JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

# MODELING OF ADSORPTION ISOTHERM FOR METHANOL LEAF EXTRACT OF *Manihot esculentum* AS GREEN CORROSION INHIBITOR OF CORROSION OF MILD STEEL IN HCl MEDIUM

Sylvester. O. Adejo[1&2*], M. M. Ekwenchi[2], John U. Ahile[1], Joseph. A. Gbertyo[1], Benjamin Ishua[1], Andrew Akombor[1]

[1]*Physical Chemistry Unit, Department of Chemistry, Benue State University, Makurdi-Nigeria*
[2]*Department of Pure and Applied Chemistry, University of Jos, Jos-Nigeria*
∗ *Author of Correspondence: sadejo@bsum.edu.ng +2348054557652*

**Abstract**

The best fit adsorption isotherm model for methanol leaf extract of Manihot esculentum as green corrosion inhibitor of corrosion of mild steel in 2 M HCl medium was determined with the help of the Adejo-Ekwenchi adsorption isotherm. The corrosion inhibition study was carried out using the weight loss method at the temperature range of 301 K to 313 K. The inhibition efficiency, %IE, of the extract was found to increase with increase in both concentration and temperature, suggestive chemisorption. Going by the values of %IE, $R^2$ and $\Delta G_{ads}$ this adsorption process would have been thought to be chemisorption and well fitted into Langmuir, Freundlich and Temkin isotherm models. However, from the information obtained through the Adejo-Ekwenchi isotherm model the adsorption process was unambiguously resolved to be physisorption and best fitted into the Langmuir isotherm model.

**Keywords:** Adsorption, Mild steel, *Manihot esculentum*, Adejo-Ekwenchi isotherm, physisorption

## Introduction

Adsorption has been adjudged to be an effective process for a wide variety of applications [1, 2]. Empirically, the process of adsorption can be described in terms of amount adsorbed as a function of pressure (or concentration) and temperature [3, 4]. For the adsorption process, the relationship between the amount of the adsorbed substance to its bulk concentration at a particular temperature and pH is known as adsorption isotherm, and many adsorption isotherms have been proposed with their characteristic parameters. The importance of the parameters of adsorption isotherms lay in the fact that they

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

useful for the deduction of the mechanism of adsorption as well as for design purposes [1, 5-9].

Several error analysis methods such as coefficient of determination, the sum of the errors, a hybrid error function, Marquardt's per cent standard, the average error and sum of absolute error, have been employed in the determination of the best-fitting isotherm for any adsorption process [1]. Among these, the method of least squares with linearly transformed isotherm equations has be acclaimed as the most widely used for finding the best fit of adsorption isotherm [10]. Also the Gibb's free energy, $\Delta G_{ads}$, value is usually employed to ascertain whether the adsorption process is physisorption or chemisorption. But, Ho and Co-workers [5] have noted the inadequacy of usage of coefficient of determination, $R^2$, for the determination of best isotherm fit thus "the transformation of non-linear isotherm equations to linear forms implicitly alters their error structure and may also violate the error variance and normality assumptions of standard least squares". Again, it has been stated by many authors that value of $\Delta G_{ads}$ below -20 kJ/mol is an indication of physisorption, while above -40 kJ/mol is ascribed to be chemisorption. However, Popova and his research team [10] argued that the use of $\Delta G_{ads}$ as a sole criterion for such distinction will be difficult, especially in the case where charged species are adsorbed due to possibility of coulombic interaction between charged species; it can increase the $\Delta G_{ads}$ value, even if no new chemical bonds are formed. Evidently, therefore, there exist ambiguities in the usage of $R^2$ and $\Delta G_{ads}$ values as sole criteria in the determination of isotherm

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

best fit of adsorption process. Unambiguously, it has been shown that the Adejo-Ekwenchi isotherm can be used to eliminate the observed inadequacies in adsorption characterisation process, especially in corrosion inhibition using plant extracts [12- 14, 13].

In this present paper we unambiguously resolved the adsorption isotherm best fit for methanol leaf extract of *Manihot esculentum* as green corrosion inhibitor of corrosion of mild steel in 2 M HCl medium.

## Research Methods

### *Material Preparations*

Leaves of *Manihot esculentum* were collected and rinsed with distilled water, then shade-dried and pounded into powder. 30 g of the powder was soaked in 300 mL of 98% methanol (BDH Chemicals Ltd, England) in a 500 mL volumetric flask for 48 hours, with occasional shaking. The extract obtained therefrom was filtered using glass wool and the methanol was slowly evaporated using thermostated water bath (Clifton: Nickel-Electro Ltd, England) at 321 K for reason given elsewhere [15]. The residue obtained was preserved in a desiccator. Stock solutions of 0.1, 0.2, 0.3, 0.4 and 0.5 g/dm$^3$ concentrations were prepared in 2 M HCl (M & B).

Coupons (2 cm x 2 cm x 0.13 cm each) were prepared as reported before [16] from a sample of mild steel of composition (%W): Fe(98.84), Mn(0.56), P(0.04),

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

C(0.27), Si(0.25) and S(0.04). The coupon surfaces were thoroughly polished to mirror finishing using different grades of emery paper, degreased by washing with ethanol (BDH), dried in acetone, and preserved in a desiccator for use.

***Experimental Methods***

The coupons, degreased in acetone (99% BDH Chemicals Ltd, England), were carefully weighed using ae Adam AFP electronic weighing balance (d ±0.0001g) and immersed in 50 mL of the acid solutions, without and with various concentrations of the inhibitor at the temperature range of 301 K to 313 K in the water bath for 8 hours. At the retrieval of each coupon, the reaction was terminated by dipping into saturated solution of ammonium acetate (97% Labtech Chemicals Limited) as outlined by Orubite-Okorosaye and Oforka [17] and the coupon stored in the desiccator until ambient temperature was attained and reweighed. An average of triplicate values was taken for each measurement. The %IE and surface coverage (θ) were calculated through equations (1) and (2), respectively [18-21].

$$IE\% = 1 - \frac{W_{inh}}{W_{uninh}} \times 100 \quad (1)$$

$$\theta = (1 - \frac{W_{inh}}{W_{uninh}}) \quad (2)$$

where $W_{uninh}$ and $W_{inh}$ are weight losses in absence and present of inhibitor, respectively.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

## Results and Discussion

Table 1 shows the variation of *%IE* of the methanol leaf extract of *Manihot esculentum* as eco-friendly corrosion inhibitor of the corrosion of mild steel sample in 2 M HCl with the extract concentration and temperature. The Table clearly shows that the %IE increases with increase in both concentration of the extract and rise in temperature. The increase in the %IE with rise in temperature is suggestive of chemisorption [22, 23].

**Table 1. Variation of Inhibition Efficiency (%IE) with Concentration and Temperature of Leaf Extract of *Manihot esculentum***

| Conc. (g/dm3) | %IE | | | |
|---|---|---|---|---|
| | 301 K | 305 K | 309 K | 313 K |
| 0.1 | 29.28 | 47.40 | 51.35 | 52.76 |
| 0.2 | 44.77 | 60.86 | 66.66 | 65.22 |
| 0.3 | 58.08 | 70.32 | 73.63 | 74.49 |
| 0.4 | 77.21 | 77.87 | 77.31 | 78.77 |
| 0.5 | 79.19 | 82.54 | 84.40 | 85.06 |

The inhibitive action of organic compounds has been ascribed to the formation of surface layers and films on the metal surface, thereby reducing the accessibility of the corrodant to the metal surface. Adsorption isotherms have been used to characterise this inhibitive action. The most frequently used of such isotherms are the Langmuir, Freundlich, Frumkin, Temkin, Flory-Huggins, Sips, Bockris-Swinkels and the El-Awady thermodynamic-kinetic model and the recent proposed Adejo-Ekwenchi isotherm [1, 12, 24, 25]. The linearised forms of the various equations are given below.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

Langmuir $\frac{C}{\theta} = \frac{1}{K} + C$ (3)

Freundlich $\log\theta = \log K_F + n_F \log C$ (4)

Frumkin $\log\frac{\theta}{[(1\ \theta)]C} = \log K + \frac{2a\theta}{2.303}$ (5)

Flory-Huggins $\log \frac{\theta}{C} = \log K + x\log[1 - \theta]$ (6)

Temkin $-2\alpha\theta = \ln KC$ (7)

El-Awady $\log \frac{\theta}{1-\theta} = \log K' + y\log[C]$ (8)

Sips $\log \frac{\theta}{1-\theta} = \log A + x\log[C]$ (9)

Adejo – Ekwenchi $\log\frac{1}{(1-\theta)} = \log K_{AE} + b\log[C]$ (10)

The fitness adsorption data to an adsorption isotherm has been determined by many authors through the use of the value of regression coefficient, $R^2$, from the plot of the surface coverage against the bulk concentration of the adsorbate (extract). Going by this it can be asserted that the data for this extract fitted into the Langmuir, Freundlich, Temkin, El-Awady and Adejo-Ekwenchi isotherms (Table 2), not fitting other popular two-parameter isotherm like Flory-Huggins, Frumkin and El-Awady.

The equilibrium constant, $K_{ads}$, values of the isotherms (Table 2) are all positive, implicitly, indicative of favourable adsorption in all the isotherms [8]. The S-shaped curve of the plot of %IE against the logarithm of concentration in Figure 1 (at 301 K) further attests to the fact that an adsorbed layer was actually formed on the metal surface by the extract [8, 26].

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

**Table 2. Various Adsorption Isotherm Parameters for Adsorption of Leaf Extract of *Manihot esculentum* onto the mild steel surface**

| Isotherm | Temp (K) | $R^2$ | Slope | Intercept | $K_{ads}$ | | $\Delta G_{ads}$ (kJ/mol) |
|---|---|---|---|---|---|---|---|
| Langmuir | | | | | | | |
| | 301 | 0.9948 | 0.6512 | 0.2955 | 3.3841 | | -13.10 |
| | 305 | 0.9949 | 0.9748 | 0.1247 | 8.0192 | | -15.47 |
| | 309 | 0.9393 | 1.0128 | 0.0985 | 10.1523 | | -16.28 |
| | 313 | 0.9815 | 0.9977 | 0.0996 | 10.0402 | | -16.46 |
| Freundlich | | | | | | n | |
| | 301 | 0.9876 | 0.6492 | 0.1128 | 1.2966 | 0.6492 | -10.70 |
| | 305 | 0.9986 | 0.3492 | 0.0270 | 1.0641 | 0.3492 | -10.34 |
| | 309 | 0.9839 | 0.2979 | 0.0172 | 1.0404 | 0.2979 | -10.42 |
| | 313 | 0.9967 | 0.2945 | 0.0190 | 1.0447 | 0.2945 | -10.57 |
| Temkin | | | | | | α | |
| | 301 | 0.9589 | 0.4820 | -3.0297 | 0.0483 | -1.4597 | -2.47 |
| | 305 | 0.9967 | 0.3465 | -4.4070 | 0.0331 | -2.2582 | -5.84 |
| | 309 | 0.9909 | 0.3343 | -4.9053 | 0.0074 | -2.5189 | +2.29 |
| | 313 | 0.9956 | 0.1754 | -4.9284 | 0.0072 | -2.5143 | +2.39 |
| Adejo- Ekwenchi | | | | | | b | |
| | 301 | 0.8908 | 0.7995 | 0.8890 | 7.7446 | 0.7995 | -15.18 |
| | 305 | 0.9582 | 0.6765 | 0.9205 | 8.3272 | 0.6765 | -15.56 |
| | 309 | 0.9540 | 0.6532 | 0.9455 | 8.3206 | 0.6532 | -15.91 |
| | 313 | 0.9507 | 0.6805 | 0.9728 | 9.3929 | 0.6805 | -16.28 |

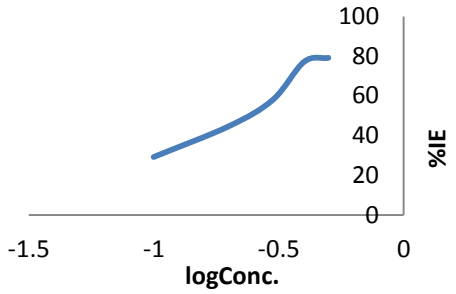


Figure 1. Relationship between Inhibition Efficiency and logarithm of Concentration at 301K for the Extract of *Manihot esculentum*

Equations (11) and (12) are conventionally used to calculate $\Delta G_{ads}$ for an adsorption process.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

$$\Delta G_{ads} = -2.303RT\log(55.5\kappa) \quad (11)$$

where

$$\kappa = \frac{\theta}{(1-\theta)C} \quad (12)$$

C is the concentration of the extract and 55.5 is concentration of water expressed in moles (i.e. ~ 1000 g/dm$^3$) [12, 27]. The values of $\Delta G_{ads}$ evaluated through the equation (11) are presented in Table 3.

The slope and intercept of ideal Langmuir isotherm plot should be unity and zero, respectively [28, 29]. The slopes of the Langmuir plot obtained are close to unity and intercepts almost equal to zero, with good $R^2$ values, indicative of suitability of the Langmuir isotherm model to the adsorption behaviour of this extract. Moreso, the values of $\Delta G_{ads}$ obtained through this isotherm are also in good agreement with those evaluated through the conventional method as shown in Table 3. Langmuir isotherm is applicable to both physisorption and chemisorption.

**.Table 3. Values of $\Delta G_{ads}$ obtained through equilibrium constant**

| Conc.(g/dm$^3$) | - $\Delta G_{ads}$ (kJ/mol) | | | |
|---|---|---|---|---|
| | 301 K | 305 K | 309 K | 313 K |
| 0.1 | 13.77 | 15.76 | 16.38 | 16.73 |
| 0.2 | 13.56 | 15.39 | 16.24 | 16.28 |
| 0.3 | 13.88 | 15.43 | 16.05 | 16.38 |
| 0.4 | 15.40 | 15.70 | 15.82 | 16.25 |
| 0.5 | 15.13 | 15.88 | 16.44 | 16.78 |

The parameter n of the Freundlich isotherm relates to the adsorption intensity, and it varies with the heterogeneity of the material [30] and it has a typical value is 0.6 [24], of which no value is close (Table 2), except at 301 K. And the values of $\Delta G_{ads}$ obtained through this isotherm model are also not comparable to those

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

of the conventional method. Therefore, the adsorption process of leaf extract of *Manihot esculentum* onto the metal sample in HCl cannot be modelled by the Freundlich isotherm, in spite of the seemly good values of $R^2$.

The Temkin isotherm mostly is a feature of chemisorption [31] and an indication of interaction of uncharged molecules on a heterogeneous surface [32]. The negative values of parameter α are clear indication of the existence of repulsive interaction among the molecules of the adsorbed layer. The values of $R^2$ are good, but those of $\Delta G_{ads}$ show no favourable adsorption by this extract onto the metal surface, a complete contrast to the observation above, and hence cannot be modelled by Temkin isotherm.

The Adejo-Ekwenchi isotherm is centred on the fact that for an adsorption process, the amount of adsorbate uptake from bulk concentration has inverse relationship with the difference between the total available surface on the adsorbent surface and the fraction that is covered by the adsorbate at a given temperature, prior to the attainment of maximum value of surface coverage [12]. Decrease in the value of *b* of the isotherm with rise in temperature signifies physisorption, while increase or fairly constant value indicates chemisorption [12, 13, 33]. From Table 2 it is obvious that the adsorption of this plant extract onto the metal surface is physisorption as *b* decreases with rise in temperature. Supportively, the values of $\Delta G_{ads}$ obtained through this isotherm are close to those of Langmuir isotherm and the conventional method.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

## Conclusion

Going by %IE, $R^2$ and $\Delta G_{ads}$ values, the adsorption process of methanol leaf extract of *Manihot esculentum* as an inhibitor for the corrosion of mild steel in 2 M HCl which would have been thought to be chemisorption and the data fitted into Langmuir, Freundlich, and Temkin isotherm models, was resolved through Adejo-Ekwenchi isotherm to be physisorption and best fitted only to the Langmuir isotherm model.

## References

[1] 'Selection of optimum sorption isotherm', Y. S. Ho, *Carbon,* **42**, pp2113 – 2130, 2004.

[2] 'Removal of aluminium from aqueous solutions by adsorption on Date-pit and BDH activated Carbons', S. A. Al-Muhtaseb, M. H. El-Naas, M. A. Abdallah, *J. Hazardous Mat.* 158, pp300-307, 2008.

[3] 'Adsorption of Aromatic Trace Compound from Organic Solvents on Activated Carbons- Experimental Results and Modeling of Adsorption Equilbria', T. C. Graf, C. Pasel, M. Luckas, *Adsorption*, **18**, pp127-141, 2012.

[4] 'Physical Chemistry of surfaces', sixth ed. John Wiley and Sons Inc., USA A. W. Adamson, A. P. Gast, pp390-422, 1997.

[5] 'Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems', Y. S. Ho, J. F. Porter, G. McKay, *Water, Air and Soil Poll.***141**, pp1-33, 2002.

[5] 'Isotherm and kinetics of Fe(II) adsorption onto Chitosan in a batch process', H. Radnia, A. A. Ghoreyshi, H. Younesi, *Iranian J. Energy Environ,* **2**, 3, pp250-257, 2011.

[6] 'Inhibition by *Newbouldia leavis* leaf extract of the corrosion of aluminium in HCl and $H_2SO_4$ solutions', L. A. Nnanna, V. U. Obasi, O. C. Nwadiuko, K. I. Mejeh, N. D. Ekekwe, S. C. Udensi, *Archives Appl. Sci. Res.,* **4**,1, p207-217, 2012.

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

[7] 'Adsorption characterization of ethanol extract of leaves of *Portulaca oleracea* as green corrosion inhibitor for corrosion of mild steel in sulphuric acid medium', S. O. Adejo, M. M. Ekwenchi, F. Momoh, E. Odiniya, *Inter. J. Modern Chem,* **1**, 3, pp125-134, 2012.

[8] 'Adsorption Behaviour of 1-pheny-3-methypyrazol-5-one on Mild Steel from HCl Solution', O. K. Abiola, J. O. E. Otaigbe, *Inter. J. Electrochem. Sci.,* **3**, pp191-198, 2008.

[9] 'Modeling of equilibrium data for free cyanide adsorption onto activated carbon by linear and non-linear regression methods', M. M. Salarirad, A. Behnamfard, *Proc. 2011 Inter. Conf. Environ. Ind. Innov. IPCBEE, Vol. 12 IACSIT Press, Singapore,* 2011.

[10] 'Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part I: Gravimetric and Voltammetric Results', A. Popova , M. Christov, A. Vasilev, A. Zwetanova, *Corr. Sci.,* **53,** pp679-686, 2011.

[11] 'Proposing a New Empirical Adsorption Isotherm known as Adejo-Ekwenchi isotherm', S. O. Adejo, M. M. Ekwenchi, *IOSR- J. Appl. Chem.,* **6**, 5, pp66-71, 2014.

[12] 'Resolution of adsorption characterisation ambiguity through the Adejo-Ekwenchi Adsorption Isotherm: A case study of leaf extract of *Hyptis suaveolen* Poit as green corrosion inhibitor of corrosion of mild steel in 2 m HCl', S. O. Adejo, M. M. Ekwenchi, J. U. Ahile, J. A. Gbertyo, A. Kaior, *J. Emerging Trends in Eng. Appl. Sci. (JETEAS),* **5**, 8, pp201-205, 2014.

[13] 'Determination of adsorption isotherm model best fit for methanol leaf extract of *Securinega virosa* as corrosion inhibitor for corrosion of mild steel in HCl', S. O. Adejo, M. M. Ekwenchi, J. A. Gbertyo, T. Menenge, J. O. Ogbodo, *J. Advances Chem.*, **10,** 5, pp2737-2742, 2014.

[14] 'Inhibitive properties and adsorption consideration ethanol extract of *Manihot esculentum* leaves for corrosion of aluminium in 2 M $H_2SO_4$', S. O. Adejo, J. A. Gbertyo, J. U. Ahile, *Inter. J. Modern Chem.,* **4**, 3, pp137-146, 2013.

[15] 'Inhibitory effect and adsorption parameters of extract of leaves of *Portulaca oleracea* of corrosion of aluminium in $H_2SO_4$ solution', S. O. Adejo, S. G. Yiase, J. U. Ahile, T. G. Tyohemba, J. A. Gbertyo, *Archives Appl. Sci. Res.,* **5**, 1, pp25-32, 2013.

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

[16] 'Corrosion inhibition of zinc on HCl using *Nypa fruiticans* Wurmb extract and 1, 5-Diphyeny carbazone', K. Orubite-Okorosaye, N. C. Oforka, *J. Appl. Sci. Environ. Mgt.,* **8**, 1, pp57-61, 2004.

[17] 'Organic corrosion inhibitors for aluminium in sodium hydroxide', A. K. Maayta, *The J. Corr. Sci. Eng.,* **3,** pp25-30, 2002.

[18] '*Emblica officinalis* (AMLA) leaves extract as corrosion inhibitor for copper and its alloy (Cu- 27Zn) in natural sea water', D. Rani, S. Selvaraj, *Archives Appl. Sci. Res.,* **2**, 6, pp140-150, 2010a.

[19] 'FTIR spectroscopic information on the corrosion inhibitor potentials of ampicillin in HCl solution', A. A. Siaka, N. O. Eddy, S. O. Idris, A. Muhammad, C. M. Elinge, F. A. Atiku, *Innov. Sci. Eng.,* **2**, pp41-48, 2012.

[20] '*Manihot esculentum* root peel ethanol extract as corrosion inhibitor of aluminium in 2 M $H_2SO_4$', S. O. Adejo, J. A. Gbertyo, J. U. Ahile, T. G. Tyohemba, *Inter. J. Sci. Eng. Res*., **4,** 9, pp2308-2313, 2013.

[21] 'Inhibitive and adsorption of *Punical granatum* extract on brass in acid media', D. Rani, S. Selvaraj, *J. Phytology,* **2**, 11, pp58-64, 2010b.

[22] 'Aqueous extract of Kalmegh (*Andrographis paniculata*) leaves as green inhibitor for mild steel in hydrochloric acid solution', A. Singh, V. K. Singh, M. A. Quraishi, *Inter. J. Corr*., **2010**, 1, pp01-10, 2010.

[23] 'Adsorption mechanism of benotriazole for corrosion inhibition of coppper-nickel alloy in hydrochloric acid', A. A. Khadom, A. S. Yaro, A. H. Abdul, *J. Chilean Chem. Soc.,* **55,** 1, pp150-152, 2010.

[24] 'Correlation with different models for adsorption isotherms of m-xylene and toluene on zeolites', Z. Benmaamar, A. Benguedach, *J. Appl. Sci. Environ. Sanitation,* **2**, 2, pp43-56, 2007.

[25] 'Adsorption of methionine onto mild steel', O. K. Abiola, *J. Chilean Chem. Soc.,* **50**, 4, pp685-690, 2005.

[26] 'The isotherm slope: A criterion for studying the adsorption mechanism of benzotriazole on copper in sulphuric acid', D. M. Bastidas, P. P. Gomez, E. Cano, *Revista Metallurgy*, **41,** pp98-106, 2005.

[27] 'The inhibitive effect of *Solanum melonena L.* leaf extract on the corrosion of aluminium in tetraoxosulphate (VI) acid', I. M. Mejeha, A. A. Uroh, K. B. Okeoma, G. A. Alozie, *Afri. J. Pure Appl. Chem,* **4**, pp158-165, 2010.

ISSN 1466-8858 Volume 17, Preprint 46 submitted 25 September 2014

[28] 'Experimental and quantum chemical studies of the corrosion inhibition of mild steel in acidic media by malachite green dye', C. O. Akalezi, C. K. Enenebaku, C. E. Ogukwe, E. E. Oguzie, (2012). *J. Chem. Soc. Nigeria,* **37**, 1, pp117-124, 2012.

[29] 'Enhanced adsorption of congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide', S. Chatterjee, D. S. Lee, M. W. Lee, S. H. Woo, *Bioresource Technol.,* **100**, pp2803-2809, 2009.

[30] ch.ntu.edu.tw. http://www.ch.ntu.edu~cymou/catalyst94/0922_C: retrieved 29/04/2014.

[31] 'Synergistic inhibition between polyvinylpyrollidone and iodide ions on corrosion of aluminium in HCl', S. A. Umoren, I. B. Obot, I. O. Igwe, *The Open Corr. J,* **2**, pp1-5, 2009.

[32] 'Adsorption Characteristics of ethanolic extract of roots of *Portulaca oleracea* as eco-friendly inhibitor of Corrosion of Mild Steel in $H_2SO_4$ Medium', S. O. Adejo, M. M. Ekwenchi, P. O. Olatunde, F. E. Agbajeola, *IOSR-Journal of Applied Chemistry,* **7**, 4, pp55-60, 2014.