

# Chapter 2

## Inhibitor

### 2.1. Background of Corrosion Inhibitor

A studied topic in the field of corrosion inhibitor is one of the most important tools for mitigation of material. Large numbers of books and journals have been published on this subject [1-5]. Several **seminars** and **conferences** on corrosion discuss the development and application of corrosion inhibitor [6-33]. The natural products that have been used as corrosion inhibitors for metallic protection could be traced to the last half of the **19<sup>th</sup> century** [34]. The first research in corrosion inhibition was given to **Baldwin** [35] which involved the use of **molasses and vegetable oils**. Organic molecules operating as corrosion inhibitors were developed in the petroleum industry in the 1950's and concrete industry in the early 1990's. **Marangoni and Stephanelli** used extract of *glue, gelatin and bran* to inhibit the corrosion of metal in HCl acid [36-38].

### 2.2. Corrosion Inhibitor

Corrosion inhibition is reversible and a minimum concentration (**e.g.~10<sup>-4</sup>M**) of the inhibiting compound is required to maintain the inhibiting surface film. Inhibitors are usually too high to be commercially feasible for the reduction of the corrosion rate of the metal [39-41]. Good circulation and the absence of any stagnant areas are also needed to maintain inhibitor concentration. While using a corrosion inhibitor for a specific problem it is essential to make a proper selection of corrosion inhibitor, as **no universal corrosion inhibitor** exists. Inhibitor being a complicated subject may cause potential hazards also. Inhibitor efficiency (IE) is given as:

$$IE \% = \frac{I_{\text{Corr}} - I_{*\text{Corr}}}{I_{\text{Corr}}} \times 100$$

Where  $I_{\text{Corr}}$  &  $I_{*\text{Corr}}$  is the corrosion current with inhibitor & without inhibitor respectively.

### 2.3. Importance of Corrosion Inhibition

In India professional organization such as the *Central Electrochemical Research Institute (CECRI)* and other parts of the world *National Association of Corrosion Engineers (NACE)* provide **Corrosion Education and Training which includes research, Degree programs, Certification program and General education.** Few **National Universities and Colleges** offer courses in Corrosion and Corrosion Control as part of their engineering curriculum [42-44].

There are two important reasons why **Scientists and Engineers** are interested in methods to control or inhibit corrosion by the use of corrosion inhibitor. The first is the issue of **safety**. The second reason is an **Economical Impact** [45-48].

### 2.4. Classification of Inhibitors

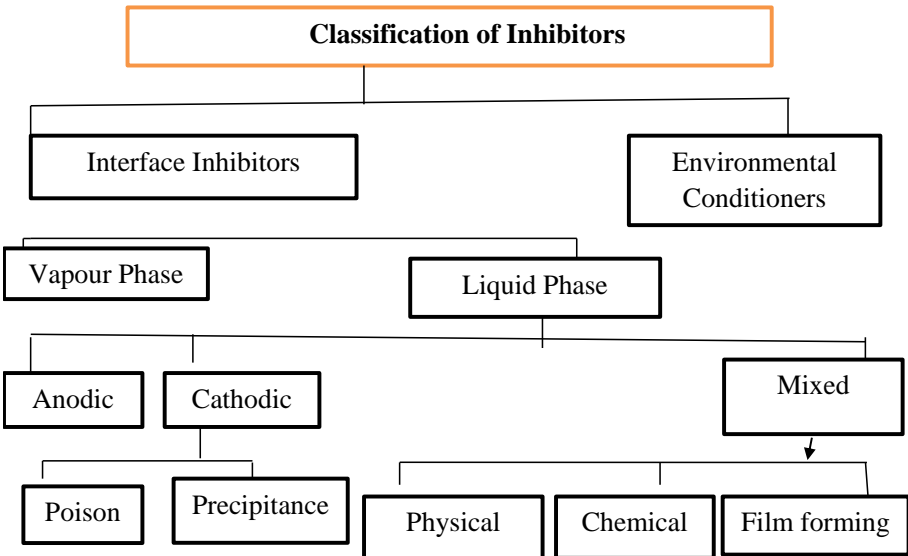
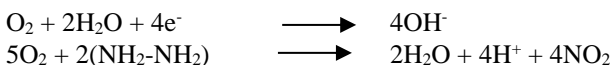


Fig. 8. Classifications of Inhibitors

### 2.5. Environmental Conditioners (Scavengers)

Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called Environmental Conditioners or Scavengers



## 2.6. Interface Inhibitors

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid and vapor-phase inhibitors.

## 2.7. Liquid-Phase Inhibitors

When adsorption occurs (or may occur) at the interface between a fluid phase and a solid, the solid is usually called the adsorbent; for gas/liquid interfaces it may be in some, but not in all cases useful to call the liquid/gas phase adsorbent as Liquid-phase inhibitors. This system is classified as anodic, cathodic or mixed inhibitors, depending on whether they inhibit the anodic, cathodic or both electrochemical reactions.

## 2.8. Vapor-Phase Inhibitors (VPI)

The process of vapor-phase inhibition involves two steps: transport of inhibitor to the metal surface and interaction of inhibitor on the surface. AVPI may first dissociate and then vaporize. Example: dicyclohexylamine.

## 2.9. Anodic Inhibitors

Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. Anodic inhibitors are often called passivating inhibitors.

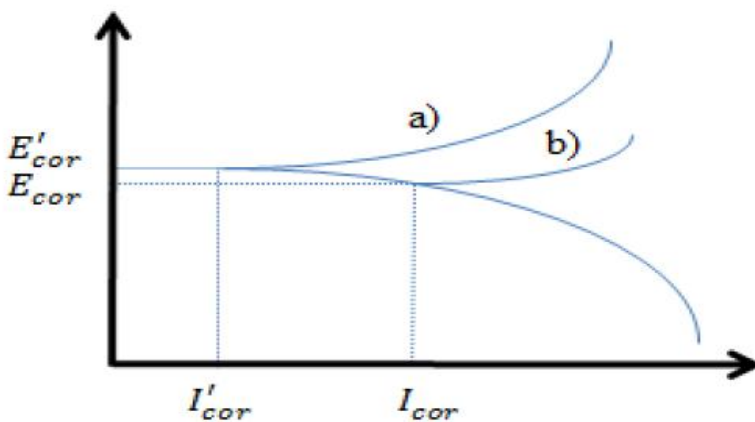
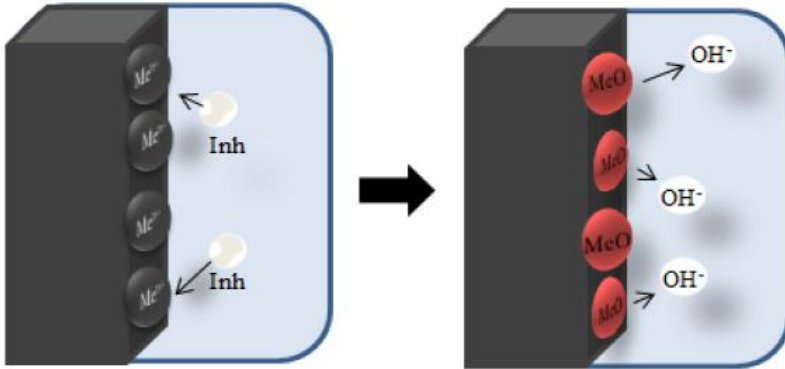


Fig. 9. Mechanism of Anodic Inhibitor

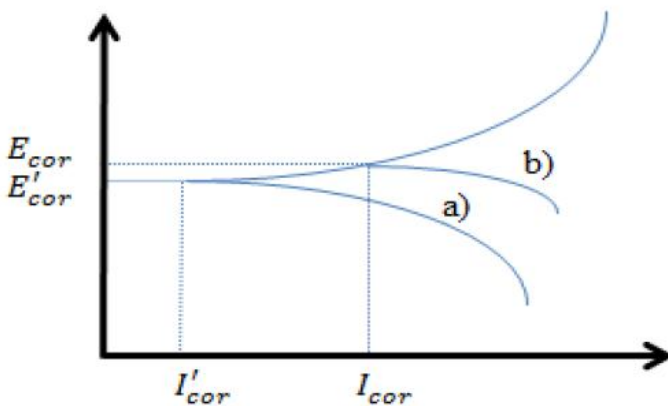
The mechanism of anodic inhibition can be explained using the polarization diagram of an active passive metal. In the absence of inhibitors, the metal corrodes in the active state at a rate corresponding to point. As the concentration of inhibitor is increased, the corrosion rate also decreases until a critical concentration and a critical corrosion rate (*Fig. 10*) are reached.



**Fig. 10.** Anodic aspects of Corrosion Inhibition

## 2.10. Cathodic Inhibitors

Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons example; sulfides and selenides) or by precipitating selectively on the cathodic areas (cathodic precipitators Examples arsenic, bismuth, and antimony).



**Fig.11.** Mechanism of Cathodic Inhibitor

The effect of a cathodic inhibitor on the polarization curves is shown in *Fig. 12*. In

this case, the slope of the anodic polarization curve is unaffected, but the slope of the cathodic polarization curve is changed [49-50].

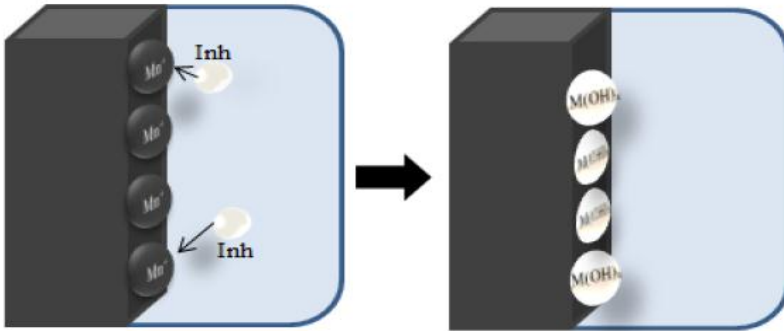


Fig. 12. Cathodic aspects of Corrosion Inhibition

## 2.11. Mixed Inhibitors

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation [51-56].

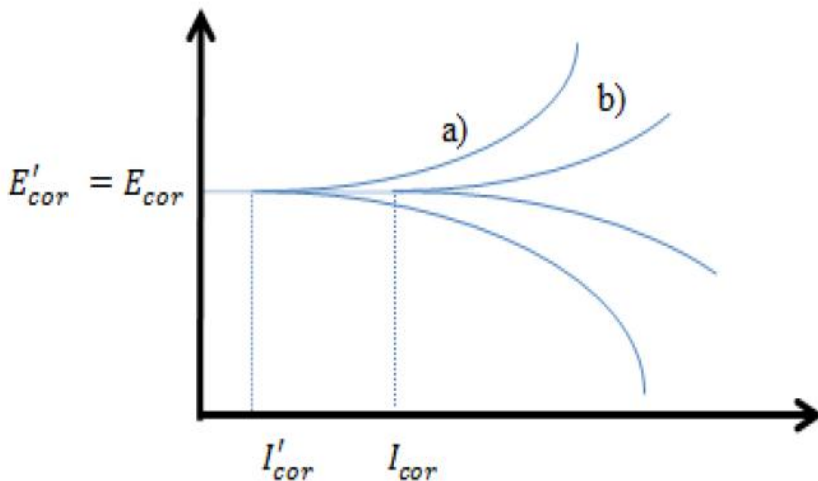


Fig. 13. Mechanism of Mixed Inhibitor

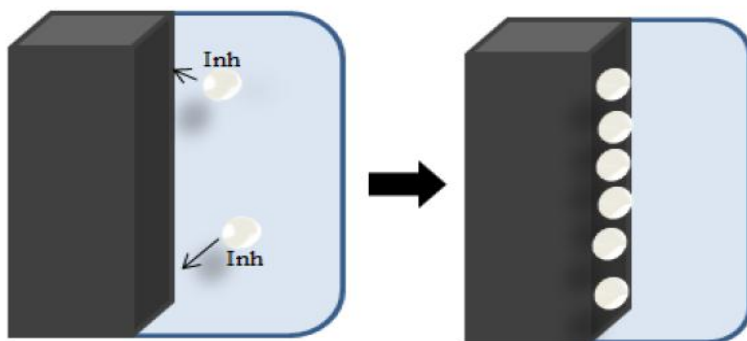


Fig. 14. Mixed aspects of Corrosion Inhibition

## 2.12. Adsorption Studies

The material in the adsorbed state is called the *adsorbate*. Adsorption is the enrichment (positive adsorption) or depletion (negative adsorption) of one or more components (or both of the bulk phases and capable of being adsorbed) of the phases forming the interface. It is said to form a spread layer (often spread monolayer when the layer is known to be only one molecule in thickness). The adsorption theory of protective activity has been proposed by most workers, which says that inhibitors are absorbed (the term adsorption may also be used to denote the process) on the metal surface forming a protective layer.

## 2.13. Types of Adsorption

The adsorption was considered either as Physical or Chemical adsorption.

### 2.13.1. Physisorption

Physisorption (or physical adsorption) is an adsorption in which the forces involved are intermolecular forces (Vander Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term Vander Waals adsorption is synonymous with physical adsorption, but its use is not recommended.

### 2.13.2. Chemisorptions

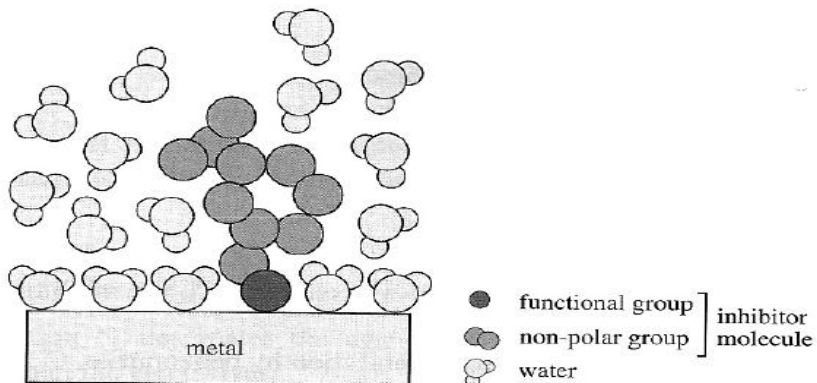
Chemisorptions (or chemical adsorption) is an adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. No absolutely sharp distinction can be made and intermediate cases exist. For example, adsorption involving strong hydrogen bonds or weak charge transfer.

**Table 1.** Difference between Chemical and Physical Adsorption

<b>Physisorption</b>	<b>Chemisorption</b>
Forces of attraction are Vander Waals' forces	Forces of attraction are chemical bondforces
Low enthalpy of adsorption (20-40) KJ/mole	High enthalpy of adsorption (200-400) KJ/mole
This process is observed under conditions of low temperature	This process takes place at high temperatures
Not specific	Highly specific
Multi-molecular layers may be formed	Generally, monomolecular layer is formed
This process is reversible	This process is irreversible

## 2.14. Adsorption from Liquid Mixtures

Adsorption from liquid mixtures is said to have occurred only when there is a difference between the relative composition of the liquid in the interfacial layer and that in the adjoining bulk phase(s) and observable phenomena results from this difference. For liquids, accumulation (positive adsorption) of one or several components is generally accompanied by depletion of the other(s) in the interfacial layer which is smaller than the adjoining bulk liquid. Negative adsorption may occur also in the case of adsorption from highly compressed gas mixtures. For liquid/liquid interfaces an arbitrary unsymmetrical nomenclature may not be appropriate [57].

**Fig.15.** Mechanism of Adsorption

## 2.15. Adsorption isotherm

In this section, different adsorption isotherms are discussed. Isotherms describe adsorption using the relationship between the amounts of adsorbate (inhibitor molecules) which is adsorbed on the adsorbent (surface of mild steel). The adsorption isotherms explored are the **Langmuir isotherm, Hasley, Freundlich, Pearson, Bockris-swinkless, De Boer, Hills El-Awardy, Dhor-Flory-Huggins, Temkin isotherm, Flory-Huggins (FH) isotherm** and **Frumkin isotherm**. From the suitable plot, the free energy of adsorption of the organic inhibitor can be obtained [58-61].

**Table 2.** Various isotherms and the corresponding equation

S.No	Adsorption	Plots
1	Temkin Isotherm	$\theta$ versus $\log C$
2	Frumkin Isotherm	$\log C$ versus $\theta$
3	Langmuir isotherm	$C/\theta$ versus $C$
4	Flory-Huggins Isotherm	$\log (\theta/C)$ versus $\log (1 - \theta)$
5	Freundlich isotherm	$\log (\theta/C)$ versus $\theta$

## 2.16. Gibbs Free Energy

The equilibrium adsorption constant (K) is determined from the adsorption isotherm and can be used to find the standard Gibbs free energy of adsorption using  $\Delta G_{ads} = -2.303 RT \log (55.5 K)$

Where T is the temperature in Kelvins and R is the universal gas constant.

## 2.17. Industrial applications of corrosion inhibitors

1. Petroleum Production
2. Internal Corrosion of Steel Pipelines
3. Water
4. Automobile
5. Paint

## 2.18. Corrosion behaviour of mild steel in different selective media

1. Acidic environment included HCl, H<sub>2</sub>SO<sub>4</sub>
2. Sea Water environment
3. Base medium



---

## References

- [1] P. Muthukrishnan, B. Jayaprabha and P. Prakash, *Arabian J Chem*, Vol. no. 5, 288-291, 2013.
- [2] L. Y. S. Helen, A. A. Rahim, B. Saad, M. I. Saleh, P. Bothi Raja, *Int. J. Electrochem. Sci.*, Vol. no. 9, 830-846, 2014.
- [3] H. Elmsellem, M. H. Youssouf, A. Aouniti, T. Ben Hadda, A. Chetouani and B. Hammouti, *Russian J. Appl Chem*, Vol. no. 87(6), 744-753, 2014.
- [4] Patchaiah Kalaiselvi, Subbaiah, Chellammal, Seeni Palanichamy and Gopalan Subramanian, *Mat. Chem and Phy* Vol. no.120, 643-648, 2010.
- [5] E. E. Oguzie *Corr. Sci*, Vol. no. 50, 2993-2999, 2008.
- [6] F. Zucchi and I. H. Omar, *Surface Technology*, Vol. no. 24(4), 391-399, 1985.
- [7] Subramaniam Leelavathi, R. Rajalakshmi, *Adv. mater and corr*, Vol. no 1(1), 47-56, 2012.
- [8] K. F. Khaled, *Int.J.Electrochem. Sci*, Vol. no. 3 462-475, 2008.
- [9] M. Shyamala and A. Arulanantham, *J. Mat. Sci and Tech*, Vol. no. 25(5), 633-636, 2009.
- [10] P. R. Sivakumar and A. P. Srikanth, *Asian Journal of Chemistry*, Vol. no. 29(2), 274-278, 2017.
- [11] A. Bouyanzer, B. Hammouti, and L. Majidi, *Materials Letters*, Vol. no. 60(23), 2840-2843, 2006.
- [12] S. Subhashini, R. Rajalakshmi, A. Prathipa, and A. Mathina, *E-J Chemistry*, Vol. no.7 (4), 1133-1137, 2010.
- [13] P. R. Sivakumar, A. P. Srikanth, *Inter J. Physical and App Sci*, Vol. no. 3(1), 10-20, 2016.
- [14] R. Saratha and V. G. Vasudha, *E-J. Chem*, Vol. no. 7(3), 677-684, 2010.
- [15] A. Singh, I. Ahamad, B. K. Singh, and M. A. Quraishi, *J. Solid State Electrochemistry*, Vol. 15, 1087-1097, 2011.
- [16] M. Karuppusamy, P. R. Sivakumar, S. Perumal, A. Elangovan and A. P. Srikanth, *J. Environ. Nanotech*, Vol. no. 4(2), 09-15, 2015.
- [17] M. Shyamala and A. Arulanantham, *Asian J. Chem*, Vol. no. 21(8), 6102-6110, 2009.
- [18] P. C. Okafor, E. E. Ebenso, and U. J. Ekpe, *Int J Electrochem Sci*, Vol. no.5 (7), 978-993, 2010.
- [19] M. Mobin, M. A. Khan, M. Parveen, *J. Appl. Poly. Sci.*, Vol. no. 121, 1558-1565, 2011.
- [20] S. Ashok Kumar, M. Gopiraman, M. Saravana Kumar, A. Srikanth, *Ind Eng Chem Res*, Vol. no. 50, 7824-7832, 2011.
- [21] N. O. Eddy, F. E. Awel, C. E. Gimbal, N. O. Ibisi, E. E. Ebenso, *Int. J. Electrochem. Sci.*, Vol. no. 6, 931-956, 2011.
- [22] K. O. Orubite, N. C. Oforka, *Mater Lett* Vol. no. 58: 1768-1772, 2008.
- [23] S. A. Umoren, O. Ogbobe, I. O. Igwe, E. E. Ebenso, *Corr Sci*, Vol. no. 50, 1998-2006, 2008.
- [24] A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros Sci.*, Vol. no. 45,

- 33-35, 2003.
- [25] M. Lebrini, F. Robert, A. Lecante, and C. Roos, *Corr Sci*, Vol. no. 53(2), 687-695, 2011.
- [26] A. Sharmila, A. A. Prema, and P. A. Sahayaraj, *Rasayan J. Chem*, Vol. no.5, 2008.
- [27] A. Singh, V. K. Singh and M. A. Quraishi, *Int J. Corr*, Vol. 2010, 275983, 10, 2010.
- [28] D. L. Lake, *Corrosion Prevention and Control*, 35 (4), 113, 1988.
- [29] A. Ostovari, S. M. Hoseinieh, M. Peikari, S. R. Shadizadeh and S. J. Hashemi, *Corros. Sci.*, 51, 1935, 2009.
- [30] J O'M. Bockris, B. Yang, *J. Electrochem. Soc.*, 138, 2237-2252, 1991.
- [31] G. Schmitt, *Institute of Materials, London*, 64, 1994.
- [32] V. S. Sastri, J. R. Perumareddi *Corros.*, 53, 617, 1997.
- [33] K. Babić-Samardžija, K. F. Khaled and N. Hackerman *Anti Corros. Method Mat.*, 52, 11, 2005.
- [34] B. G. Clubley, *Royal Society of Chemistry, Cambridge*, 1990.
- [35] M. A. Quraishi, M. Wajid Khan, M. Ajmal, S. Muralidharan and S. Venkatakrisna Iyer *Anti-Corros. Method. Mater*, 43, 5, 1996.
- [36] S. Muralidharan, S. Venkatakrisna Iyer, *Anti-Corros. Method. Mater*, 44, 100, 1997.
- [37] I. B. Obot, N. O. Obi-Egbedi and S. A. Umoren, *Int. J. Electrochem. Sci.*, 4, 863, 2009.
- [38] J. Sinko *Prog. Org Coat.*, 42, 267, 2001.
- [39] L. A. Nnanna, B. N. Onwuagba, I. M. Mejeha and K. B. Okeoma, *Afr. J. Pure Appl. Chem.*, 4, 11, 2010.
- [40] P. Nagarajana, J. Morris Princya, J. Christy Ezhilarasia, D. Kavithaa and N. Sulochana *J. Ind. Council Chem.*, 26, 153, 2009.
- [41] P. Deepa Rani, S. Selvaraj, *J. Phytol.*, 2, 58, 2010.
- [42] A. M. Al-Turkustani, S. T. Arab and R. H. Al-Dahiri, *Modern Applied Sci*, 4, (5), 2010.
- [43] E. Emeka Oguzie, *Portugaliae Electrochimica Acta*, 26, 303, 2008.
- [44] A. K. Satapathy, G. Gunasekaran, S. C. Sahoo, K. Amit and P. V. Rodrigues, *Corros. Sci.*, 51, 2848, 2009.
- [45] E. E. Oguzie, *Corro Sci.*, 49, 3, 1527, 2007.
- [46] M. B. M. Ali, K. Kannan, *J. Appl. Sci. Environ. Manage*, 13, 27, 2009.
- [47] S. A. Verma, M. N. Mehta, *Transact. Socie. Advan. Electrochem. Sci. Techn.*, 32,4, 1997.
- [48] A. Mesbah, C. Juers, F. Lacouture, S. Mathieu, E. Rocca, M. Francois and J. Steinmetz *Solid State Sci.*, 9, 322, 2007.
- [49] P. C. Okafor, V. I. Osabor and E. E. Ebenso *Pigment Resin Technol.*, 36, 299-305, 2007.
- [50] K. Anuradha, R. Vimala, B. Narayanansamy, J. Arockia Selvi and S. Rajendran, *Chem. Eng. Commun.*, 195, 352, 2008.
- [51] Peter C. O., Eno E. E. and Udofot J. E. *Int. J. Electrochem. Sci.*, 5, 978, 2010.
- [52] Lebrini M., Robert F., Blandinières P. A. and Roos C. *Int. J. Electrochem.*

- 
- sci., 6, 2443, 2011.
- [53] Sharma M. K., Arora P., Kumar S., Mathur S P. and Ratnani R. Corros. Eng. Sci. Technol., 43, 213, 2008.
- [54] Gopiraman M., Sakunthala P., Kanmani R., Alex R. V. and Sulochana N Int. J. Ionics., 17, 843, 2011.
- [55] Xiang-Hong L., Shu-Duan D. and Hui F. J. Appl. Electrochem., 40, 1641, 2010.
- [56] Sivaraju M., Kannan K. Int. J. Chem. Tech. Res., 2, 1243, 2010.
- [57] Chetouani A., Hammouti B. Bull. Electrochem., 19, 23, 2001.
- [58] Okafor P. C., Ebenso E. E. Pigment Resin Technol., 36, 134, 2007.
- [59] Bouyanzer A., Hammouti B. and Majidi L. Mat. Lett., 60, 2840, 2006.
- [60] Oguzie E. E., Mater. Chem. and Phys., 99, 441, 2006.
- [61] Shivakumar S. S., Mohana K. N., Adv. Appl. Sci. Res., 3, 3097, 2012.