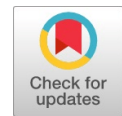


Recent Updates on Electrochemical Detection of Perchlorate Ions

Nisha Rani, Kuldeep Singh, Nitin Kumar Sharma, Anuj Singal



Abstract: Perchlorate is a highly toxic compound. It has both chemical and physical properties. Perchlorate is not easily degradable compound by both bio and non-bio degradation process because of its high stability, highly water soluble compound and low absorption. That's why perchlorate reduction becomes a big challenge. In this research work we studied different type of electrochemical technique and effect of different electrodes on these techniques. In present days, many techniques were developed for the detection or reduction of perchlorate such as bio-degradation, optical, chemical, electrochemical and microbial technique. This article gives information about application of electrochemical technique for the detection or reduction of perchlorate. The electrochemical techniques have various types for the detection of ion. These techniques grouped on the behalf of various types of electrical signal such as potential or voltage, current and impedance which were produce in the presence of perchlorate into aqueous solution. Electrochemical technique such as impedance spectroscopy, this technique was performed on the electrochemical work station by applied a constant range of frequency. In cyclic voltammetry technique we were given a constant potential range and found results in the form of oxidation and reduction current. In the reduction of perchlorate history various researcher was found results using different electrochemical technique on different types of electrodes. The perchlorate salts and perchlorate have some useful application in the defense field, batteries, automobile airbags, rocket propellants and fuels. Perchlorate contamination is become a worldwide health problems. In many western states perchlorate was found in ground and surface water. It disturbs the thyroid gland to uptake iodine the human body. So its prevention technique was needed. However, the electrochemical techniques have more advantage such as low cost, user friendly, label free and real time monitoring over all other techniques. So we focus on electrochemical detection technique for the perchlorate.

Keywords: Perchlorate treatment, electrochemical detection, electrochemical work station, electrochemical techniques, electrodes.

I. INTRODUCTION

Perchlorate means a chemical compound Perchlorate ion (ClO_4^-) which used as a strong oxidizing agent, found in more chemically stable form and as high water soluble compound. Perchlorate is found mainly in salts form but acid compound of Perchlorate is also available. ¹Corresponding author:

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Mostly Perchlorate is found in the simple white crystal and colorless form but acid compound is found in white liquid form. Mainly The five Perchlorate compounds are attracting the attention of scientist to use as an oxidizing agent and as an electrolyte; those names are as Ammonium Perchlorate (NH_4ClO_4), Sodium Perchlorate (NaClO_4), Lithium Perchlorate (LiClO_4), Potassium Perchlorate (KClO_4) and Perchlorate Acid (HClO_4). The Perchlorate anion (ClO_4^-) structure has a negative charge with Chlorine atom and a tetrahedral decorated Oxygen atom.

Salts of Perchlorate are used for properties of exploiting as a strong oxidizing agent, rocket propellants & fuels, matches, batteries, automobile airbags, in food packaging control electricity and other consumer products [1].

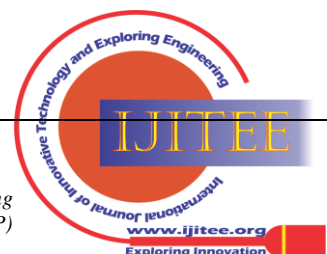
The Perchlorate water treatment technologies have been evolved into Present-day. The Recent Review of different technologies used for the treatment of Perchlorate was revealed in 2018. These Techniques grouped into three categories: Chemical treatment, Physical treatment, nZVI material treatment [2]. Perchlorate used as an electrolyte with high oxidizing property and many different applications but it plays a role of health hazards material in the environment. It has the ability to disturb with iodine uptake into the thyroid gland and thyroid hormones produce in small scale. The Thyroid gland hormones play an important role in the human body for Central Nervous System, Skeletal System, Metabolism and Growth, most essential role in the Fetuses and Birth Outcomes [3],[4]. Perchlorate can be produced by atmospherically and by the natural resources like fertilizers, due to thus generate some environmental problems and pollution diffusion [2]. Due to the great water solubility and lower adsorption [5], Perchlorate ions are hard to degrade and remove from environment. Perchlorate can be reduced by many numbers of methods like bio-degradable and non-bio-degradable techniques. Reducing of Perchlorate using bioremediation is cost-effective technique. In these techniques microorganism's function are used for enzymatic reduction of Perchlorate mixing with reducing agents including inorganic or organic compounds (e.g. Lactate [6], Hydrogen [7], Acetate [8], Ethanol [9] or Methane [10]). When ClO_4^- anion concentration is high in polluted water, cost of perchlorate reduction using bioremediation technique comparatively low. Reverse to this, when Perchlorate concentration is in fewer amounts in contaminated sample, enzymatic reduction is very costly because need of large reducing medium [11] and rate of reaction is comparatively slow [2].

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In addition, the microorganisms have metabolic products which may produce harmful byproduct and cause other health problems when technique is performed in drinking water treatment [4]. Therefore, forthcoming treatment techniques are needed to displace the potential pathogens and biological process nutrients supplied into water [12]. Physical treatment includes ion-exchange, membrane filtration and absorption process and Chemical treatment includes Catalytic, Chemical and Electrochemical or Electro-catalytic reduction. Chemical and Physical technologies are normally used for removal of trace-level of Perchlorate ion. In Chemical reduction, ClO_4^- ion is completely converted into non-toxic or harmless Chlorine ion. Theory of Thermodynamic says reduction of Perchlorate by Chemical technique kinetically interrupted because so long as it's high activation energy (120kJ/mol) and process are slow due to stable structure of ClO_4^- anion. These both Chemical and Physical treatment techniques have advantage of easy operation, low cost and high treatment efficiency [14]-[16]. But, Some Catalysts have application to conquer this energy barrier and ClO_4^- anion completely converted into Cl^- ion. Many metals (e.g. Pt[17], Pd[18], Pd-Re[19]) are supported Catalysts or Electrode in which ClO_4^- anion are reduce at surface of catalytic electrodes or metals[4]. Catalytic hydrogenation and electrochemical reduction can be parallel happened in the electrochemical hydrogenation instrument (ECHI). So, metal electrode and catalysts supporting both electro-catalytic & catalytic process. Many Researchers explored electrode and catalytic material (Homogeneous Catalyst [19], Poly-Electrode [20] and Pt-Ni [21]) for reduction of Perchlorate in aqueous solution. When we use both types of reduction process then biggest challenge is to improve the activity of catalytic, absorption capacity, fouling resistance, and catalytic stability, selectivity of reduction products, the reusability and electrodes. Nevertheless, Researchers are still working on these technologies and finding some new ideas for reduction of Perchlorate from environment and solve the problem of perchlorate contamination.

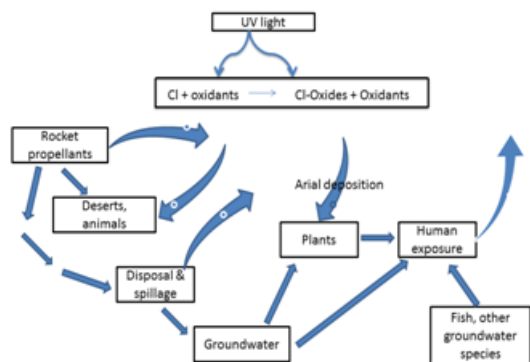


Fig.1. Flow, transformation pathways and transport of perchlorate in the environment

This review gives the information about recent electrochemical techniques of perchlorate reduction and effort to supply a holistic entry, by including many probabilities. Starting with introducing nature and resources of perchlorate contamination and gives hazards status of perchlorate in the environment and discuss some health issues. In this study also gives some brief introduction about

electrochemical experiment setup, electrochemical techniques and electrode which were used for perchlorate detection or reduction. There have been few interesting points to control the perchlorate pollution and possibly of 'innovative' outcome.

II. BACKGROUND

In order that generate a hopeful process, it is requisite to survey the background which belongs to perchlorate contamination. The chemistry was discussed hunted by the survey on origin, toxicity and health issues.

A. Origin of Perchlorate

Perchlorate found from both manufactured and natural compound. Discussion on sources and uses of perchlorate are important because it will help to direct us to investigate perchlorate and as also in treatment techniques. Perchlorate is a high oxidizing agent, due to this property of perchlorate synthesis process of perchlorate come into picture. Because high oxidizing agent are used in numerous application, which is as rocket propellants, rocket fuel, air bags, fireworks, explosives and in other pyrotechnics & industrial products [22]. Perchlorate has a worldwide use, that's why ClO_4^- contamination is general in Europe, western U.S and other industrialized countries [23]. Natural resources of perchlorate are found in abnormal condition. Perchlorate produce by serial reaction in environment involving electrical discharge lighting, oxidation of ozone and UV exposure [24],[26],[27]. The perchlorate has also produce by natural sources through photochemical reaction in the environment including inorganic chlorine with ozone [24] and organic chlorine species like methyl chlorine which converted into a inorganic species [25]. After that it contributes to make perchlorate in stratosphere. With the help of dry or wet deposition ClO_4^- found in rain water samples. China and Ireland collected the rain samples and detect manifold concentration of perchlorate from those rain samples [28]. The perchlorate has poor absorption and high water solubility properties, due to this it is easily transported to groundwater sources [29]. Dry deposition of perchlorate can get formation of dust, gases and atmospheric aerosols [30]. Some resources of perchlorate are human made products. These Perchlorate synthetic products are uses such as electrolyte solution with chlorine ions, rocket propellants, glitters for road safety and fireworks [31]. United States found that ammonium perchlorate manufacturing is the key origin of anthropogenic perchlorate [12], [33]. NH_4ClO_4 is mostly used in missiles and rockets propellants, because of its strong oxidizing property. In the sites of military and NASA facilities establishments high perchlorate contamination are found where perchlorate contaminated wastewater was poured at the ground without doing proper perchlorate treatment [33]. March 2005, the EPA catalogued 25 various states from 150 distinct locations by known groundwater and soil perchlorate contamination [33], [34]. Since major sites of contamination are controlled by either DOD (Department of Defense) or NASA, both have started doing research to finding alternative of perchlorate which used in their further operations [33].

In area of laboratories, pharmaceuticals and other industries, perchlorate has bounded application [33]. Few geographical places may have combination of both naturally and man-made occurring ClO_4^- . Further Doing researches to finding methods of distinguish between man-made and naturally occurring perchlorate in atmosphere [31]. Isotopic Mass ratio separation is one of them in which a result found that naturally occurring perchlorate has less mass than isotope of chlorine [42]. Further research on this technique is being conducted [31].

B. Health effect and pollution status

After 1990's observed that, the perchlorate detection rang was decrease from $400\mu\text{g/L}$ to $4\mu\text{g/L}$ [2] and going near about $1.05\mu\text{g/L}$ [28] because researchers are modified many detection and separation techniques.

Perchlorate is more stable compound due to that more difficult to reduce and it is an easily mobilized compound in atmosphere because it have inherent characteristics. Therefore, it found in several environment media and cause health & environmental problems. The perchlorate as a chemical was firstly research in 1985 by the U.S. EPA [2].

The ammonium perchlorate is found as a pure salt of perchlorate. Its dilute solution is not much effect on skin but pure salt is absorbed in the skin [34]. Perchlorate exists in various forms like water contamination, food, milk and dust. Perchlorate anion radius and charge both similar as iodine ion so it disrupts the iodine uptake in thyroid gland. Perchlorate as a dust compound contact with eyes, skin and membranes and irritates them. Shortness of breath and coughing problems also cause due to vapors and dust particles of perchlorate [34]. It also caused annihilation of red blood cell and kidney or liver damage [34]. The ecosystem may be affected by the perchlorate [34].

In 1996, Howard et al. found that using radioiodine reduces the perchlorate by transfer into animals [43]. Tests on female mice and male rats are also performed by increasing drug concentration of potassium perchlorate in water and observed harmless tumor growths [34]. On Frog embryos tests is done with ammonium perchlorate.

Thyroid is essential and play important role for the human body. In human body nervous system development and growth of the body is done by it [33]. Study on perchlorate give more information about health effect related to pregnant woman and fetus is serious effects. Quantity of iodine is low then development delay is take place in infancy, memory and language skills and in subclinical disease [2]. Perchlorate contamination has been found in atmospheric media of various countries. In laurentain great lake, a survey by America was done with use of isotope ratios to found sources of perchlorate and nature of ClO_4^- anion. This survey was found 0.05 to $0.13\mu\text{g/L}$ concentration of perchlorate [37]. In Japan, research was done on 30samples of tap water. Author found higher than 10mg/L in 13 samples and more than 1mg/L in 19 samples of tap water [48]. In 2011, South Korea researcher Her et al. also investigated perchlorate in tap water, sea water and local water bottled samples and conclude that local water also affected by perchlorate pollution [49]. Tamil Nadu also research on perchlorate and observed that at surface water contamination range from 0.005 to $30.2\mu\text{g/L}$, in groundwater contamination $0.005\text{-}7690\mu\text{g/L}$ and in tap water perchlorate contamination range from 0.063 to $0.393\mu\text{g/L}$ [2]. Many researchers have found that in

groundwater due to fireworks factory areas are most pollutant by perchlorate [2]. Perchlorate contamination also found in vegetables, serum, milk, breast milk and saliva this concludes by China research [50]. Atacama Desert also most polluted by perchlorate contamination than other sites this was found by Lybrand et al. in 2016 [51].

By adding all results we conclude that perchlorate found in different countries of various environment means that pollution by perchlorate has turn into universal environmental problem.

I -Table. Perchlorate found because of natural sources. Adapted from Ref. [25]

Location	Perchlorate source	Concentration of ClO_4^-	References
Texas, USA	Atmospheric deposition	25 samples 70% contained measurable ClO_4^- ($\text{N}10\text{ ng}\cdot\text{L}^{-1}$) Max value = $1.6\mu\text{g}\cdot\text{L}^{-1}$	[27]
Great Lakes, USA and Canada	Atmospheric deposition	From 0.05 to 0.13 $\mu\text{g}\cdot\text{L}^{-1}$	[22], [37]
Atacama Desert, Chile	Arid and semi-arid deserts	From 744 to 1480 $\mu\text{g}\cdot\text{L}^{-1}$	[38]
Atacama Desert, Chile	Arid and semi-arid deserts	From 1 to 10 $\text{mg}\cdot\text{L}^{-1}$	[39]
Southern High Plains, USA	Atmospheric deposition and ET enrichment/irrigation	Max value = $200\mu\text{g}\cdot\text{L}^{-1}$	[40], [41] [44], [45] [35]
Atacama Desert, Chile	Arid and semi-arid deserts	From 50 to $150\mu\text{g}\cdot\text{L}^{-1}$	[39]

III. ELECTROCHEMICAL SYSTEM SETUP FOR DETECTION OF PERCHLORATE

An electrochemical work station has an experiment setup for the detection of any ion. Electrochemical detection of perchlorate consist a process in which charge is transfer through chemical phases at the specific interface. It consist an electrode (electronic conductor) and an electrolyte (anionic conductor) for the electrochemical process [68]. Perchlorate contenting solutions act as an electrolyte. On the electrode/electrolyte interface when electric potential is applied current passes through chemical phase. The electric cell potential is calculated at electrode/electrolyte interface. The whole chemical reaction or independent two half-cell reaction is done in electrochemical cell as a real chemical change on two electrodes. One half-cell reaction is take place on working electrode (WE) and other on reference electrode (RE). The cell potential is measured with respect to reference electrode which has fixed potential. External power supply is used in electrochemical experiment for providing excitation signal and calculate the function of response in the electrolyte solution in which some variables are kept constant as shown in figure2.



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Electrochemical system also has a three cell electrode configuration in which third electrode used as a counter electrode (CE). The electrical current is travel from working to counter electrode and vice-versa.

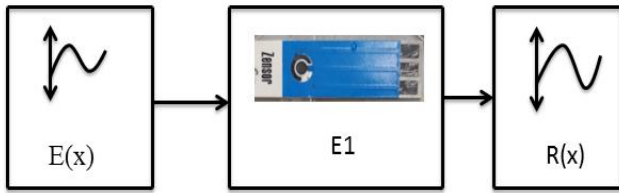


Fig.2. General concept for performing electrochemical experiment. (Where, $E(x)$ is excitation signal, $R(x)$ is response signal, E1 is electrode)

In addition, a three electrode experimental setup has three electrodes placed into an electrolyte solution and show the modified working interface by different materials for high detection sensitivity. Working and counter electrode materials choose such as counter electrode material doesn't affect the Working Electrode and put in different section from working electrode. The electric cell potential is calculated between the RE and the WE with device which has input impedance high in order to current prevention drawn from reference electrode.

Electrochemical workstation is a lab apparatus or portable in-field embedded system which has measuring units for calculating and receiving response signal and internal power supply system for giving excitation signal to connected input electrode.

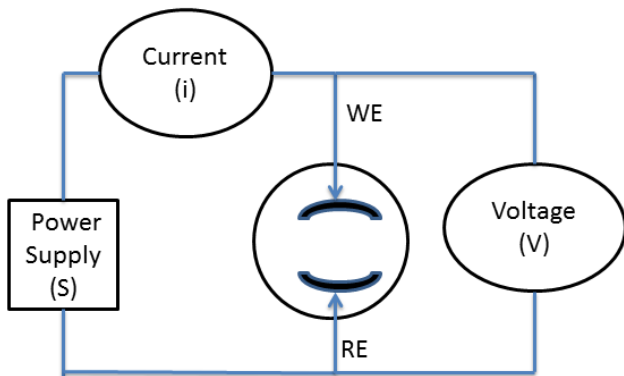


Fig.3. Two electrode electrochemical cell setup (Where, WE is working electrode, RE is Reference electrode)

CHI instrument Software installed in a computer which attached with electrochemical work station is used for analyzing and interpretation of the experiment data. A two electrode electrochemical cell setup which has RE and WE is used to calculate resistance of the small solution. The figure3 shows the two electrode system. Even so, for the non-aqueous solutions a three electrode electrochemical cell setup which used for electrochemical practical having with resistance of large solution is shown in figure4.

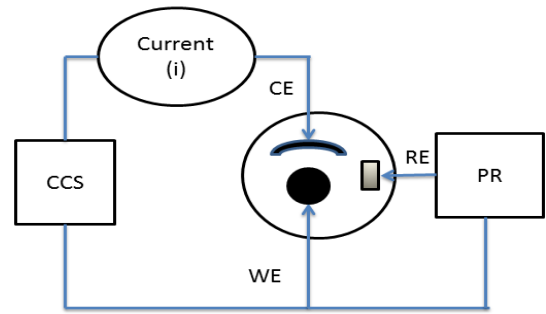


Fig.4. Three electrode electrochemical cell setup (Where, CCS is controlled current source, PR is potential recording device, WE is working electrode, RE is Reference electrode, and CE is Counter electrode.)

IV. ELECTROCHEMICAL TECHNIQUES FOR PERCHLORATE DETECTION OR REDUCTION

The perchlorate can be destroyed by conversion and/or partition processes. Some common partition technologies for removal or detection of perchlorate such as activated carbon adsorption [52], electro dialysis [53], ion-exchange [54], reverse osmosis [55] and membrane filtration [56] can use effectively. Some Chemical and biological technologies are used as conversion techniques for this process [57]-[59]. In [57], author show that bacteria species are also capable for degradation of perchlorate. Nevertheless, these methods are not preferred for the treatment of drinking water because some secondary byproducts re-contaminate the finished water. Some researchers are also show that the combination of two or more technologies is more effective for removal or reduction of perchlorate. In [58], author found that the combination of biological and membrane based technology of perchlorate reduction is more effective. Zero-valent iron techniques are also used for the perchlorate removal but the problem is further treatment of drinking water to remove iron from water [59], [60]. For example zero-valent iron techniques are used for perchlorate reduction but it produces byproduct during reduction process. So we need further treatment of water to remove iron from water. That's why; if we need total removal of perchlorate the above techniques are not better option.

Now, question is that which technique is gives without producing byproduct and further treatment of water. Solution of this problem is that chemical and electrochemical techniques are gives total conversion of perchlorate into chlorine ion.

Electrochemical reduction method also reported for the removal or detection of perchlorate. This is a promising method for removal of ClO_4^- anion because it completely converts ClO_4^- anion into Cl^- ion. This method is used to reduce perchlorate as like chemical reduction but the main difference is the electrochemical reduction can also take place without use of catalyst. Catalyst is use to reduce the activation energy of the reaction.

In this study, we discuss about reduction of perchlorate at the transition metal, carbon nanoparticles and polymer based experiment.

In [61], the author used titanium electrode for perchlorate and nitrate removal from water. In this paper indirect electrochemical method are used for water treatment. In [62], the author investigated ruthenium electrode behavior in aqueous solution for removal perchlorate. As like this many researches are done on removal of perchlorate by electrochemical reduction. We discuss electrochemical method of perchlorate removal.

Generally, the electrochemical techniques for the perchlorate detection are processed with or without any pretreatment of the sample because of its dependency on complexity of the sample matrix. The electrochemical techniques for reduction or detection of perchlorate are grouped according to different electrical signals produced in the aqueous solution because of perchlorate presence. The presence of perchlorate can bring changes in several electrical parameters such as potential, current, charge, electroluminescence and electrochemical impedance. Based on several electrical signals, the electrochemical techniques are grouped into voltammetric, chronoamperometry, impedance measurement and potentiometric. Mostly the potential or current can controlled to calculate the other parameter values with respect to change.

Potential and current can't be controlled at a time making basis for galvanostatic or potentiostatic measurement techniques [69]. Change in charge transfer resistance, double layer capacitance and solution resistance are occurs due to perchlorate presence, such type of technique is called impedance measurement technique. Another type of electrochemical technique in which potential is measured, this technique is called potentiometric technique. Cyclic voltammetry measurement was used by several authors for reduction of perchlorate in [20]-[21], [62], [65]-[66], [71]-[76], [78]-[82] on various electrodes. Some researchers are used other electrochemical technique for perchlorate reduction such as chronoamperometry [65], potentiostatic [72]-[73], [75] and electrochemical impedance spectroscopy [63], [65].

Perchlorate detection electrochemical techniques are classified and described below:

A. Cyclic voltammetry

For the study of perchlorate detection or reduction, mostly used electrochemical technique is cyclic voltammetry. Cyclic voltammetry provides friendly conditions for investigating working parameters for the electro active perchlorate, such as scan rate, potential range and pH of electrolyte. CV provides information about thermodynamics process of redox processes for aqueous solution, on-coupled absorption processes or chemical reactions and also kinetics information of heterogeneous electron-transfer reaction. Linear sweep voltammetry is beneficial for the anodic scan of oxidation peak for aqueous solution in the presence of perchlorate rather than cyclic voltammetry. Linear sweep voltammetry is gives same results as CV forward or backward scan, but measurement time is reduced by half effectively.

In [71], Author used cyclic voltammetry for reduction of perchlorate in aqueous solution on platinum platinized electrode. An electrolyte solution 0.5M H₂SO₄ in 3M HClO₄ aqueous solution was used to measure parameter of cyclic voltammetry like current at different sweep rate and also show that at different sweep rate current is changing. This

study also shows that anodic cathodic treatment lead to decrease the perchlorate reduction capability of that electrode in 3M HClO₄ solution. In this research author not able to find out the relationship between voltammetry curves produces by catalytic activity of platinized electrode and electrolyte H₂SO₄ solution during perchlorate reduction. In [65], cyclic voltammetry was performed on the rhodium disc electrode using 3M HClO₄ solution for reduction of perchlorate ion. A curve was obtained at different sweep rate with 3M HClO₄ aqueous solution on disc electrode at 25°C temperature and area of electrode is 0.196cm². Author found that if number of scan is changed then negative current is continuously decreasing during positive sweep of the cycle.

B. Potentiostatic techniques

Potentiostatic is an electrochemical technique which used to control the potential using a potentiostat instrument between counter and reference electrode to keep up a potential difference between working and reference electrode as shown in below figure5. The resulted value of current is recorded and calculated consequently to predict the concentration of analysts. Controlled Potential techniques are also having that type of experiments. According to type of applied voltage signal and resultant current waveform, this technique is further grouped into basic categories like Chronocoulometry, Amperometry and voltammetry. Some authors applied potentiostatic technique for perchlorate reduction [72]-[73], [75].

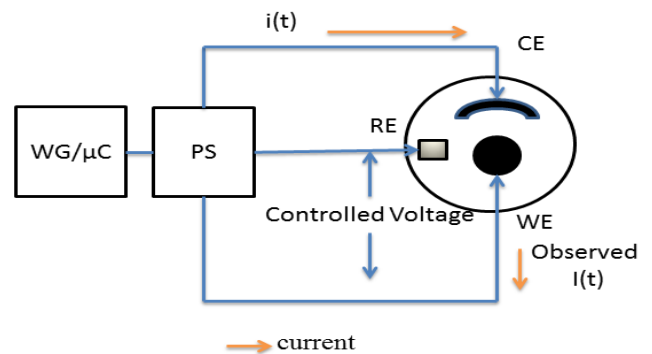


Fig.5. Potentiostatic electrochemical experiment setup (Where, WG is waveform generator, μC is Micro-controller, PS is Potentiostat, WE is working electrode, RE is Reference electrode, CE is Counter electrode)

C. Chronoamperometry

Chronoamperometry (CA) is a part of amperometric technique that used for measurement of diffusion coefficient of active area of working electrode surface and electro-active species. It also involved the potential step application and measuring the current as function of time for working electrode. This electrochemical technique has a small time scale than other amperometric techniques. CA technique requires more expansive and complex specialized apparatus and proper handling. So these are time consuming and specialized personal needed techniques. Nevertheless it provides most accurate data or results.

In [65], the chronoamperometric electrochemical technique is performed on rhodium disc electrode for perchlorate reduction. During chronoamperometric measurement electrode potential kept constant at 45°C temperature and recorded electrical current in time function. Author study behavior of current with respect to change in rotation rate of disc electrode and conclude that current is depended on potential of electrode and rotation rate of rhodium electrode.

D. Impedance measurement techniques

Electrochemical Impedance spectroscopy (EIS) is most widely used technique for the measurement of impedance for investigating analysts concentration in aqueous solution. This technique is hired to study the interfacial characteristics of the modified electrodes such for multilayer films. Many researchers proved that EIS was an efficient tool for investigating interface properties of the modified electrode which could be used for bio-sensing application.

EIS is a very suitable technique for electrochemical detection in terms of ac theory. It describes behavior of a circuit to a voltage or alternative current in terms of frequency. Electrochemical instrument technique impedance spectroscopy used for moderate and cheap experiments. It used for sensitive toxic metal detection in chemical & biological matrices rather than other electrochemical techniques. In this technique the experiment is performed in electrochemical cell in terms of an electrical equivalent circuit (EEC). An electrochemical reaction is take place on electrified interface through that current is passing and leads to charge transfer along this interface which produces non-faradaic & faradaic components. The figure6 shows the EEC for impedance measurement. In this figure low-frequency component are show in the right side and high-frequency component are show in left side. For calculating randles circuit parameter and RC (resistive-capacitive) parameter, firstly we find out perchlorate concentration in the electro-active aqueous solution. Frequency response analyzer (FRA) is a technique which used in determining concentration of analysts. However frequency response analyzer is not a part of impedance measurement techniques. A single sine method is used in impedance measurement. In this method a 5-15mV small signal of required frequency is clamped by a dc voltage that also provides biasing and also gives result in the form of ac current. In impedance measurement gives a range of frequency and then calculating various impedance values for different current and voltage measurement. Nevertheless, this technique needed high data acquisition time. In [65], electrochemical impedance spectroscopy (EIS) measurement was also done on rhodium electrode. In this measurement area of electrode and potential were taken as a constant and temperature of the system is maintained at 45°C. In this measurement the electrode impedance in the 1M HClO₄ solution is calculated at different rotating speed of the rhodium electrode disc with potential applying E=0.01V at 45°C temperature. A Randles circuit fitting experiment was also performed and calculated parameters of circuit at different rotating speed. At last author conclude that impedance of the rhodium electrode in 1M HClO₄ solution is gives stationary change with rotating speed.

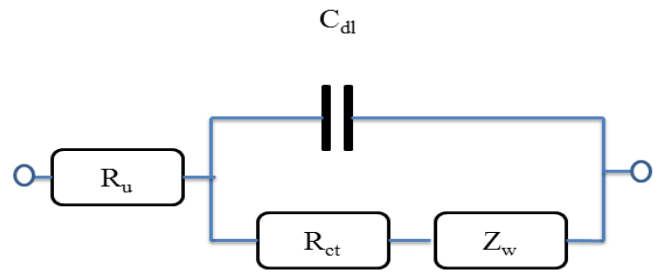


Fig.6. an idealized Randles electrical equivalent circuit for an electrochemical reaction (Where, R_u is solution resistance, R_{ct} is charge transfer resistance, Z_w is Warburg impedance, C_{dl} is a double-layer capacitor)

V. ELECTRODE FOR THE DETECTION OF PERCHLORATE

In many years HClO₄ and ClO₄⁻ anion were used as stable and inert electrolyte compound in several electrochemical measurements without creating any problem. These days most compelling evidence is supplied by multiple authors to prove that reduction of perchlorate in acidic electrolyte solution on various electrodes can be occurred. The perchlorate reduction in acidic electrolyte media was reported on Rh [63], [65], [74], [77]-[79], Pt [21], [71], [80], [82], Re [72], [81], Ti [73], Ir [76], Tc [72], Ru [62], and Wc [66] electrodes. The investigative study of perchlorate reduction by electrochemical measurement was defined in [65]. On the Ruthenium and Iron surface electrode perchlorate reduction process are completely described. In these studies cyclic voltammetry measurement was used to prove perchlorate reduction without any problem on various electrodes. In [65], Reduction of perchlorate was done on polycrystalline rhodium electrode using electrochemical techniques. In this study experiments were performed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chromoamperometry techniques on a rotating disc electrode. Experiments were done using 3M HClO₄ aqueous solutions at different rotation rate of electrode. The author concludes that ClO₄⁻ ion converted into Cl⁻ ion using electrochemically on rhodium electrode. The absorption of Cl⁻ ion takes place on electrode by reduction process. But in this experiment desorption of Cl⁻ ion come into picture and the desorption rate is depending on hydrodynamic conditions of perchlorate reduction process. In 1980s various author research on single crystal Rhodium electrode were performed in HClO₄ electrolyte solution. In all measurement evidence was not in favour of positive result of perchlorate reduction process even after that cyclic voltammetry reading was measured. These experiment results were not taken into account for positive results of perchlorate reduction [13]. In 1990s researchers were proved by evidence of positive results that antithetical measurement obtained during electrochemical process. This perchlorate reduction information could be elaborate if we suppose that perchlorate reduction process is characteristic on both rhodized electrode surface and polycrystalline surface [78]-[79], [46].



In 2007, author show that reduction of perchlorate was also possible on rhodium rotating disc electrode. In this study experiments were performed using CV, EIS and chronoamperometry techniques on a rhodium rotating disc electrode. Experiments were performed in 3M HClO₄ solution at different rotation rate of disc electrode. The absorption of Cl⁻ ion takes place on electrode by reduction process. But in this experiment desorption of Cl⁻ ion come into picture and the desorption rate is depending on hydrodynamic conditions of perchlorate reduction process [65]. By this information, mainly all problems regarding perchlorate reduction encountered in the explanation of several methods have been removed since last some years.

In [61], author finds out a method for perchlorate and nitrate reduction using transition metal titanium. Titanium is a metal which commonly used as an industrial material. It has many properties like non-toxic in nature, resistant to corrosion and found at normal payable prize. The reaction is performed on anode at the place of cathode that's why it called indirect electrochemical reduction. Author also examines the co reduction of nitrate and perchlorate on water-titanium electrode interface. At last results conclude that nitrate is not interfering in the reduction of perchlorate on Ti electrode. Chloride or nitrite is found as a last product. In [62], colom et al. is recorded in aqueous solution of perchlorate on ruthenium electrode. He concluded that perchlorate reaction with any solution is depending on pH and concentration of present anion in the solution which going to be reduced. It shows that perchlorate reduction is effectively affected by pH changing.

In [63], A Rhodized electrode is used to anion electrosorption using electrochemical impedance spectroscopy. In this study a three electrode system is used in which on working Platinum electrode rhodium is deposited using electrodeposition method. Impedance and cyclic voltammetry measurement is take place in 0.5M H₂SO₄ +1M HClO₄ electrolyte solution adding without or with Chloride ion and (bi)Sulfide ion. Author was investigated a method of decomposition of perchlorate anion in an HClO₄ electrolyte solution. Results are show by change in impedance spectra and potential shift by deposition of anion on rhodium electrode. A theory on study of Roughness factor of electrode surface is come into picture. The Roughness factor of electrode surface was depended on applied potential, absorption pseudo-capacitance and charge transfer resistance of the electrode in HClO₄ solution. In [74], Rhodium electrode is used to reduction of Perchlorate into Chloride ion using cyclic voltammetry. Author developed a cell for impinging jet technique using electrochemical cyclic voltammetry in 1M HF +0.0001M HCl with the presence of HClO₄.

In [64], Lee et al. work on zero-valent titanium electrode for perchlorate reduction. They concluded that for perchlorate reduction, zero-valent iron and its aqueous solution had a large thermodynamic potential. For 100mM perchlorate solution authors calculated pitting potential 12.77±0.04V of zero-vzlent iron. In [71], platinized platinum electrode is used for perchlorate reduction. In this paper cyclic voltammetry technique is used on platinized platinum electrode for perchlorate reduction from aqueous solution using with 0.5M H₂SO₄ electrolyte solution. The anodic-cathodic treatment was done by applying potential range from 0.05V to 1.4V to the platinized electrode. This

research gives information about the behavior of catalytic activity by changing parameters of platinizing technique.

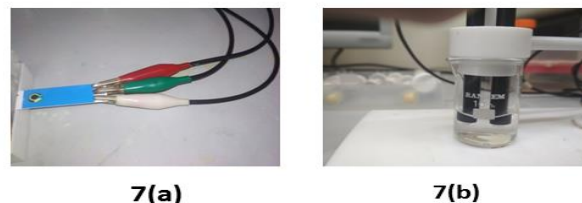


Fig.7. (a) Carbon paste screen printed electrode, (b) solid electrodes

VI. DISCUSSION OF STUDY

In past years, perchlorate was removed by using different types of techniques such as biological, activated carbon absorption, chemical and electrochemical technique. Perchlorate removed by chemical and electrochemical techniques is much better than other techniques because other techniques give byproducts during reduction process. In past few years, solid and rotating disk electrodes of different materials are used for removal of perchlorate using electrochemical technique. However currently we studied perchlorate removal on screen printed electrode. We were taken screen printed electrode and modifying them using different materials. In past few years many nano-materials was used for modifying electrodes [32], [47], [70]. After modifying samples are performed on that electrode using following equation:



Here we mixed X1 solvent into HClO₄ solution at different terms and conditions and performed electrochemical experiment. At last we found different electrical signal waveform as a result. Further work is going on this technique for perchlorate detection.

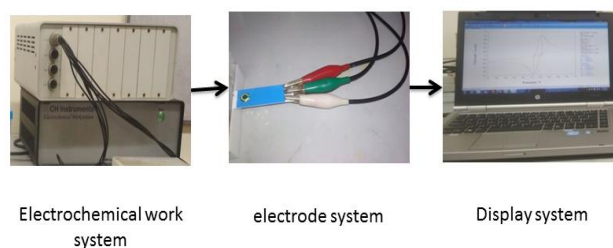


Fig.8. Electrochemical detection of perchlorate using mention equation and above instrument

VII. CONCLUSION

Perchlorate contamination has been become biggest challenge to treat and control by using different treatment technologies. Perchlorate caused several health problems and environment pollution. Perchlorate and salts of perchlorate are mostly used in defense field, manufacturing rockets, matches, fireworks and in solid propellants. Perchlorate has humanoid and natural both resources.



It is a toxic and highly water soluble compound. Perchlorate has many other characteristics such as high stability, less absorption and less volatility. This paper discussed the electrochemical technique for the detection of perchlorate. Electrochemical technique is better for perchlorate reduction in compare with other bio and non-bio technique. This technique was not produce any secondary pollutant compound and mainly its convert toxic ClO_4^- to non-toxic Cl^- . But this technique also faces many problems for the detection of perchlorate. The electrochemical technique is based on the time, electrode property and environmental condition. It needs proper environment and experimental condition and knowledge of chemical reaction of perchlorate with different electrolyte. Perchlorate reduction can become batter if we use combine reduction process such as chemical and electrochemical together. Further development of new technique and research in the electrochemical perchlorate detection should be focused to reduce these barriers and increase the application of electrochemical detection or reduction.

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