CHAPTER II

REVIEW OF LITERATURE, SCOPE AND
AIM OF THE PRESENT WORK

Aluminium is a very attractive anode material for energy storage and conversion. The electrochemistry of aluminium in alkaline solutions is of technical interest, due to its high voltage and energy density of aluminium-air batteries. Concentrated alkaline solutions are generally used in batteries owing to the need of improving battery performance. The efficiency of Al/air battery can be improved, by reducing the idle time corrosion of aluminium in alkaline media, without reducing the high potential of the working anode. Therefore, for commercial applications of the aluminium air battery, addition of corrosion inhibitors to the alkaline solution is recommended. Inhibitors reduced the magnitude of corrosion of aluminium in alkaline solution to a large extent. Corrosion inhibitors are able to increase the overpotential of parasitic hydrogen evolution without decreasing the oxidation rate of aluminium.

2.1. Brief historical survey

Dissolution of aluminium occurred when aluminium comes in contact with aqueous solutions of alkalis such as sodium and potassium hydroxides. Alkalis attack aluminium with particular vigour the hydroxide of it showing the properties of amphoteric compounds. Inhibitors of alkali corrosion were known as far as back to the early 1900s when pickling of aluminium in alkaline solutions was widely applied in practice. Pickling in 5% caustic soda was done to degrease aluminium and aluminium alloys before being anodized. Components that were stored for long periods are washed with a 2% solution of a mixture of sodium hydroxide, sodium carbonate and water-glass that acted as an inhibitor. Pickling in solutions of caustic alkalis was done to give an attractive matte finish aluminium articles and to reveal defects in the metal [1].

It was necessary in many cases to reduce the solution rate of aluminium during its pickling with alkalis and inhibitors were added to alkalis. Rohrig [2] reported the protective power of agar-agar and gum arabic at 0.75% concentrations in caustic soda solutions of different concentrations. The protective power of 4-6%
concentrations of gelatine was 80% when added to a 4% caustic soda solution [3]. Glucose at a concentration of 18% in a 4% caustic soda solution almost completely protected aluminium against corrosion [4]. Corrosion rate of aluminium in a 0.3N caustic soda solution at 23°C reduced to 70% in the presence of 0.3% meat peptones. The corrosion of aluminium in 0.3N sodium hydroxide at 40°C decreased by 82-87% in the presence of 0.43% gum tragacanth and by a factor of 8% in 0.64N potassium hydroxide in the presence of a hydrochloric acid extract of sapropel [5]. Zaromb and co-workers made earlier efforts for the development of the Al/ air battery with alkaline electrolytes. The efforts were made to modify the electrolyte by adding inhibitors, additive agents or complexing agents in order to make the electrolyte less corrosive [6-8].

2.2. Corrosion of aluminium in alkaline medium

Pure aluminium is too reactive to be used directly in concentrated alkaline solutions. High reactivity of pure aluminium resulted in an unacceptably high corrosion rate of aluminium anode, which is responsible for the main loss of aluminium fuel. So it is important to understand the corrosion mechanism of the aluminium anode in alkaline solution for the development of aluminium /air batteries. Since aluminium ions are not thermodynamically stable in alkaline solution [9], the direct ejection of aluminium ions from the oxide lattice in to the solution is unlikely to occur in alkaline solution. So, it is expected that the dissolution mechanism of anodic oxide films in alkaline solution should be different from the mechanism in acidic solution.

Awad et al. [10] studied the electrode potential and the corrosion rate of aluminium in 0.001-2M NaOH solutions at 30°C. Above 0.5M, both the potential and corrosion rate increased rapidly with concentration. This was attributed to adsorption of Na⁺ ions, which lead to the formation of active cathodic areas at the expense of the anodic ones. Aluminium suffered substantial corrosion in alkaline solutions, which induced coulombic loss in discharge and fuel loss during standby.

The anodic dissolution mechanism of aluminium in strong and weakly alkaline solution was investigated by several researchers. MacDonald et al. [11]
proposed a model for anodic dissolution involving stepwise addition of hydroxide ions to surface aluminium atoms. Chu and Savinell [12] suggested a similar anodic dissolution mechanism in which two fast steps of aluminium ionization and hydroxide formation reactions were combined with last slow film dissolution reaction by hydroxide attack. However, the native oxide film could be inherently present on the surface of aluminium metal in alkaline solutions, the anodic dissolution mechanism should include the presence of surface oxide film on aluminium in alkaline solution [13-17].

Armstrong and Braham [18] reported the extent of corrosion of aluminium in weakly alkaline solutions (pH 11). The results indicated that the rate of the cathodic reaction which occurred when aluminium corrodes in weakly alkaline solution, is a function of electrode potential but not of pH.

Doche et al. [19] studied the corrosion dissolution properties of pure aluminium in a 4M sodium hydroxide electrolyte using steady state techniques and voltammetric analysis. Presence of impurities such as As, Fe, Mg, Zn, Ni, and Cd in sodium hydroxide solution affected the corrosion rate of aluminium.

Emreguil and Aksut [20] reported the polarisation and impedance measurements carried out on aluminium in 0.1, 1 and 3 mol/L sodium hydroxide. The behaviour of the system was characterized by a high frequency capacitive loop related to the charge transfer process due to dissolution of the metal and an inductive loop at medium frequency attributed to surface roughening.

Zhang et al. [21] discussed in detail about aluminium chemistry and mechanism of aluminium corrosion in alkaline medium in a review paper. Corrosion of pure aluminium in alkaline solution involved two consecutive partial anodic reactions and a partial cathodic reaction [13-17]. The successive electrochemical film formation at the aluminium/surface oxide film interface (owing to the movement of OH through the film towards aluminium) and chemical film dissolution (due to OH attack at the film/solution interface) were given as anodic partial reactions.

\[
\text{Al} + \text{OH}^- \rightarrow \text{Al(OH)}_3 + 3e^- \tag{2.1}
\]
\[ \text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{Al(OH)}_4^- \] ................................. (2.2)

The electrons produced by the partial anodic reaction were consumed immediately by such partial cathodic reaction as the oxygen reduction reaction or the water reduction reaction which were represented as follows:

\[ \frac{3}{4} \text{O}_2 + \frac{3}{2} \text{H}_2\text{O} + 3\text{e}^- \rightarrow 3 \text{OH}^- \] ................................. (2.3)

\[ 3\text{H}_2\text{O} + 3\text{e}^- \rightarrow 3/2 \text{H}_2 + 3\text{OH}^- \] ................................. (2.4)

Cathodic reaction of water reduction takes place simultaneously with the dissolution of aluminium metal. The gas bubbles observed on the corroding aluminium surface were due to the corrosion of aluminum in alkaline solution which occurred mainly by water reduction reaction.

Therefore the overall mechanism of corrosion reaction of aluminium in alkaline solution was given as follows:

\[ \text{Al} + 3\text{H}_2\text{O} + \text{OH}^- \rightarrow 3/2\text{H}_2\text{O} + \text{Al(OH)}_4^- \] ................................. (2.5)

2.3. Chemical inhibitors

Organic compounds, containing mainly oxygen, nitrogen, and sulfur atoms, and having multiple bonds, are recognized as effective inhibitors for the corrosion of many metals and alloys [22-26]. Corrosion inhibition occurs via adsorption of the organic molecule onto the corroding metal surface, consistent with certain known adsorption isotherms, with the polar groups acting as the reactive centers in the molecules [27]. Net efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the resulting adsorption layers.

2.3.1. Inhibitors for aluminium corrosion in sodium hydroxide medium

Sundararajan and Rama char [28] evaluated the corrosion rates for commercial aluminium, containing 4 per cent manganese and 3 per cent iron in sodium hydroxide solution. The inhibition efficiencies were calculated for the following substances, the efficiency decreasing from 90 to 60 per cent in the order: agar-agar, gum-acaciae, dextrin, gelatin, glue. Corrosion potentials were measured with and without dextrin inhibitor, and cathodic and anodic polarization studies were carried out. The results revealed that the dissolution of the metal was
electrochemical in character. The corrosion process appeared to be under mixed control with predominant inhibitor action on the anodic areas of the metal surface.

The corrosion of aluminium in 3M HCl and 2M NaOH solutions of different concentrations was examined by Abd El Kader and Shams El Din [29]. The effect of concentration of a number of alklyamines were examined. The results indicated that metal dissolution in each medium followed a different mechanism. The alkylamines were strongly adsorbed than the alkylammonium ions and interfered with the anodic reaction. Inhibition increased with the chain length and number of alkyl group of amines. Retardation in dissolution of aluminium was due to the blocking of the aluminium surface by the additive.

Desai and Desai [30] studied the influence of sodium alginate as corrosion inhibitor for Al-3S in 0.2, 0.4 and 0.6N NaOH solutions. 70-79% IE was obtained in 0.2 and 0.4N NaOH for up to 2 h. However IE was only up to 52-68% in 0.6N NaOH. It was also noted that a combination of 1% sodium alginate with 2% sodium borate and 0.26% potassium selenate was very effective in retarding the corrosion of Al-3S in all the three concentrations of sodium hydroxide.

Subramanyan et al. [31] studied the influence of glycerol, acetyl alcohol, hexyl alcohol, isopropyl alcohol and phenolic compounds on the corrosion of commercial Al (2S) in 0.01M and 0.1M NaOH. Weight loss and polarisation measurements showed that the inhibition efficiency of phenolic compounds was greatly influenced by the electron releasing and withdrawing groups substituted in the benzene ring.

Subramanyan and Krishnan [32] studied the influence of sucrose, glucose, fructose, mannose and mannitol on the corrosion and anodic polarization behaviour of aluminium (2S) in 1M NaOH in the presence and absence of calcium chloride using potentiostatic polarisation measurements. The results showed that considerable inhibition of corrosion was obtained by adding calcium chloride to sucrose, glucose, and fructose whereas corrosion was accelerated in mannose and mannitol.

Ramakrishnaiah and Subramanyan [33] reported the effect of some nitrogen containing organic compounds namely formamid, pyridine, gramine, dipyridyl piperidine benzoyl piperidine and dibenzyl disulphide, on the corrosion of 2S
aluminium in 1M solutions of sodium hydroxide and hydrochloric acid with and without calcium. All the compounds were not effective as inhibitors in 1M NaOH solution. But inhibitor when combined with calcium the inhibition efficiency was enhanced to a greater extent. Inhibition efficiency in 1M HCl was higher than in 1M NaOH. Potentiostatic polarisation experiments in 1M HCl revealed that the action of pyridine, gramine, piperidine and benzoyl piperidine were under cathodic control whereas dibenzyldisulphide was under mixed control.

Krishnan and Subramanyan [34] examined a set of aliphatic and aromatic aldehydes as inhibitors for preventing the corrosion of aluminium (2S) in 1M NaOH solution using weight loss and polarisation experiments. The results showed that the aromatic compounds were generally more effective as corrosion inhibitors than the aliphatic compounds and the inhibitive nature of the compounds was not related to compound solubility in sodium hydroxide solution.

Awad et al. [35] studied the effect of anions on the corrosion of aluminium in 0.1-0.5M NaOH solution containing 0.0001-1M Na₂CrO₄ using galvanostatic anodic polarization measurements. At large dilutions the chromate ion markedly promoted the corrosion of aluminium. The promoting effect increased with concentration up to 0.001M. At higher concentrations the ion behaved as inhibitor, and the corrosion rate decreased sharply with concentration. The inhibition action was attributed to the formation of a protective layer of chromium oxide.

Fouda and Elasmy [36] prepared and treated five phenylthiosemicarbazide derivatives, (1-(p-methoxybenzoyl)-4-phenyl-3-thiosemicarbazide, 1-(p-methylbenzoyl)-4-phenyl-3-thiosemicarbazide, 1-(o-chlorobenzoyl)-4-phenyl-3-thiosemicarbazide, 1-Benzoyl-4-phenyl-3-thiosemicarbazide, 1-(p-nitrobenzoyl)-4-phenyl-3-thiosemicarbazide) as inhibitors for the corrosion of aluminium in 2M sodium hydroxide. All the five compounds afforded 75 to 98.5% protection to aluminium in sodium hydroxide. 1-(p-methoxybenzoyl)-4-phenyl-3-thiosemicarbazide was the most efficient inhibitor. Thermometric and weight loss methods indicated that inhibition was principally governed by the adsorption of inhibitor compounds on the surface of the aluminium metal. The adsorbability of inhibitor was due to basicity of oxygen and sulphur sites involved.

31
Moussa et al. [37] investigated the effect of 4-Phenyl-3-thiosemicarbazide, 1,4-Diphenyl-3-thiosemicarbazide, 4-Phenyl-(2,4-dinitrophenyl)-1,3-thiosemi carbazide, 4-Phenyl-1-cyanoacetyl-3-thiosemicarbazide and 4-Phenyl-1-benzoyl-3-thiosemicarbazide derivatives on corrosion of aluminium in 2M sodium hydroxide using thermometric, weight loss and hydrogen evolution techniques. The rate of corrosion depended on the nature of inhibitor and its concentration, heat of hydrogenation, mode of interaction with the metal surface and formation of metallic complexes. The compounds were weakly adsorbed on the surface of aluminium and formed a monolayer of adsorbate.

John Albert et al. [38] studied the effect of calcium chloride and sodium chloride on the electrochemical properties of various grades of aluminium namely 2S, 3S, 26S and 57S in alkaline citrate solution. Among the different grades of aluminium the 57S grade was found to be the promising galvanic anode material in 4N NaOH containing 20% wt/vol of sodium citrate and 2.5% wt/vol of CaCl₂.2H₂O.

Mourad et al. [39] studied the inhibition of corrosion of aluminium in 1M NaOH solution by some cyclodiphosphazane derivatives (N,N’- Diphenyl hexachlorocyclodiphosphazane(I), N,N’-Di(p-tolyl)hexachlorocyclodiphosphazane(II), spiro-cyclodiphosphazane derivative of thiourea(III) using hydrogen evolution technique. The results indicated that the additives reduced the corrosion rate. The inhibitory action was found to depend upon the concentration and chemical composition of the additive compounds.

Mourad et al. [40] studied the dissolution of Al in 2M HCl and 2M NaOH in the presence of dimethyltin dichloride as corrosion inhibitor using hydrogen evolution and thermometric methods. The two methods gave consistent results. The higher inhibition efficiency of the compound in acidic media than in alkaline media was due to the less negative potential of Al in HCl solution, favouring adsorption of the additive. The adsorption of the compound was found to obey Frumkin adsorption isotherm.

Hassan et al. [41] revealed the inhibition of Al corrosion in solutions of hydrochloric acid and sodium hydroxide using aromatic acid derivatives as inhibitors by weight loss and hydrogen evolution methods. The results showed that
benzoic acid and its derivatives inhibited acidic and alkaline corrosion effectively. The efficiency of inhibitors increased in the order benzamide < benzaldehyde < acetophenone < benzoic acid < benzophenone (100%). The inhibition efficiency of acid anhydrides followed the sequence: pyromellitic > naphthalic > trimellitic.

Mourad and Ibrahim [42] investigated the inhibitive effect of butyltin trichloride on dissolution and localized corrosion of aluminium in 2N HCl and 2N NaOH using hydrogen evolution and thermometric methods. The experimental findings indicated that the inhibition effect of butyltin trichloride takes place through an adsorption mechanism following the Frumkin’s isotherm. Butyltin trichloride acted as a weakly adsorbed inhibitor in NaOH and as a strongly adsorbed inhibitor in hydrochloric acid medium.

Moussa et al. [43] studied the inhibition of some carboxylic acids on aluminium corrosion in 2M HCl and 2M NaOH solutions, using weight loss and hydrogen evolution methods. The order of inhibitive action of aromatic acids varied with the number and position of the carboxylic groups and the other substituents in the benzene ring. Increase of the chain length increased the inhibiting power of aliphatic acids. The inhibition efficiency in NaOH was higher than that in HCl solution.

Ahmed et al. [44] studied the inhibition of corrosion of aluminium in 2M hydrochloric acid and 1M sodium hydroxide solution by S-phenyl-isothiouronium derivatives using weight loss and hydrogen evolution methods. The inhibition efficiency depended on the type of solution and the nature of derivative. It was found that the inhibition efficiency in acidic medium was more than in alkaline medium. The adsorption of all the compounds followed Langmuir adsorption isotherm. The efficiency of the inhibitors on the acid and alkaline corrosion of aluminium followed the order S-benzyl-isothiouronium iodide > S-benzyl-isothiouronium bromide > S-methylisothiouronium chloride > S-benzoyl-isothiouronium bromide > S-benzyl-isothiouronium chloride > N,N’-diphenyl-S-methylisothiouronium chloride > urea.

Paramasivam et al. [45] examined the self corrosion and electrochemical properties of different grades of aluminium (2S, 3S, 26S and 57S) as galvanic anodes in 4M NaOH containing 0.01 to 0.6 M zinc oxide by weight loss and
polarisation studies. The studies revealed that 3S and 57S aluminium were the most suitable anode materials and 4M NaOH solution containing 0.6 M zinc oxide was the best electrolyte to get satisfactory performance as battery anodes.

Sarkar et al. [46] studied the inhibitive action of rubeanic acid on corrosion of aluminium alloy (Cu 0.5, Mn 0.59, Si 0.06, Ni 0.02, Mg 0.001 and 98.83% Al) in 1M NaOH using gasometry, weight loss and polarisation studies. Activation energy (Ea), the thermodynamic function for adsorption i.e. heat of adsorption were evaluated. The standard free energies for adsorption were calculated using Bockris-Swinkels isotherm equation where one molecule of water eas replaced by ne molecule of inhibitor. The efficiency of the inhibitor decreased with rise in temperature. The shifting of polarisation curves towards the left indicated that the metal was more and more anodically protected.

Gnana Sahaya Rosilda et al. [47] investigated the influence of sodium stannate, sodium citrate and calcium oxide combinations as corrosion inhibitors for anode utilization behaviour of different grades (99.0%, 99.5 to 99.7% pure, 99.8% pure, 99.999%) of aluminium in 4M NaOH solution. All the grades of aluminium irrespective of the differences in iron and silicon contents, showed that overall corrosion kinetics was predominantly under anodic control in 4M NaOH solution.

Jeyaraj et al. [48] evaluated the effect of some bakelites such as phenolformaldehyde and, salicylic-formaldehyde resins, sulphonated resins of salicylic acid and formaldehyde on the corrosion of aluminium (2S) in 1M NaOH by weight loss, open circuit potential, polarisation and thermometric measurements. Phenol-formaldehyde resin was found to inhibit the corrosion process when used in small concentration and the inhibition efficiency decreased with increasing concentration of the resin. The OCP (open circuit potential) and polarization studies revealed that the inhibitive action of the resins occurred predominantly by the retardation of the anodic process.

Pyun et al. [49] investigated the effect of the anions Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\) on the anodic dissolution of pure aluminium in 0.01M NaOH solution using potentiodynamic polarisation experiments, AC impedance spectroscopy and potentiostatic current transients. It was found that the addition of Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\)
ions to 0.01M sodium hydroxide solution reduced the anodic dissolution rate of pure aluminium.

Scholl and Jimenez [50] reported the application of 1-hydroxy imidazole -3-N-oxide as aluminium corrosion inhibitor in 0.01M NaOH, 0.01M NaOH +3% NaCl and 0.1 M Na₂CO₃. The 3-N-oxides shifted the corrosion potential of aluminium to more positive potentials and decreased the corrosion current (i_cor) by two orders of magnitude. Polarisation measurements, AC impedance measurements and electrochemical noise experiments were adopted for the investigation. The adsorption of inhibitors coupled with the redox reactions of the 3-N-oxides and the creation of a polymer layer on the aluminium surface were suggested from the results obtained.

Solymos et al. [51] evaluated the corrosion of aluminium and aluminium-magnesium-silicon alloys in alkaline solution with chloride ions. The protective effect of silatrane as inhibitors were investigated. The corrosion rate of aluminium and the inhibition efficiency of the applied compounds were determined by weight loss and electrochemical measurements. The m-chlorophenoxy-silatrane was investigated as the good corrosion inhibitor for aluminium in alkaline solution containing chloride ions at pH = 12.3.

Paruthimal Kalaignan et al. [52] studied the electrochemical behavior of commercial aluminium (2S) and alloys in 3N NaOH medium. Electrochemical characteristics of binary alloy of commercial aluminium containing 4% Zn and ternary alloy of commercial aluminium with 4% Zn containing various percentage of In, Sb and Bi were examined for the purpose of utility as galvanic anode in alkaline battery. Polarisation measurements revealed that the addition of alloying elements shifted the corrosion potential values in negative direction when compared to 2S aluminium at all current densities.

Madkour et al. [53] investigated the kinetics of substituted Bis and Mono-azo dyes as corrosion inhibitors in 2M HCl and 2M NaOH solutions using weight loss, thermometric and polarization measurements. Weight loss of Al decreased with increase in concentration of the inhibitors. A positive shift in the corrosion potential
in the presence of investigated azo dyes, indicated mixed type inhibition with predominant anodic action.

Jeyaraj et al. [54] studied the inhibitive effect of S-benzyl-iso-thiuronium chloride on the corrosion of aluminium (2S) in 1N sodium hydroxide, prepared by dissolving in water as well as in a water and propan-2-ol mixture containing 40% (v/v) propan-2-ol. Weight loss, polarisation and thermometric measurements were employed and the inhibition efficiency, determined by the three methods was compared. The polarisation studies revealed that both the anode and cathode were polarised in the presence of the inhibitor and thus it appeared as a mixed type of inhibitor.

Ansari and Quraishi [55] investigated the inhibitive effect of sodium silicate on corrosion of aluminium-lithium alloy in 3% NaOH by weight loss and electrochemical methods. The results indicated that sodium silicate inhibited significantly the corrosion of aluminium-lithium alloy in alkaline medium. The inhibition was further increased by the addition of 0.25% of barium chloride due to synergistic effect. The plausible mechanism of corrosion inhibition was also discussed.

Maayta [56] studied the corrosion inhibition of aluminium in aqueous solutions of sodium hydroxide in the presence of sulphonic acid, sodium cumene sulphonate and sodium alkyl sulfate in relation to the concentration of inhibitor and concentration of corrosive medium using weight loss method. The additives tested were found to be good inhibitors for aluminium corrosion in sodium hydroxide in the studied concentration range. Due to the adsorption of the additive molecules on the metal surface the inhibition efficiency increased with increasing additive concentration, Sulphonic acid showed the best inhibition capability for aluminium corrosion in sodium hydroxide, due to the planar orientation of the adsorbed additive molecules. Inhibition efficiency of the inhibitors increased with decreasing sodium hydroxide concentrations. The higher the temperature the lower was the inhibition efficiency, which was due to physical adsorption of inhibitor molecules on aluminium surface.

Meena et al.[57] reported the corrosion inhibition of tartaric acid, citric acid, maleic acid and malic acid in both acidic (0.1N HCl) and alkaline (0.1N NaOH)
solutions using Tafel polarisation method. Inhibition increased with concentration of inhibitors in acidic media while inhibition decreased with increase in inhibitor concentration in alkaline media.

Dhayabaran et al. [58] studied the influence of fluorescein in conjunction with calcium oxide on corrosion of aluminium in 1N NaOH by galvanostatic and weight loss techniques. It was found that the inhibition of aluminium corrosion increased with increase in concentration of the inhibitor. The inhibition was found to be of mixed type.

Jeyaraj et al. [59] investigated the effect of arginine in conjunction with calcium oxide on the corrosion of aluminium in 1.0 N sodium hydroxide. The results showed that arginine acted as a good inhibitor. A combination of calcium oxide and arginine showed maximum inhibition efficiency of 60.65%. Polarisation studies revealed that the corrosion process was found to be under anodic control in the presence of inhibitor. The adsorption of arginine obeyed Langmuir adsorption isotherm.

Jeyaraj et al. [60] studied the effect of 2, 3-dicarboxylato-4-hydroxy azobenzene on the corrosion of aluminium in 1M NaOH using weight loss and electrochemical techniques. The inhibitive effect increased with the increase in concentration of the inhibitor. The polarisation studies revealed that the corrosion of aluminium in the presence of inhibitor was under the anodic control. The corrosion inhibition was found to be of mixed type.

Al-Rawashdeh and Maayta [61] studied the inhibiting effect of cationic surfactant cetyl tri methyl ammonium chloride (CTAC) on aluminium in 1.5M hydrochloric acid and sodium hydroxide using weight loss measurements. Both in acidic and basic media, increase in temperature, resulted in decrease of the inhibition efficiency of CTAC. Adsorption of inhibitor followed Temkin isotherm in HCl and Langmuir isotherm in NaOH. Polarisation studies carried out in 0.5M HCl and 0.5M NaOH revealed that the inhibitors controlled the cathodic reaction.

Oguzie et al. [62] evaluated the adsorption and corrosion inhibition of bismark brown on aluminium (AA 1060) in 0.1M NaOH solution at 35°C and 70°C using gravimetric technique. The results indicated that bismark brown acted as an
inhibitor in the alkaline environment by adsorption on the metal surface and the inhibition efficiency was found to increase with dye concentration.

Rajendran et al. [63] studied the inhibition efficiency of methyl orange in controlling corrosion of aluminium in an aqueous solution at pH 11, in the absence and presence of Zn\textsuperscript{2+} by weight loss method. The combination of 80 ppm methyl orange and 50 ppm Zn\textsuperscript{2+} showed 90% IE. The influence of N-cetyl-N,N,N-trimethylammonium bromide and sodium dodecyl sulphate on the IE of the methyl orange-Zn\textsuperscript{2+} was also examined. IE decreased as the immersion period was increased. Polarisation studies revealed that methyl orange-Zn\textsuperscript{2+} system functioned as a mixed inhibitor. AC impedance and FT-IR spectral studies revealed the presence of protective film formed on the metal surface.

Al-Juaïd [64] reported the effect of some mono azo dye compounds on the dissolution of aluminium in 0.01M NaOH solution using weight loss and galvanostatic polarisation techniques. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with increasing temperature. The inhibition mechanism was discussed on the basis of the formation of complex compound adsorbed on the metal surface. The adsorption process followed Frumkin isotherm.

Umoren et al. [65] investigated the corrosion inhibition of aluminium in 0.1M NaOH in the presence of polyvinyl alcohol at 30 and 40°C using weight loss and hydrogen evolution methods. The synergistic effect produced by the addition of halides (KCl, KBr, and KI) to the inhibitor was also tested. Results obtained showed that inhibition efficiency of polyvinyl alcohol increased with increase in concentration and synergistically increased on the addition of halides. But IE of the polymer was found to decrease with increase in temperature.

Vasanthi et al. [66] studied the corrosion control of aluminium by phenyl thiourea polymers in 2N NaOH medium. Simple phenylthiourea compounds were known for their high solubility in alkaline medium and also for good corrosion control. The monomer N-(4-hydroxy-3-methoxybenzal)-N’-(4’-hydroxyphenyl) thiourea was condensed with pimeloylchloride and azeloylchloride through interfacial polycondensation method to synthesize the polymers. The polymers were
dissolved in 2N sodium hydroxide and the corrosion controlling efficiency on aluminium was studied through AC impedance and potentiodynamic polarisation methods.

Elango et al. [67] studied the corrosion inhibition of 57S aluminium in 2 M NaOH solution using polyaniline-ZnO. Results obtained showed that as the amount of polyaniline is increased, the self-corrosion rate of 57S aluminium alloy decreased appreciably. The open circuit potential was more in the case of 700 ppm level of polyaniline (-1.630 V) compared to 600 ppm level of polyaniline (-1.587 V). It was also observed that the anodic polarisation was greater than the cathodic polarisation, and the overall corrosion of 57S alloy in 2 M NaOH containing 0.2 M ZnO and 700 ppm of polyaniline was under anodic control. Hence the 57S grade aluminium was suggested as a potential candidate (anode) for alkaline batteries.

Elango et al. [68] investigated the novel polymeric inhibitor for corrosion of 57S aluminium in 2M NaOH solutions using gravimetric and polarisation measurements. The results clearly revealed that the 0.2M ZnO with 700ppm polyaniline in N-methyl-2-pyrrolidone solution offered inhibition up to 71.2 per cent.

Lashgari and Malek [69] reported the studies of Al corrosion in 0.5M HCl and NaOH environments using phenol inhibitor by theoretical calculations and experimental observations. The studies confirmed that the rate of corrosion in alkaline solution was substantially greater than in HCl media. Moreover phenol acted as a potential molecule showing mixed type inhibition mechanism.

Edrah and Hasan [70] studied the inhibition of thiourea derivatives on aluminium corrosion in sodium hydroxide solution. The inhibition efficiency of thiourea, phenyl thiourea (PTU) and 4-carboxy phenyl thiourea (CPTU) in 0.3, 0.4, 0.6 and 1.0M NaOH solution were calculated by weight loss measurements. It was found that the corrosion of aluminum in NaOH solution was considerably reduced in presence of inhibitors. Thiourea formed a protective film on the surface of metal through adsorption. The extent of adsorption depended on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosive media.
Lashgari [71] studied the corrosion inhibition mechanism of Al/NaOH system in the presence of some p-phenol derivatives. The results revealed a complicated proton / deprotonation cycle for inhibitor species inside electrochemical double layer. The corrosive agents in the vicinity of metal surface become locally and pushed away.

3-methyl-4-amino-5-mercapto-1,2,4, triazole (MAMT) was synthesized and its inhibition action on the corrosion of 6061 aluminium in 0.5M NaOH was investigated by Reena kumari et al.[72] using potentiodynamic polarisation and electrochemical impedance spectroscopy techniques. The surface morphology of metal surface was investigated by scanning electron microscope. The inhibition efficiency increased with increase in concentration of the inhibitor, but decreased with increase in temperature. The adsorption of 3-methyl-4-amino-5-mercapto-1, 2, 4, triazole on the base alloy was found to be through physisorption and it obeyed Langmuir’s adsorption isotherm.

Soliman [73] examined the effect of 8-hydroxyquinoline on the corrosion inhibition of commercial aluminium and Al-HO411 alloys in 0.1, 0.15 and 0.2M NaOH solutions. With increasing inhibitor concentration corrosion resistance shown by Al-HO411 alloy was higher than that of commercial aluminium. The essential role played by the protective film formed on the aluminium surface was proved by studies of optical microscope, energy-dispersive X-ray spectrometer, and x-ray diffractometry.

Umasankareswari and Jeyaraj [74] studied the inhibitive influence of salicylideneaniline (a schiff base) on the corrosion of aluminium in 1.0N sodium hydroxide by weight loss, potentiodynamic polarisation and electrochemical impedance measurements. The inhibition efficiency of the compound increased with increasing concentration. The addition of tetrabutylammonium bromide (TBAB) to varying concentrations of the schiff bases enhanced the inhibition efficiency at each concentration.

Princey and Nagarajan [75] studied the anticorrosive effect of 3-Hydroxyflavone (3HF) in combination with quaternary ammonium bromide and iodide salts (QAB and QAI) for aluminium corrosion in NaOH medium at the
temperature range of 303K-323K using weight loss study, potentiodynamic polarisation study and impedance spectroscopic measurements. The results revealed that the inhibition efficiency increased with the inhibitor concentration and it further increased on the addition of quarternary ammonium bromide and iodide salts. The enhanced inhibition efficiency of the inhibitor in the presence of quarternary ammonium salts was due to synergistic effect. The adsorption process of 3HF on the aluminium surface obeyed Langmuir’s adsorption isotherm. The mechanism of adsorption was further supported by Scanning Electron Microscope (SEM) study.

Rajendran et al.[76] studied the inhibition efficiency (IE) of diethylene triamine penta (methylene phosphonic acid) (DETAPMP) in controlling the corrosion of aluminium metal in a medium containing 0.01M NaOH and Zn\(^{2+}\) ions using weight loss measurements and electrochemical polarisation studies. Similar investigations were carried out by adding the second inhibitor viz. adipic acid (AA) also. The combined IE of the above two inhibitors was found to be more than 90%. All the synergism factor values calculated were greater than unity, confirming the synergistic effect of the two inhibitors. The protective film formed on the metal surface consists of Zn (OH)\(_2\) and complexes of Al\(^{3+}\) and Zn\(^{2+}\) with DETAPMP and AA. The film formation was confirmed by UV-Visible spectra, FT-IR spectra and Atomic Force Microscopy (AFM). Surface morphological studies were done using scanning electron microscopy (SEM) and AFM. Both inhibitors acted as mixed type inhibitors and obeyed Langmuir adsorption isotherm.

Rajendran et al. [77] studied the inhibition efficiency (IE) of succinic acid (SA) in conjunction with Zn\(^{2+}\) and diethylene triamine penta (methylene phosphonic acid) [DTPMP] on the corrosion of aluminium in 0.01M NaOH by weight loss and electrochemical techniques. The ternary system SA (240ppm) – Zn\(^{2+}\) (20 ppm) - DTPMP (20ppm) showed 98% IE and the protection efficiency values calculated from electrochemical polarisation studies were in good agreement with those calculated from weight loss studies. Effect of temperature on corrosion rate of aluminium was also studied to calculate E\(_a\) and \(\Delta H^*\). Surface morphology studies were done using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The inhibitors acted as mixed inhibitors and obeyed Langmuir adsorption isotherm.
Umasankareswari and Jeyaraj [78] studied the inhibition effect of vanillideneanthranilic acid on the corrosion behaviour of commercial aluminium in 1.0N NaOH using mass loss, potentiodynamic polarisation, electrochemical impedance measurement methods and SEM technique. The maximum inhibition efficiency was found to be 59.25% at 30°C. The investigation of adsorption isotherms indicated that the inhibitor fitted Langmuir and Temkin isotherms fairly well. The phenomenon of physisorption was attributed to the values of $E_	ext{ad}$, $Q_	ext{ad}$ and $\Delta G_	ext{ad}$ . The potentiodynamic polarisation results revealed that the inhibitor acted as a mixed type inhibitor.

Rani and Jeyaraj [79] reported the inhibitive, thermodynamic and adsorptive properties of 1-(phenyl)-3-(2-hydroxy phenyl)-propenone (PHPP) and tetrabutyl ammonium bromide (TBAB) for the corrosion of aluminium in 1.0M NaOH solution using weight loss measurements at 303K and 323K and electrochemical measurements at 303K . It was found that the inhibition efficiency increased with PHPP concentration but decreased with increase in temperature. A synergistic effect was observed between TBAB and PHPP. The experimental results suggested that the presence of TBAB stabilized the adsorption of PHPP molecules on the metal surface and therefore improved the inhibition efficiency. The phenomenon of physisorption was proposed from the trend of inhibition efficiency with temperature and also from the values of $\Delta G_	ext{ad}$, $\Delta H^*$ and $\Delta S^*$. Langmuir and Flory-Huggins adsorption isotherms were tested to ascertain the adsorption of the inhibitor on the aluminium surface in 1M NaOH.

Edouk et al. [80] studied the inhibition of 4-(4-nitropherylazo)-1-naphthol (44NIN) on the corrosion of Al in a binary mixture of 0.1M NaOH-0.1M KOH by chemical and spectrophotometric methods at 303-333 K. 44NIN exhibited an excellent inhibiting property. IE increased with the azo dye concentration but not with temperature.UV-visible absorption spectra of the Al specimen after immersion in the aggressive solution containing the dye indicated the possible formation of a 44NIN-Al type complex. FT-IR results showed a correlation between the inhibitive effect and molecular structural information of 44NIN in the studied alkaline system.
2.3.2. Inhibitors for aluminium corrosion in potassium hydroxide medium

Hirai et al. [81] investigated the inhibition effect of polymers with ammonium cation for Al corrosion in primary cells containing Al anodes and alkaline electrolyte (1N KOH). Two polymers polyvinylbenzyltrimethyl ammonium chloride (PVBA) and polydiallyldimethyl ammonium chloride (PDDA), inhibited Al corrosion effectively. The selective cathodic inhibiting effect of the polymer inhibitors was due to the thick layer of polymer cation, which inhibited H⁺ cations approaching the Al surface.

Onuchukwu [82] studied the corrosion inhibition of aluminium in 0.5M KOH in the presence of hard bases using potentiodynamic polarisation measurements. The hard bases such as Cr₂O₇²⁻, HCO₃⁻, B₄O₇⁻² which acted as anode inhibitors revealed high % inhibition. IE (%) of borax was greater than bicarbonate and dichromate in alkaline medium.

Onuchukwu [83] reported the corrosion inhibition of aluminium in alkaline medium by amines and ethanediithiol using hydrogen gas evolution technique in 0.2 M KOH. The corrosion inhibition efficiency of the inhibitors followed the order: ethylamine < ethylenediamine < ethanediol. Rapid and more reliable results were obtained in the H₂ gas evolution technique compared to the ex-situ measurement such as weight loss method.

Mukherjee and Basumallick [84] examined the behaviour of aluminium dissolution in 1M KOH using aqueous 2-propanol over a wide range of concentrations (0 to 56 vol. %) by potentiodynamic polarisation measurements. The results obtained revealed that 2-propanol acted as a corrosion accelerator at low concentrations. However at high concentrations, corrosion was abated markedly, and at a concentration of 56 vol. % the corrosion rate almost vanished. A blocking effect of the inhibitor occurred at high concentration through interaction via the oxygen centre of the 2-propanol molecule.

Shao et al.[85] examined the corrosion behaviour of aluminium in 1M KOH solution with and without calcium tartarate by weight loss measurement, open-circuit potential measurement, potentiodynamic polarisation and electrochemical impedance spectroscopy. Experimental results showed that the corrosion of
aluminium was inhibited by the addition of calcium tartarate. At high concentrations of calcium tartarate both anodic and cathodic processes were greatly inhibited. At low concentrations of calcium tartarate, selective adsorption of the inhibitor on anodic sites was suggested as the cause for the much stronger effect of the inhibitor on anodic processes than the cathodic processes. The cooperative effect of saturated calcium hydroxide containing 0.02M tartarate in 4M KOH for the corrosion of aluminium was also investigated [86] by hydrogen collection, electrochemical methods and XPS. The results indicated that the inhibitive effect of calcium ion was enhanced by the addition of tartrate ion, while tartrate ion itself showed little inhibition effect.

Oguzie et al. [87] studied the inhibitory action of methylene blue dye in the corrosion of aluminium in aerated KOH at 303 -333K using gravimetric method. The effect of halide additives (KCl, KBr and KI) on the inhibition efficiency of methylene blue dye was also studied. Corrosion rate increased with increase in temperature. The inhibition efficiency of methylene blue dye increased with increase in its concentration and synergistically increased on the addition of halides. The adsorption characteristics of the inhibitor was explained by Freundlich, Langmuir and Frumkin adsorption isotherms.

Oguzie et al. [88] reported the inhibitive effect of congo red (CR) dye for Al corrosion in 2M KOH solution and also evaluated the synergistic effect of halide ions (KCl, KBr, and KI) on the IE of the dye using gravimetric technique. CR inhibited Al corrosion by physical adsorption mechanism. Dye adsorption was increased in the presence of halides in the order: KCl < KBr <KI. In presence of KI IE was increased up to 48.63 and 41.70 per cent at 30 and 60°C respectively.

Wang et al. [89] investigated the influence of zinc oxide and dimethylamine epoxy propane (DE) on the electrochemical behaviour of pure aluminium in 4M KOH solution by means of hydrogen collection, polarisation curves and electrochemical impedance spectroscopy technique. The corrosion of pure aluminium was greatly inhibited by the addition of ZnO and dimethyl amine epoxy propane. It was also found that the addition of DE greatly improved the deposition of zinc layers on aluminium.
Wang et al. [90] reported the corrosion and electrochemical behaviour of pure aluminium in alkaline methanol solutions (1-6M KOH). The results of hydrogen collection experiments revealed that corrosion rate of aluminium in alkaline methanol solutions was lower compared to water based solutions and the corrosion rate increased with increasing water content of the solution. Polarisation measurements revealed that addition of water to KOH methanol solutions improved the anode performance. Scanning electron microscopy and energy dispersive analysis of X-ray revealed the formation of a Al(OH)₃ layer on the surface of the anode.

Oguzie [91] investigated the inhibiting effect of crystal violet dye (CV) on aluminium corrosion in HCl (1mol dm⁻³) and KOH (0.5mol dm⁻³) in the temperature range 30⁰ – 60⁰ C using the gravimetric technique. The effect of iodide ions on the inhibiting effect of CV was also evaluated. IE was 83.6% in 1M HCl and 23.0% in 0.5M KOH. In alkaline solution the IE of CV was synergistically increased in the presence of iodide ions up to 85.3%. The calculated values of activation energy, free energy of adsorption and heat of adsorption confirmed the physisorption mechanism. Freundlich adsorption isotherm was used to explain the adsorption characteristics of CV.

Mercier and Labrousse [92] investigated the influence of 1, 2- diaminoethane (DAE) on the mechanism of aluminium corrosion in 0.1 mol L⁻¹ solution at pH 13 by inductively coupled plasma optical emission spectroscopy, open circuit potential measurements and X-ray photoelectron spectroscopy. In KOH solutions at pH 13 DAE initially behaved as a strong corrosion accelerator due to synergistic effects with the hydroxyl ions.

2.4. Natural inhibitors

Natural products are emerging out as effective inhibitors and are found to be better alternatives for organic and inorganic inhibitors due to their biodegradability, easy availability and non-toxic nature. In recent years, large number of green inhibitors are developed from plant products. Various parts of plants, such as seeds, leaves, flowers, fruits etc., are used as corrosion inhibitors. Plant materials are dried in shade so as to reduce the moisture content present in the various parts of the
plants. Then the active principle is extracted with acids or organic solvents or water. Plant products exhibited good protection even at 60°C. Natural products are organic in nature. Some of the phytoconstituents such as tannins, alkaloids, flavonoids, proteins, aminoacids, pigments and polysaccharides are known to exhibit good corrosion inhibiting abilities [93,94]. Several authors have reported the applications of natural inhibitors for the corrosion of different metals in acidic and alkaline media [95,96].

2.4.1. Inhibitors used in sodium hydroxide medium

Naturally occurring organic compounds such as tannins, gelatin, saponin and agar-agar were often used as inhibitors for aluminium in alkaline medium. It was surmised that the inhibitors extended the pH stability range of the amphoteric oxide and hydroxide layers, repaired the defective oxide and hydroxide films, decreased the diffusion rate of reactant to the surface and also removed the corrosion products from the surface of the metals [97].

El Horary et al.[98] studied the effect of inhibition of Al (in 2N HCl and 1.5M NaOH) and Zn (in 3N HCl and 1N NaOH) using different concentrations of hibiscus subdariffa (karkade) extract using thermometric, weight loss and galvanostatic polarisation methods. The retarding effect on the dissolution of Al and Zn observed was attributed to the presence of small amount of free acids such as citric and malic acid of karkade extract.

Saleh et al. [99] investigated the corrosion inhibition by naturally occurring substances. The effect of the aqueous extract of some seeds (Fenugreek, Lupie), leaves (Opuntia ficus indica, Aloe eru), fruits (Doum) and fruit-peels (Orange, Mango, Pomegranate) on the corrosion of aluminium in 0.1, 1.0 and 1.5M NaOH. The results revealed that most materials afforded comparable inhibition in the three examined NaOH solutions. The high IE obtained for opuntia ficus indica in 1.0 and 1.5M NaOH (85%) reduced to 74% in 0.1M NaOH solution. Orange peels and aloe eru extracts provided more protection 1.0M NaOH than in the other two concentrations.

Priya et al. [100] evaluated the inhibitive effect of aqueous extract of garlic for the corrosion of aluminium in sodium hydroxide solution at pH 11 and 12 in the
absence and presence of Zn$^{2+}$ by weight loss method. The results obtained revealed that the extract accelerated Al corrosion in the absence and presence of Zn$^{2+}$ at pH11.

Umoren et al. [101] studied the inhibitive effect of gum arabic (GA) for the corrosion of aluminium in NaOH (0.1-2.5N) medium and determined its adsorption characteristics using hydrogen evolution and thermometric methods at 30 and 40°C. The results revealed that inhibition efficiency increased with increase in GA concentration and with increase in temperature. Phenomenon of chemical adsorption was proposed for the inhibition and the adsorption process followed the Langmuir and Freundlich adsorption isotherms.

Ayeni et al.[102] studied the corrosion inhibition of Hibiscus teterifa on chill cast Al-Zn- Mg alloy in 0.5M NaOH solution using weight loss method. Various concentrations of the inhibitor (5-20 % v/v) were tested at temperatures of 30, 50 and 70°C. The inhibitive action of the extract was explained on the basis of thermodynamic and kinetic calculations.

Abdel-Gaber et al. [103] reported the inhibition of Al corrosion in 2M NaOH solution in the presence and absence of 0.5M NaCl using damissa extract by using chemical and electrochemical techniques. Damsissa extract was found to be more effective in the presence of chloride ions than in its absence. IE was found to increase with increasing concentration of extract but decreased with increasing temperature.

Umoren et al. [104] investigated the adsorption behaviour and inhibitive effect of vigna unguiculata extract for aluminium corrosion in 0.5M NaOH and H$_2$SO$_4$. The inhibitive effect of the plant extract was assessed using weight loss method at 30 and 60°C. Vigna unguiculata extract effectively inhibited aluminium corrosion in both alkaline and acidic media. Inhibition efficiency of the extract increased with increase in concentration of the extract and temperature. For 0.5 g/L of the extract concentration IE of 77.78% obtained at 30°C was increased to 79.63% at 60°C. Inhibitor adsorption characteristics were approximated by Freundlich and Temkin adsorption isotherms at all the concentrations and temperatures studied.

Umoren [105] studied the influence of iodide ion on the inhibiting effect of gum arabic for the corrosion of aluminium in 0.1M NaOH using weight loss and
hydrogen evolution techniques at 303 and 313 K. The results obtained showed that the inhibiting action of gum arabic was considerably increased by the addition of KI. The adsorption of KI, gum arabic and gum arabic + KI on the aluminium surface followed the Temkin’s adsorption isotherm. With 0.1g/L gum arabic and 0.05 M KI concentration of inhibitor 62.7% IE and 46.9% IE were obtained for weight loss and hydrogen evolution methods respectively at 313K.

Rajendran et al. [106] evaluated the inhibition efficiency of aqueous extract of hibiscus rosasinensis (white) in controlling corrosion of aluminium at pH12 by weight loss method in the absence and presence of Zn$^{2+}$. Polarisation studies revealed that the formulation functioned as a cathodic inhibitor. AC impedance spectra revealed the presence of a protective film formed on the metal surface. FT-IR spectra revealed that the protective film consisted of a complex formed between the active principle of the flower extract and Al$^{3+}$.

Abiola and Otaigbe [107] studied the effect of the extract of phyllanthus amarus leaves on the corrosion of aluminium in 2M NaOH solution using chemical technique. The adsorption of the inhibitor on aluminium surface was in accordance with the Langmuir adsorption isotherm. The inhibition efficiency increased with increase in concentration of the extract. A zero-order kinetic relationship was obtained from the kinetic treatment of the weight loss measurements.

Noor [108] evaluated the potential of aqueous extract of hibiscus sabdariffa leaves for inhibiting the corrosion of Al in 0.5M NaOH using chemical and electrochemical measurements. Results obtained from potentiodynamic polarisation studies showed that the inhibition efficiency increased from 23.09% to 82% with the increase of extract concentration. The protection efficiency of the extract calculated from the weight loss and hydrogen evolution methods were found to be almost 92%. Electrochemical measurements revealed that extract acted as a mixed type inhibitor. Adsorption of inhibitor species was found to follow Langmuir and Dubinin-Radushkevich isotherm models.

Abiola et al. [109] investigated the corrosion inhibition properties of gossipium hirsutum leaves extract and seed extract in 2M NaOH using chemical technique. The leaves extract was found to be more effective than the seed extract.
The inhibition efficiency increased with increasing concentration of the extracts. The leaves extract gave 97% IE and the seeds extract gave 94% at the highest concentration. The inhibitory action was ascribed to the presence of organic compounds in the extract.

Obot and Egbedi [110] investigated the corrosion inhibition of aluminium by ipomoea involcrata in 1M NaOH using the gasometric technique at 30 and 60°C. Results obtained showed that ipomoea involcrata acted as an efficient inhibitor for aluminium corrosion in 1M NaOH. Inhibition efficiency increased with increase in concentration of the inhibitor and decreased with increase in temperature. The adsorption of inhibitor was in accordance with Langmuir adsorption isotherm at the temperatures studied.

Rajalakshmi et al. [111] evaluated the inhibition efficiency of abrus precatorius extract in 4N NaOH at ambient temperature using conventional weight loss and polarisation measurements. The seed extract of abrus precatorius acted as an effective inhibitor at different concentration at different time intervals.

Abdel-Gaber et al. [112] examined the inhibition efficiency of a package containing lupine seed extract and cetyl trimethyl ammonium bromide surfactant for the corrosion of aluminium in 2M NaOH using chemical, gasometry and electrochemical measurements. Potentiodynamic polarisation curve measurements showed that lupine seed extract controlled both anodic and cathodic reactions. The presence of both the surfactant and lupine seed extract did not indicate synergistic action between them.

Nanna et al. [113] studied the inhibitive effect of euphorbia hirta on the corrosion of aluminium alloy of type AA 3003 corrosion in 0.5M HCl and 0.25M NaOH using gravimetric technique at 30 and 60 °C. Results obtained showed that the IE of the leaves extract varied with concentration, temperature and exposure time. The inhibiting effect of euphorbia hirta and dialum guineense leaves extracts in 0.25M NaOH for the AA 3003 alloy was also studied using weight loss method [114]. The %IE depended on the concentration of the leaves extracts as well as on the time of exposure of the aluminium samples in 0.25M NaOH solutions containing the leaves extracts. Best inhibition of 87 % at 303 K and 82.4% at 333 K for Al
corrosion was shown by dialum guineense leaves extracts and it was attributed to the planar orientation of the adsorbed extract molecules.

Singh and Quraishi [115] reported the corrosion inhibition properties of piper longum fruit extract and bacopa monnieri stem extract in 1M NaOH using chemical technique. Both extracts inhibited the corrosion of aluminium in NaOH solution. The inhibition efficiency increased with increasing concentration of the extracts. The piper longum fruit extract was found to be more effective than bacopa monnieri stem extract. 95% IE was obtained for the fruit extract.

The stem extract of bacopa mannieri was investigated as a corrosion inhibitor in 0.5M NaOH using potentiodynamic polarisation, EIS and weight loss measurements by Singh et al. [116]. The results obtained in potentiodynamic polarisation technique, revealed that the extract was proved to be a mixed type inhibitor for aluminium in alkaline solution by suppressing both anodic and cathodic reaction on the metal surface. The Langmuir adsorption isotherm model fitted well with the results obtained from weight loss measurements.

Singh and Quraishi [117] investigated the corrosion behavior of Al in 0.5M NaOH solution in presence of Azwain (Trachyspermum copticum) seed extract by weight loss and electrochemical techniques. Adsorption of inhibitor molecules on the surface of aluminium followed Langmuir adsorption isotherm model. Tafel polarisation data indicated that the studied compound was a mixed type inhibitor.

Ambrish singh et al.[118] investigated the inhibiting action of piper longum seed extract for the corrosion of aluminium in 1M NaOH using potentiodynamic polarisation, electrochemical impedance spectroscopy methods and weight loss measurements. The extract behaved like a mixed type inhibitor for aluminium in alakline solution.

The effect of aqueous extract of adathoda vasica leaves (AVL) on the corrosion inhibition of Al in 1N NaOH solution was studied using chemical and electrochemical techniques by Lakshmi prabha et al. [119]. IE of the extract increased with the increase of AVL extract up to a concentration of 800 ppm. Electrochemical measurements revealed that AVL extract acted as a mixed type inhibitor. The protective film formed on the metal surface by the adsorption
of water soluble chemical constituents of AVL extract was confirmed using SEM study.

Lakshmi Prabha et al. [120] studied the effect of aegle marmelos leaves (AML) extract on the corrosion inhibition of aluminium in 1N NaOH solution using chemical and electrochemical techniques. It was found that the inhibition efficiency increased with the increase of AML extract upto 800 ppm. The results obtained from chemical and electrochemical measurements are in reasonably good agreement. The potentiodynamic polarisation studies revealed that the AML extract acted as mixed type inhibitor. Adsorption of AML extract on aluminium surface followed Langmuir adsorption isotherm. The surface characteristics of the inhibited and uninhibited aluminium were investigated by scanning electron microscope studies.

Irshedat et al. [121] evaluated the effect of the extract of Lupinus varius L. for the corrosion of Al in 1M NaOH solution using weight loss technique. Lupinus varius L. extract inhibited the corrosion of Al in 1M NaOH solution and the inhibition efficiency increased with increasing concentration of the extract and decreased with increasing temperature. The adsorption of the inhibitor molecules on Al surface followed Langmuir and Temkin adsorption isotherms.

Sangeetha et al [122] reviewed the significance of extracts of green inhibitors for corrosion inhibition of aluminium and its alloys. The various methods employed for the estimation of effectiveness of the corrosion inhibitors were also discussed.

2.4.2. Inhibitors used in potassium hydroxide medium

Oguzie et al.[123] evaluated the inhibiting effect of ocimum basilicum extract on aluminium corrosion in 2M HCl and 2M KOH solutions by gasometric technique at 30 and 60° C. The extract inhibited Al corrosion in the acidic and alkaline environments. IE increased with increase in concentration of inhibitor but decreased with increase in temperature. For the system with10 per cent extract and 5.0mM KI 84.46% IE was obtained in 2M HCl and 77.19% was obtained for 2M KOH at 30° C. Physisorption mechanism was explained by analyzing the data obtained from kinetic and activation parameters for corrosion and adsorption.
process. Halide additives synergistically increased the IE of ocimum basilicum extract in the order Cl<sub>1</sub> < Br<sub>1</sub> < I<sub>1</sub>.

Oguzie [124] examined the inhibitive action of leaves extract of sansevieria trifasciata on aluminium corrosion in 2M HCl and 2M KOH using the gasometric technique. The results revealed that the extract acted as a good inhibitor in both environments and inhibition efficiency increased with concentration of the extract. IE of 94.3% and 95.3% were obtained for the 50 v/v% concentration of the extract in 2M HCl and 2M KOH respectively at 30<sup>0</sup> C. Synergistic effect of halides increased the IE of the extract. A decrease in IE was observed with increase in temperature and corrosion activation energies increased in the presence of the extract. Physical adsorption mechanism was proposed for the inhibition behaviour.

Oguzie et al. [125] reported the effectiveness of gongronema latifolium extract as an environmentally friendly corrosion inhibitor for aluminium in 2M HCl and 2M KOH environments. Corrosion rates were determined using the gas-volumetric technique. The IE increased with concentration up to 97.54 and 90.82 per cent in 2M HCl and 2M KOH respectively. Temperature studies revealed that the extract was chemically adsorbed on the aluminium surface at all concentrations in 2M HCl and physically adsorbed in 2M KOH.
2.5. SCOPE AND AIM OF THE PRESENT WORK

Aluminium and its alloys are widely used in many industrial applications, mainly in aerospace, reaction vessels, pipes, and in marine applications. But due to high reactivity of aluminium these materials undergo corrosion. Alkaline solutions are employed in industrial operations such as pickling, chemical or electrochemical etching and cleaning of aluminium and to improve efficiency of aluminium/air batteries. Al/alkaline systems are also found in nuclear reactors during a loss of a coolant accident. The pH of the chemical environment produced by the introduction of coolant into the emergency cooling system is around 10. Generally in industrial processes corrosion inhibitors are added to alkaline media to mitigate corrosion of aluminium due to dissolution of the protective oxide film on the surface of aluminium.

Research works have been reported earlier for the corrosion of aluminium in alkaline medium using organic and inorganic inhibitors. It is a challenging task to develop new environment friendly, renewable, cost effective natural inhibitors as successful alternatives to chemical inhibitors which are currently employed in industrial processes. While using plant extracts as inhibitors complicated preparative steps are not required, operating cost is reduced and it involves economical usage of chemicals. Various parts of plants such as root, stem, leaves, seed, and fruit peel are reported earlier as natural inhibitors for aluminium in acidic, alkaline and neutral environments. But so far no published information is available in literature about the use of five different plants namely Coleus aromaticus, Mentha piperita, Moringa oleifera, Solanum nigrum and Vitex negundo for the corrosion of aluminium in 1M NaOH solution.

The present work aims to investigate the anti-corrosive properties of aqueous extract of the above mentioned plants for the corrosion of aluminium in 1M NaOH aggressive medium. The work aims to estimate the effectiveness of the inhibitors using chemical and electrochemical techniques. It is aimed to examine the adsorption of inhibitor molecules on the aluminium metal surface using surface morphological studies. The work also aims to confirm the functional groups of the active principles of the leaves extract, and the presence of Al\(^{3+}\) leaves extract complex on the metal surface by means of FT-IR spectral study.
2.5.1. Objectives of the present work

Work plan of the present investigation includes the following objectives:

- To study the inhibition efficiency of five leaves extracts in 1M NaOH for aluminium corrosion at room temperature.
- To evaluate the effectiveness of the leaves extracts at different immersion time intervals.
- To estimate the effect of temperature on the corrosion of aluminium in the absence and presence of inhibitors using weight loss method.
- To determine the inhibition behaviour of leaves extracts from the volume of hydrogen gas evolved during corrosion of aluminium in 1M NaOH using gasometric method.
- To calculate corrosion current density, corrosion potential and to classify the inhibitor as anodic, cathodic or mixed type using Tafel extrapolation method.
- To evaluate solution resistance, charge transfer resistance and double layer capacitance of the metal/solution interface by electrochemical impedance spectroscopy.
- To reveal the presence of the adsorbed film on the metal surface by surface examination study.
- To analyze the adsorption film on aluminium surface using Fourier Transform-Infrared spectral study.
- To reveal the nature and mechanism of adsorption using kinetic and thermodynamic calculations.
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58