) (mol/L)	8.21 × 10^{-6}(mol/L)	[**166**]
GC free tyrosinase sensor	Chrono coulometry	(0- 0.629) × 10^{-6}(mol/L)	13.7× 10^{-9}(mol/L)	[**167**]
Unmodified carbon felt	Cyclic voltammetry	(0.006-0.1) × 10^{-3}(mol/L)	0.006× 10^{-3}(mol/L)	[**168**]
Unmodified GCE, transduction by free $K_4[Fe(CN)_6]$	Preconcentration step and flow injection analysis	0.01× 10^{-3}(mol/L)	(0.01-0.53)× 10^{-3}(mol/L)	[**169**]
Nafion-Modified GCE	Stripping voltammetry	(8×10^{-9}- 1×10^{-5}) (mol/L)	1 × 10^{-9}(mol/L)	[**170**]
Chitosan/laponite/polyphenol oxidase/GCE	Amperometry	(1.1×10^{-8}- 4×10^{-5}) (mol/L)	11 × 10^{-9}(mol/L)	[**171**]
Co/Al LDH	Amperometry	(3×10^{-7}- 3×10^{-4}) (mol/L)	0.3 × 10^{-6}(mol/L)	[**172**]
Laccase and Tyr based biosensor	Amperometric	(1-10) × 10^{-6}(mol/L)	0.15 × 10^{-6}(mol/L)	[**173**]
MWCNT/Polyethlenimine/GCE	Amperometric	(2.5-20) × 10^{-6}(mol/L)	0.21 × 10^{-6}(mol/L)	[**174**]
MWNT/Nafion/Tyr/bio-composite/GCE	Amperometric	(1-19) × 10^{-6}(mol/L)	0.13 × 10^{-6}(mol/L)	[**175**]
GCE	DPV	(0.5-5) × 10^{-6}(mol/L)	---	[**176**]
GNP	DPV	(0.08-0.8) × 10^{-6}(mol/L)	0.05 × 10^{-6}(mol/L)	[**177**]
Pt-MWCNT-SO3--PB	LSV	(0.0-69.8) × 10^{-6}(mol/L)	7.04 × 10^{-6}(mol/L)	[**178**]
Polypyrrole and polyvinylpyrrolidone	CV	(1-100) × 10^{-6}(mol/L)	0.1 × 10^{-6}(mol/L)	[**179**]
Tyr/CPE	Amperometric	(2-25) × 10^{-6}(mol/L)	0.006 × 10^{-6}(mol/L)	[**180**]
Tyr/ZnO	Amperometric	(0.015-6.5) × 10^{-6}(mol/L)	0.005 × 10^{-6}(mol/L)	[**181**]
BDD film electrode	DPV	---	1.82 × 10^{-6}(mol/L)	[**182**]
Polyazure B-clay-enzyme	CV	(0.004-18) × 10^{-6}(mol/L)	0.004 × 10^{-6}(mol/L)	[**183**]
Poly(N-3-aminopropyl pyrrole-co-pyrrole)-tyr	Amperometric	(1.35-222.3) × 10^{-6}(mol/L)	0.7 × 10^{-6}(mol/L)	[**184**]
ZnO/SPE	LSV	(0.01-50) × 10^{-6}(mol/L)	0.0041 × 10^{-6}(mol/L)	[**185**]
MCN/Tyr/GCE	i-t	(0.05-9.50) × 10^{-6}(mol/L)	0.01024 × 10^{-6}(mol/L)	[**186**]
Tyro/SBM Based biosensor	Chronoamperometric	(0-200) × 10^{-6}(mol/L)	0.2 × 10^{-6}(mol/L)	[**187**]
ZnO/CNT/HPDB/CPE	Amperometric	(1-750) × 10^{-6}(mol/L)	500 × 10^{-6}(mol/L)	[**188**]
Poly diphenlamine/CNTs/GCE	SWV	(9.8-80) × 10^{-6}(mol/L)	500 × 10^{-6}(mol/L)	[**189**]
Ag@C@Ag/GCE	DPV	(0.5-50) × 10^{-6}(mol/L)	41.5 × 10^{-6}(mol/L)	[**190**]
Tyr-AuNps/GCE	SWV	(0.1-1.1) × 10^{-6}(mol/L)	0.07 × 10^{-6}(mol/L)	[**191**]
Tyr-Aucoll-graphite-teflon	Amperometric	(0.025-4) × 10^{-6}(mol/L)	0.02 × 10^{-6}(mol/L)	[**192**]
Tyr-TiO_2 sol-gel/CE	Amperometric	(0.44-11) × 10^{-6}(mol/L)	0.13 × 10^{-6}(mol/L)	[**193**]
PDPA-MWCNT/GCE	Amperometric	(3.96-177.8) × 10^{-6}(mol/L)	0.5 × 10^{-6}(mol/L)	[**194**]
Pt-RuO_2	Chronoamperometric	(0.7-5) × 10^{-8}(mol/L)	1 × 10^{-9}(mol/L)	[**195**]
Tyr-BSA-GA	DPV	(1.0-100) × 10^{-6}(mol/L)	4 × 10^{-6}(mol/L)	[**196**]
GO-ZnO/GCE	SWV	(5-155) × 10^{-6}(mol/L)	2.2 × 10^{-9}(mol/L)	[**197**]

Conclusion and future perspectives

Phenolic pollutants are generated from various sources such as coal, plastic, oil, and so on and are released in the form of waste. Because of the carcinogenic risk that may take place in human being, the phenol detection process is considered to be significant in the field of environmental science. Phenols are the form of organic pollutant, which is toxic or even resistant towards the microorganisms clarifying that it is not capable of getting treated through any biological action or mechanism. The inhalation, as well as the dermal exposure of phenol, seems to be irritating for eyes, mucous membrane, the skin of human beings. Even oral exposure is highly toxic for human beings. The 1g ingestion of phenol is lethal, showing different symptoms such as paralysis, respiratory, convulsions, loss of coordination, tremors and muscle weakness. Hence, because of such circumstances, phenol is induced in environmental legislation. As there occurs a binding of the hydroxyl group in phenol, the derivatives of phenol are generally weak acids and get oxidised very easily.

The process of characterisation and quantification of the phenol is considered as an important as well as a challenging topic for environmental science and electrochemistry. Various methods such as chromatographic, spectrophotometric, and electrochemical process are used to detect phenol. But such approaches are complicated, consumes lots of time and even needs costly tools and implements. These methods are not adequate for active monitoring in *situ*. But in practical use, the electrochemical process is considered to be convenient for analysis of organic compounds. The electrochemical phenol detection consummated through the process of oxidation on the solid electrodes. It is assumed that if the phenol oxidation is achieved directly on the surface of the electrode, the surface tends to passivates because of the formation of the polymer due to oxidation. To get rid of such circumstances, various techniques need to be implemented, namely polymerisation. For an electrochemical system, the controlling process is very often like the precipitation, adsorption of undesirable species, the reaction between surface and collateral species by modifying the surface of electrodes. The species holds on their specific features allowing the development of different approaches like electrocatalysis, bioassays, preconcentration, and detection of few particular compounds.

The new electroanalytical methods are used for electroactive as well as electrochemically inert compounds. Such features have enabled the electroanalytical technology to exhibits its influence in the research fields in the form of electrochemical transduction. The most significant is the biocompatibility and the ability to integrate chemical species without any defaults in the operating medium. They need to follow specific essential condition such as possessing good electrical conductivity, sensitivity towards analytes along with the physical and chemical inertia in contrast to the contraction solution. The electrodes should mainly possess some underlying properties such as easy modification, renewable surface, low costing, reproducibility, sensitivity, biocompatibility etc. But a chance may arise in future that the use of such electrochemical devices may elaborate showing substantial effects in various areas namely conversion of energy, green electroanalytical chemistry catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors acknowledge the Knowledge Resource Centre, CSIR-NEERI, (CSIR-NEERI/KRC/2018/JUNE/EMD/3) for their support.

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