Available online at http://www.journalijdr.com

International Journal of DEVELOPMENT RESEARCH

ISSN: 2230-9926

International Journal of Development Research
Vol. 6, Issue, 03, pp. 7007-7011, March, 2016

Full Length Research Article

CORROSION INHIBITION EFFECT OF TEA BYPRODUCT WATER EXTRACT ON MILD STEEL IN H_2SO_4 AND APPLICATION

[1]Vu Minh Tan, [2]Luc Van Thu and *[3]Le Xuan Que

[1]Hanoi University of Industry
[2]Thainguyen Teacher Training College,
[3]Institute for Tropical Technology –VAST, Vietnam

ARTICLE INFO

Article History:

Received 21st December, 2015
Received in revised form
28th January, 2016
Accepted 11th February, 2016
Published online 31st March, 2016

Key Words:

Green tea, Byproduct,
Corrosion Inhibition, Tea Glue

ABSTRACT

Water extract of green tea byproducts was examined as a corrosion inhibitor for mild steel in H_2SO_4 acid solution using the open circuit potential (E_{oc}) measurement, the polarization technique and electrochemical impedance spectroscopy. The E_{oc} measurement and polarization studies showed a strong corrosion inhibition of the extract. E_{oc} and the inhibition efficiency (H) were found to increase with increasing the extract quantity in the acid solution. The corrosion inhibition of the extract affected both anodic and cathodic reactions. The mechanism of inhibition is an adsorption forming different barriers on the metal surface in both anodic and cathodic branches. The results showed that the extract could play significant role as a corrosion inhibitor for mild steel in H_2SO_4 environment, and that contributed forward an application for preparation of an industrial pickling solution.

INTRODUCTION

Metal is one of the most popular materials even for long next time in 21st century. The largest industrial application of metal has been in construction with well known family of mild steel, in the other word construction steel. This steel is also largely used in many other industrial processing. Unfortunately the steel is not resistant in acid solutions which are used widely in industry, mostly as acid pickling, industrial acid cleaning, acid descaling and oil well cleaning. In order to restrain the oxidation attack of the acid solution on metallic materials it is necessary to add different corrosion inhibitors to the acid solutions. Corrosion inhibitors can be defined as chemical compounds that are capable to prevent metal from further degradation (corrosion) only with a small concentration in the aggressive environment. For example, potassium-chromate and sodium-nitrite can act as effective corrosion inhibitors in an acid solution (Okeniyi *et al*., 2014). However, these compounds are hazardous for the health and ecosystem (Fu etal., 2010; Mennucci *et al*., 2009). In fact many countries have banned the use of chromate as corrosion inhibitors. A lot of synthesized organic inhibitors have been studied, most of them containing nitrogen, oxygen and multiple bonds in the molecules, most of which can strongly adsorb on the metal surface forming a resistant inhibition layer and reducing an attack of the acid solutions. However, the toxic effects of most synthetic corrosion inhibitors have led to the research of green alternatives that are environmentally friendly and harmless (Znini *et al*., 2012; Ambrish Singh *et al*., 2012; Husnu Gerengi *et al*., 2012). Recently, most of the investigations were directed towards research for green corrosion inhibitors from natural products (Husnu Gerengi *et al*., 2012; Abiola and James, 2010; Raja, 2009; Obot, 2010; Fernando Sílvio de Souza *et al*., 2012; Trindade and Gonçalves, 2009). Instead of the synthesized corrosion inhibitors, natural products, as extract of common plants have been alternatively used because of the biodegradability, eco-friendliness, low cost and easy availability from renewable sources of materials (Afidah *et al*., 2007; Afidah, 2008; Farreira *et al*., 2004; Osman *et al*., 2003). In the context anticorrosion effects of natural polyphenol have been studied (Afidah *et al*., 2007; Yuasa *et al*., 2000). The well known polyphenol source is green tea, one of the important tropical natural products in Vietnam. The green tea principal products are very rich in polyphenol, strong antioxidants making the tea so valuable, consequently are very expensive and not suitable for the other application, excepting well known tea drinks. However there are green tea byproducts, such as old leaves, tea powders occurred during green tea production, which are cheap enough for next treatment such as recuperating polyphenol and other products.

Corresponding author: Le Xuan Que,
Institute for Tropical Technology –VAST, Viet nam.

Practically, the felling of old tea branches and leaves is a important planting technique to generate the new tea buds. Every year hundreds of thousands of tons of felled tea by-products that have not been recovered - processed, but still throw away causing pollution and emission of greenhouse gas. One of the suitable exploitation of the felled tea byproducts is a water extraction to recovery natural products such as polyphenol, caffeine, or a mix in form of tea water extract, tea glue or mix powders. Those products can be used as a corrosion inhibition in acid solutions, and forward to prepare industrial pickling liquids. This paper presents an investigation result on the possibility of tea byproduct recovery forming corrosion inhibitors for mild steel in acid environment.

EXPERIMENTAL TECHNIQUE

Tea old leaves extracts and tea glues

The tea old leaves are harvested in Tancuong village - Thainguyen province, in spring season. After being well washed using distilled water the leaves freshly extracted in boiling water, at mass ratio tea leaves / water 1:10. The extraction was repeated at the same ratio with recuperated water from previous extract concentration. The final extracts were mixed, filtrated, and then boiled down to prepare tea glues (Vietnam Pharmacopoeia, 2012).

There are four types of the glues: liquid, soft, concentrated and dried.

- Liquid glue: Liquid syrup, pouring it easy, the specific weight > 1.1 kg / liter
- Plastic glue: Liquid dense glue, with the water ratio of 20% to 25%
- Dense glue: Type plastically dense with water ratio 12% - 15%
- Dried glue: Water ratio is no more than 5%, can be pulverized, existing in powder types.

In this work the tea glue was prepared in form of plastic glue, the water rate is 22%. The glue then are well air hermetically packed and preserved in room temperature.

Electrochemical inhibition study procedure

The tea glue was washed the grease by n-Hexane to prepare corrosion inhibitors, then dissolved in H_2SO_4 1M solution at concentration 5g/l as the experimental inhibition solution. The electrochemical experiments were carried out in 200ml of H_2SO_4 1M solution, with different tea glues concentrations, which are marked as M0- 0.0g/l of the inhibition solution, M1-0.2g/l, M2-0.4g/l and M3-1.0g/l. The other examination has been carried out up to glue concentration 5g/l. Electrochemical potentiostat is AUTOLAB PGSTAT 30 (Eco Chemie B.V. Utrecht, The Netherlands) connect to a PC with Window XP. Two readily installed software GPES 4.9 and FRA 4.9 control the measurement system and also analyze the experimental data. Measurement system is three electrodes glass cell. Working electrode is a plate steel of 1cm^2 effective surface. Coating electrode of larger surface was prepared from Pt wire. Electrochemical bridges were used for connecting a compartment of saturated calomel electrode (SCE) to the cell.

Steel sample was domestic Thainguyen product, TCVN 1656-75, with composition as follow:

Elements	C	Mn	Si	P	S	Fe	Cr	Cu
Weight %	0.34	0.51	0.19	0.017	0.035	98.7	0,044	0.1

The steel samples, as a working electrode in the electrochemical cell, were cut in cylindrical form of nearly 1cm^2 profile, then polished around before being enclosed in epoxy resin with electric contact. The electrodes surface then was polished using abrasive papers of grades 400, 600, 800, 1000, 1200, and then cleaned in distilled water following rinsing in technical alcohol and then drying in hot air current. The previously prepared electrodes then were protected in an air hermetic desiccator. Inhibition effect of the glues was investigated using 3 techniques: measurement of open circuit potential (E_{oc}), corrosion current density (J_{cor}) and electrochemical impedance. The J_{cor} measurement has been realized in polarization range $\Delta E = E - E_0 = \pm 5$ mV with scan rate 0.1mV/s. E_0 is stable E_{oc} Corrosion current density J_{cor}, Tafel coefficients anodic β_a and cathodic β_c, polarization resistance R_P have been determined using readily installed GPES program. B constant has been calculated according to relation $B = R_P.J_{corr}$ and re-examined using Tafel coefficients in following equation (General Purpose Electrochemical System, 2004; Stern and Geary, 1957):

$$B = \frac{1}{2.303}\left(\frac{\beta_a\beta_c}{\beta_a+\beta_c}\right)$$

RESULTS

Open circuit potential E_{oc} measurement

Variations of E_0 in the studying solution as a function of emerge time are presented in figure 1. It is clear that the potentials obtained in the all 4 solutions increase in general with time, and those measured in the inhibition solutions M1 – M3 are significantly more positive than that of solution sample M0. The E_{oc} values determined after 1800s emerge are shown in figure 2. Variation of the open circuit potentials due to the inhibition effects (M1 – M3) in comparison with that in solution M0 is not very large, about 20mV, but the difference increases with the green tea glue concentration. It simple saturation of the green tea glue concentration for the solution M2 and M3 where E_0 is the same for both solutions (Figure 1.).

Corrosion current i_{cor} measurement

Linear polarization measurement was realized in potential interval 10mV starting at 5mV more negative than E_{oc}, scan rate 0.1mV/s. The stability of the measured electrochemical system has been examined by cyclic polarization with the same potential interval and scan rate. The typical polarization curves in log scale Tafel plot) are represented in figure 3. From these linear polarization curves J_{cor}, R_P, Tafel coefficients β_a and β_c have been determined. Variation of corrosion current density J_{cor} and of polarisation resistance R_P according to the samples is presented in Figure 4.

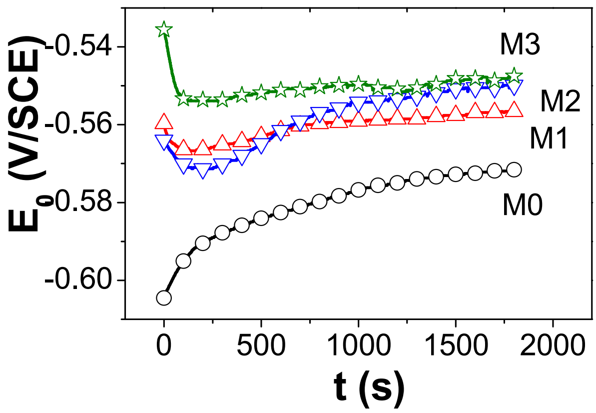

Figure 1. Variation of E_{oc} as a function of emerge time t,

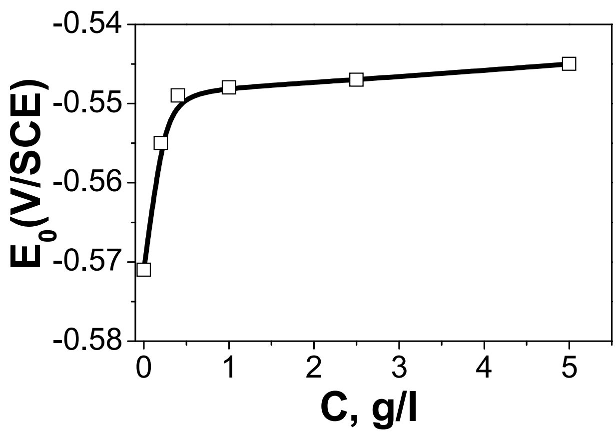

Figure 2. Variation of E_0 as a function of glue concentration C

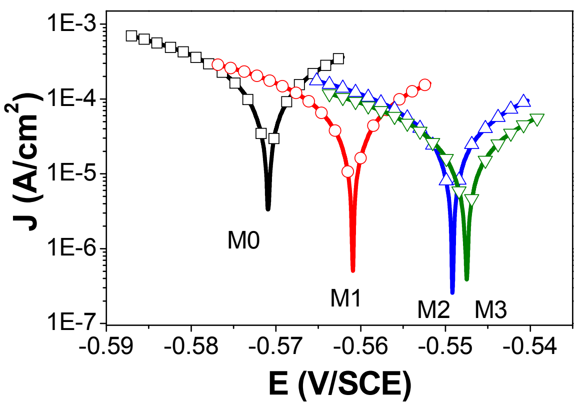

Fig. 3. Linear polarization curves, Tafel plot, 4 samples M0 – M3

In general J_{cor} decreases and R_P increases with increasing inhibitor concentration. The inhibition efficiency calculated on i_{cor} for samples M1, M2 and M3 are 65.2, 87.3 and 92.0, respectively, and calculated on R_P for these samples are 59.2, 76.1 and 84.6, respectively. These high inhibition efficiency of the green tea glue is significant in practice (Corrosion Handbook, 2006; Afidah *et al*, 2007).

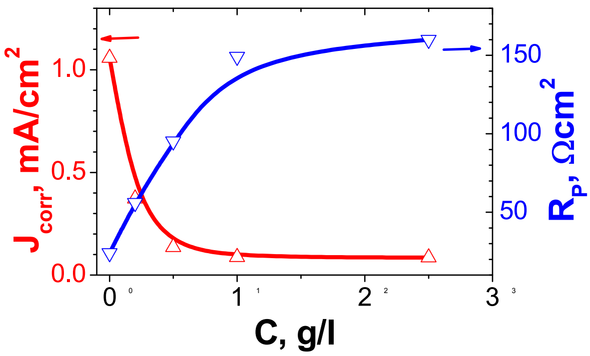

Figure 4. Variation of corrosion current as a function of the inhibitor quantities

Anodic polarisation measurement

It is interesting to examine anodic polarisation behaviour of the green tea glue inhibitor. Tea glue diminished remarkably anodic dissolving current and prolonged passive region on the curve which was not occurred for the sample M0 (Fig. 5). Inhibition efficiency, calculated at the same polarisation potential for the all 3 samples, is strongly dependent on the tea glue concentration and polarisation potential (Fig.6).

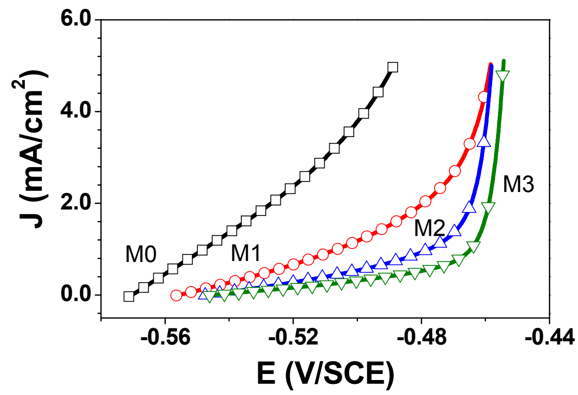

Fig. 5. Anodic polarisation curves obtained from 4 study solutions

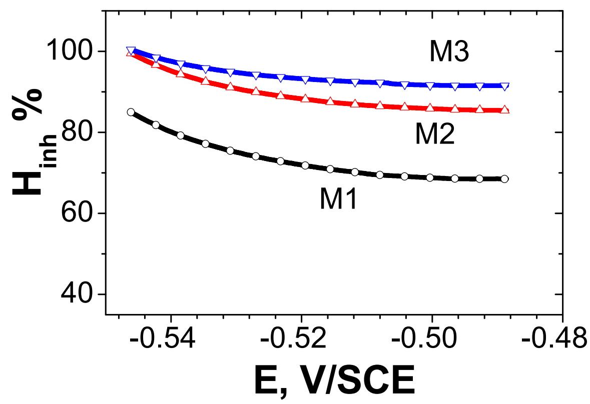

Fig. 6. Inhibition efficiency calculated at the same polarisation potential

For more negative potentials the efficiency reaches up to 100% (M2 and M3), but decreases remarkable according to increasing potential. Anodic polarisation provokes brutal augments of dissolving currents and certain diminution of the inhibition efficacy (figure 5 and 6). At closed open circuit potential the efficiency arrives nearly 100%, and then gradually decreases. Sample M3 provides obviously highest, practically acceptable inhibition efficiency, even at high polarisation, and quantitatively more than 90% (Figure 6).

Electrochemical impedance measurement

The impedance was measured at E_{oc}, and the obtained data are presented as Nyquist diagrams in figure 7. The tea glue inhibitors augment significantly the impedance of the steel electrodes. Variation of charges transfer resistance R_{ct} and double layer capacity C_{dl}, determined from obtained impedances using FRA program, as a function of the tea glue solution volumes, are presented in Figure 8.

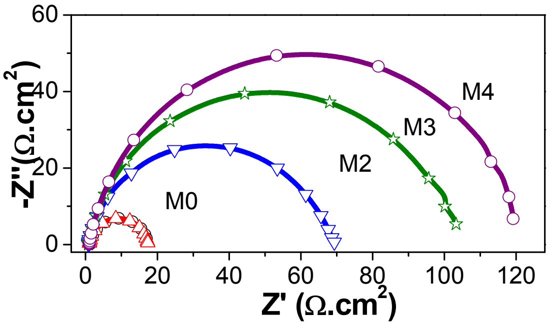

Figure 8. Nyquist diagram of EIS, samples M0, M2 and M3

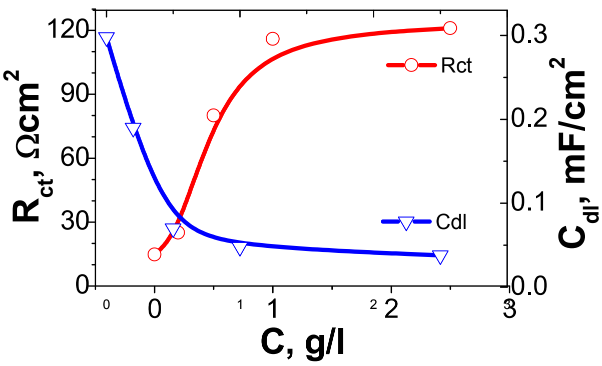

Figure 9. Variation of R_{ct} and C_{dl} of glues concentration, samples M0, M2 and M3

DISCUSSION

The obtained results from previous electrochemical investigation on corrosion inhibition of the tea glues provided good corrosion prevention of the green tea glues. The corrosion inhibition manifests not only at the open circuit potential region, but expending to large anodic region with still high efficiency up to more than 90% (Figure 5 and 6).

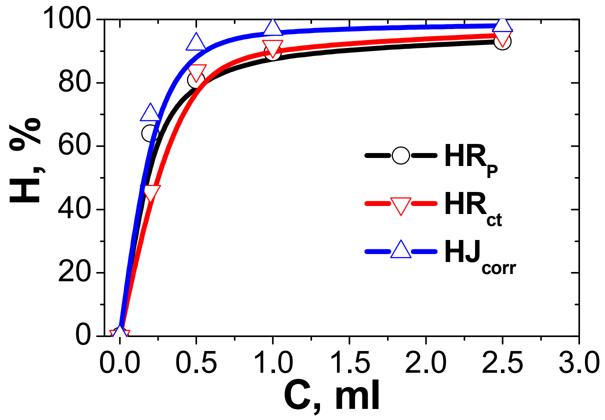

Figure 10. Variation of H (%) as a function of concentration, different experimental techniques: HR_P calculated from R_p,, HR_{ct} from R_{ct}, and HJ_{corr} from J_{corr} data

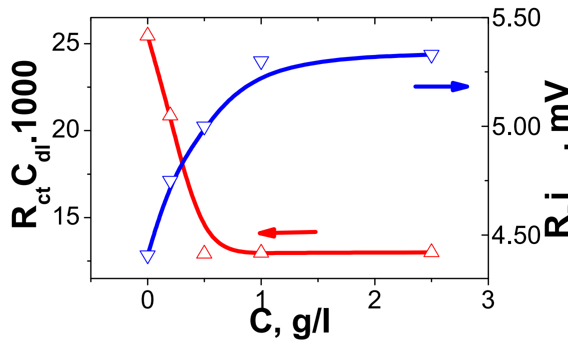

Figure 11. Variation of product $R_{ct}C_{dl}$ and $R_p i_{corr}$ with tea glues solution volumes C.

The obtained corrosion inhibition efficiency is well analysed with variable technique and calculation method. Thus HJ_{corr} is directly calculated, but HR_p and HR_{ct} are deduced using well known semi-experimental relation $J_{corr} = B/R_P$ or $= B'/R_{ct}$. Namely, R_{ct} data are calculated from impedance measurement, considered as an accurate technique, additionally capable providing reaction mechanism (Corrosion handbook, 2006; General Purpose Electrochemical System, 2004; Stern and Geary, 1957; Bard and Falkner, 2001). In fact, the decreasing of C_{dl} while tea glue concentration increases, indicating a strong adsorption into interface electrode / solution, in other word in the double layer (Raja, 2009). The adsorption mechanism of the polyphenol inhibitors has been mentioned and discussed (Afidah A. Rahim *et al.*, 2007; Afidah A. Rahim and Jain Kassim, 2008; Farreira *et al.*, 2004; Osman *et al.*, 2003; Yuasa, 2000). However in this study, using simplest model electric circuit R_{ct} in parallel with C_{dle}, and applying the characteristic relation for the maximum imaginary impedance (–Zi) of a parallel RC circuit $(RC\omega)^2 = 1$, where ω is angular frequencies (21), we have tried to examine the variation of product $R_{ct}C_{dl}$ (Figure 11), alternatively also the product $B = R_pJ_{corr}$ (Stern and Geary, 1957; Bard and Falkner, 2001). Variation of these products as a function of the concentration shows that adsorption of tea glues compounds on the steel sample surface increase strongly with concentration, and the increase of the product $R_{ct}C_{dl}$ indicates a state variation of the double layer providing a shift of the maximum characteristic frequency, from 25.1 Hz (M0) to 15.8 (M2) and finally to 12.6 (M3). Capacitance C_{dl} and characteristic frequency f_{max} diminish obviously indicate more solid absorption film, consequently preventing more efficiently metal dissolution. Product R_pJ_{corr} is a constant charactering a given active electrochemical system, such as a corrosive electrode in an aggressive solution (Bard and Falkner, 2001). Consequently B = R_pJ_{corr} remains constant uniquely when the essence of the system has been conserved. However the R_P increase in this case is not proportionally with the J_{corr} decrease so, fortunately, the product R_pJ_{corr} diminishes, providing a remarkable increase of the inhibition efficiency. The system change can be explained by an adsorption of the tea glues compounds making a barrier film.

Conclusion

Green tea old leaves can be gathered all to extract active compounds, such as polyphenol, a strong antioxidant providing values for green tea. One of the possible applications of the green tea old leaves extract is as construction steel corrosion inhibitors. In 1M H_2SO_4 solution, a small quantity of the concentrated water extract of these secondary tea products well presents acid attack up to nearly 100% efficiency at open circuit potential. The inhibition can remain at high anodic polarisation. The tea old leaves extract prevents acid corrosion on construction steel via adsorption mechanism, which modifies the nature of the interface metal surface / acid solution, probable due to create a barrier film with certain metal complex with tea polyphenol. The obtained results show a possible use of the tea secondary products presenting metal corrosion at industrial scale, as in acid pickling, cleaning, and descaling etc.

REFERENCES

Abiola, O.K. and James, A.O. 2010. Corrosion Science 52 661.

Afidah A. Rahim and Jain Kassim, 2008. *Recent Patents on Materials Science,* 1, 223-231 223

Afidah A. Rahim, E., Rocca, J., Steinmetz, M.J., Kassim, R. and Adnan, M. Sani Ibrahim, 2007. Corrosion Science 49, 402–417

Ambrish Singh, 2012. 1 Eno E. Ebenso,2 andM. A. Quraishi, *International Journal of Corrosion,* Volume 2012, Article ID 897430, p1-20

Bard, A.J. and Falkner L. R. 2001. Electrochemical methods fundamentals and applications, Second edition, printed in the United States of America.

Corrosion handbook, DECHEMA, 2006

Farreira, E.S., Giacomelli, C., Giacomelli, F.C. and Spinelli, A. 2004. Materials Chem. Phys. 83, 129.

Fernando Sílvio de Souza, Cristiano Giacomelli, Reinaldo Simões Gonçalves and Almir Spinelli, Adsorption 2012. behavior of caffeine as a green corrosion inhibitor for copper, Materials Science and Engineering C 32, 2436–2444

Fu, J.J., Li, S.N., Cao, L.H., Wang, Y., Yan, L.H. and Lu, L.D. 2010. L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution, *J Mater Sci* 45:979–986.

General Purpose Electrochemical System (GPES) 4.9 for Windows, Eco Chemie B.V. Utrecht, The Netherlands, (AUTOLAB PGSTAT 30, Manuel), 2004.

Husnu Gerengi, Katarzyna Schaefer and Ibrahim Sahin, H. 2012. Corrosion-inhibiting effect of Mimosa extract on brass-MM55 corrosion in 0.5 M H2SO4 acidic media, *Journal of Industrial and Engineering Chemistry* 18, 2204–2210

Mennucci, M.M., Banczek, E.P. and Rodrigues, P.R.P. and Costa, I. 2009. Evaluation of benzotriazole as corrosion inhibitor for carbon steel in simulated pore solution Cem Concr Compos 2009;31:418–424.

Obot, I.B. Obi, N.O. 2010. Egbedi, Journal of Applied Electrochemistry 40, 1977.

Okeniyi, J.O., Omotosho, O.A., Ajayi, O.O. and Loto, C.A. 2014. Effect of potassium-chromate and sodium-nitrite on concrete steel-rebar degradation in sulphate and saline media. Construct Build Mater, 50:448–456.

Osman, M.M., El-Ghazawy, R.A. and Al-Sabagh, A.M. 2003. Materials Chem. Phys. 80, 55.

Raja, P.B. and Sethuraman, M.G. 2009. Materials and Corrosion 60, 22.

Stern, M. and Geary, A.L. 1957. *J. Electrochem. Soc.,* Vol.104, p. 56

Trindade, L.G. and onçalves, R.S. 2009. *Corros. Sci.* 51 1578–1583.

Vietnam Pharmacopoeia (Pharmacopoeia Vietnamica) IV, Medical Minister 2012

Yuasa, M., Tokoro, K., Nakagawa, T., Sekine, I., Imahama, T., Shibata, Y. and Wake, T. 2000. Hyomen gijutsu (Hyomen gijutsu) ISSN 0915-1869, Vol. 51, no5, pp. 524-529

Znini, M., Cristofari, G., Majidi1, L., Ansari1, A., Bouyanzer, A., Paolini, J., Costa, J. and Hammouti, B. 2012. *Int. J. Electrochem. Sci.,* 7, 3959 – 3981

****