A green microwave-assisted synthesis, characterization and comparative study of new pyridazinium-based ionic liquids derivatives towards corrosion of mild steel in in acidic environment

M. Messali

Chemistry Department, Faculty of Science, Taibah University, Al Madinah Al Mounawara, 30002 Saudi Arabia.

Received in 30 Mar 2011, Revised 15 Apr 2011, Accepted 15 Apr 2011.

**Corresponding author E-mail: mouslim@mail.be; Tel:+966562441572; Fax:+96648454770*

Abstract

A green microwave-assisted procedure for the preparation of four new N-alkylpyridazinium ionic liquids with different functionality in the alkyl chain is described. For the first time, target ionic liquids were prepared using under microwave irradiation in short duration of time with quantitative yields. The newly ionic liquids were tested as corrosion inhibitors of steel in 1.0 M HCl weight loss methods. The obtained results showed that the four ILs are good inhibitors for steel in 1.0 M HCl and the inhibition efficiency increased with increasing the inhibitor concentration and reached up to 95% at 10^{-2} M.

Keywords: Green procedure, pyridazinium-salts, ionic liquids, Inhibitors, Acid corrosion.

1. Introduction

The gradually destroyed of the metallic structure via anodic dissolution by the means of electrochemical process is known as metals corrosion [1]. To avoid the metal corrosion, some specific compounds can be added and found to be effective for combating corrosion under acid condition [2]. Electronegative functional groups and л-electron in triple or conjugated double bonds as well as heteroatoms like sulphur, phosphorus, nitrogen and oxygen in their structure are the major adsorption centres. There are many condition can be controlled the modes of adsorption such as chemical structure of the molecule, solution contents, the metal surface and the electrochemical potential of the metal-solution interface. The relation between the chemical structure and corrosion inhibition is the most important issue for the corrosion researchers [3-5].

Ion liquids (ILs) are considered as good solvents which formed by the electrostatic interaction between positive and negative charges and they are liquid at room temperature [6-8]. They showed very sounding properties such as thermal stability, inflammability, moderate solubility for organic and inorganic compounds, high ionic conductivity and electrochemical potenial properties [9-13]. Variation of the ionic liquids cation and anion led to the tuning of their chemical and physical properties[14].

Recently, a variety of applications [15–21] of ILs have been widely investigated. In particular, the most extensively studied ILs is based upon the imidazolium cation.

It’s reported that, both imidazolium and pyridinium compounds are reported to represent a good corrosion inhibitors copper [22,23], mild steel [24-27] and aluminium [28]. A strong relationship between the functional groups of the ionic liquids and the metal surface due to the presence of the more electronegative nitrogen atom has been discussed.

In the same context, we synthesize and characterise four new N-alkylpyridazinium ionic liquids namely, 1-(6-ethoxy-6-oxohexyl)pyridazinium bromide (**I**), 1-benzylpyridazinium bromide (**II**), 1-phenethylpyridazinium bromide (**III**) and 1-(4-phenoxybutyl)pyridazin-1-ium bromide (**IV**), with the aim to study their applicability as corrosion inhibitors for carbon steel in 1.0 M HCl by gravimetric study. The chemical structures of the studied pyridazinium ionic liquids are given in Table1.

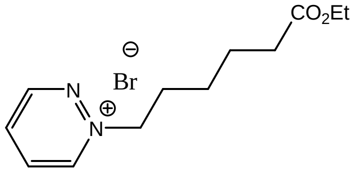
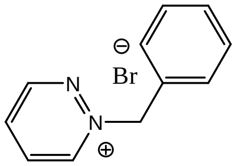
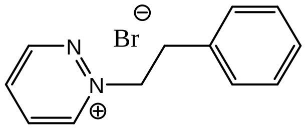
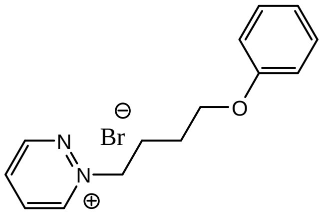
Compound	Structural formula	Molar mass
I		302.06
II		250.01
III		264.03
IV		308.05

Table 1. The chemical structure of the studied pyridazinium ionic liquids.

2. Experimental methods

2.1. Synthesis

2.1.1. Materials

The reagents: pyridazine (98%), ethyl 6-bromohexanoate (96%), benzyl bromide (97%), phenetyl bromide (97%), and 4–phenoxybutyl bromide (98%), were purchased from Aldrich and used as received. All solvents were of HPLC grade.

2.1.2. Measurements and equipments

All new compounds were synthesized and characterized by ^{1}H NMR and ^{13}C NMR spectroscopies. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in DMSO at room temperature. Chemical shifts (d) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which is used as an internal standard. The LCMS spectra were measured with a Micromass, LCT mass spectrometer. The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer as well as a pressure, temperature and power controls. The maximum operating pressure of the reactor is 20 bar. The power and temperature range are 15 - 300 W and 60 – 250 °C, respectively.

*2.1.3. Synthesis of 1-(6-ethoxy-6-oxohexyl)pyridazinium bromide (**I**)*

Pyridazine (2 g, 0.025 mol) and ethyl 6-bromohexanoate (5.66 g, 0.0275 mol) and 10 ml of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 80ºC. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 ºC. Brown crystals, yield 82%, mp 79-81 °C; IR (ν_{max}, cm^{-1}):1731 (C=O). ^{1}H NMR (400MHz, DMSO) δ: 1.15 (t, *J* = 7.2, 3H), 1.31 (quint, *J* = 7.6, 2H), 1.55 (quint, *J* = 7.6, 2H), 2.00 (quint, *J* = 7.6, 2H), 2,28 (t, *J* = 7.6, 2H), 4.03 (q, *J* = 7.2, 2H), 4.83 (t, *J* = 7.6, 2H), 8.61-8.64 (m, 1H), 8.74-7.76 (m, 1H), 9.64-9.65 (d, *J* = 4.4 1H), 10.03-10.04 (d, *J* = 4.8 1H). ^{13}C NMR (100MHz, DMSO) δ: 14.1 (CH_3), 23.7 (CH_2), 24.8 (CH_2), 29.0 (CH_2), 33.1 (CH_2), 59.7 (CH_2), 64.2 (CH_2), 136.0 (CH), 136.6 (CH), 149.9 (CH), 154.5 (CH), 172.7 (C); LCMS: m/z 302 (M^+).

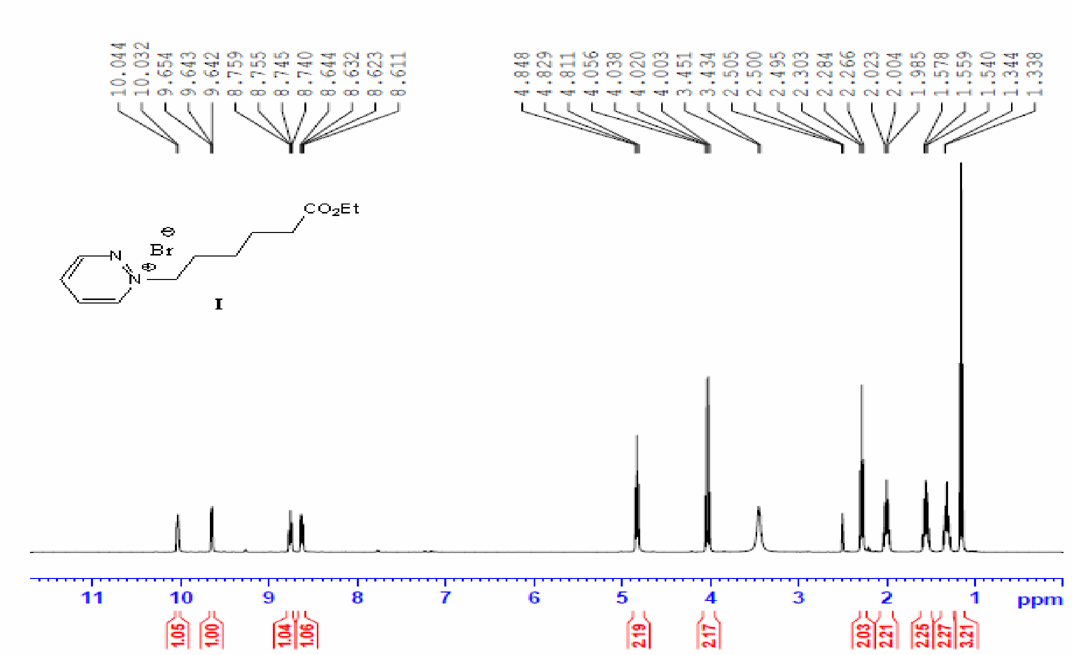


Figure 1. ^{1}H NMR spectrum (DMSO) of 1-(6-ethoxy-6-oxohexyl)pyridazinium bromide (**I**)

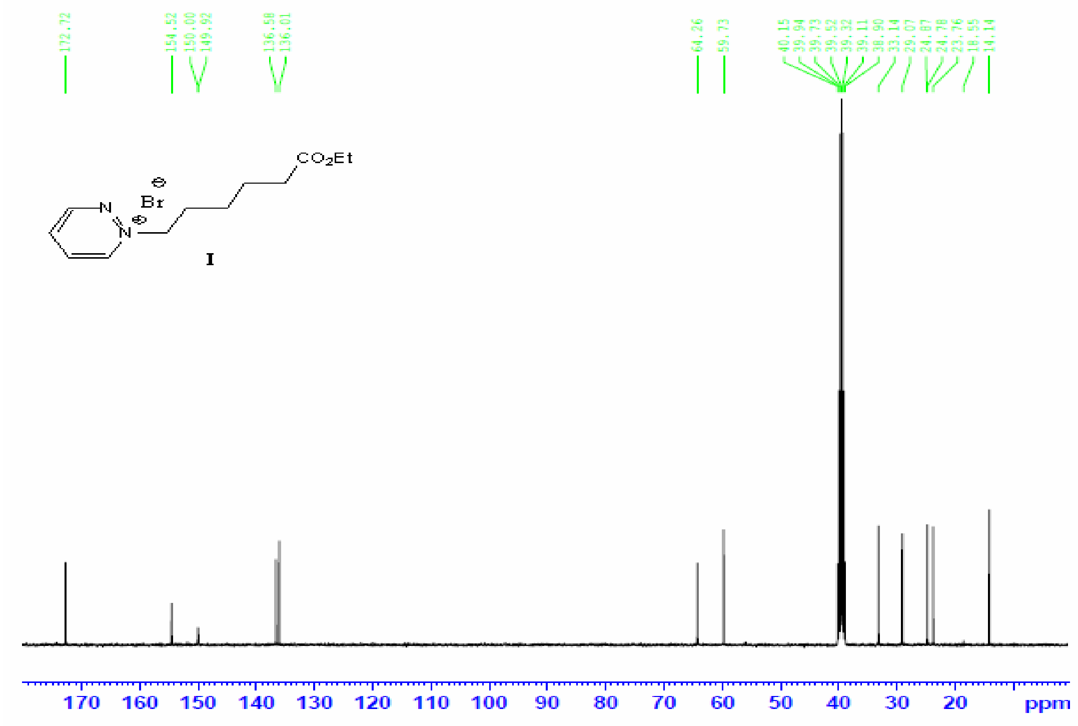


Figure 2. ^{13}C NMR spectrum (DMSO) of 1-(6-ethoxy-6-oxohexyl)pyridazinium bromide (**I**)

*2.1.4. Synthesis of 1-benzylpyridazinium bromide (**II**)*

Pyridazine (2 g, 0.025 mol), benzyl bromide (4.67 g, 0.0275 mol) and 10ml of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 80 ºC. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 ºC. Brown crystals, yield 87%, mp 165-168 ºC. ^{1}H NMR (400MHz, DMSO) δ: 6.12 (s, H), 7.39-7.43 (m, 3H), 7.56-7.57 (m, 2H), 8.62-8.65 (m, 1H), 8.78-7.82 (m, 1H), 9.62-9.64 (d, *J* = 4.8 1H), 10.32-10.34 (d, *J* = 6 1H). ^{13}C NMR (100MHz, DMSO) δ: 67.1 (CH_2), 128.9 (CH), 129.3 (CH), 129.5 (CH), 133.2(C), 136.3(CH), 136.8(CH), 150.1 (CH), 154.8 (CH); LCMS: m/z 250 (M^+).

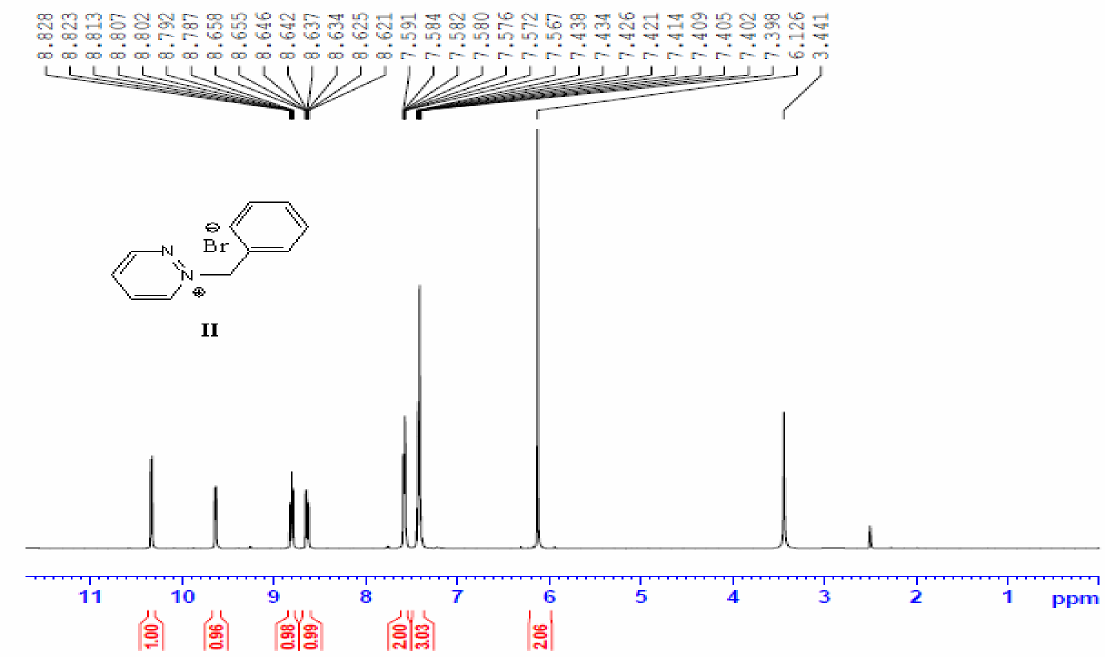


Figure 3. ^{1}H NMR spectrum (DMSO) of 1-benzylpyridazinium bromide (**II**)

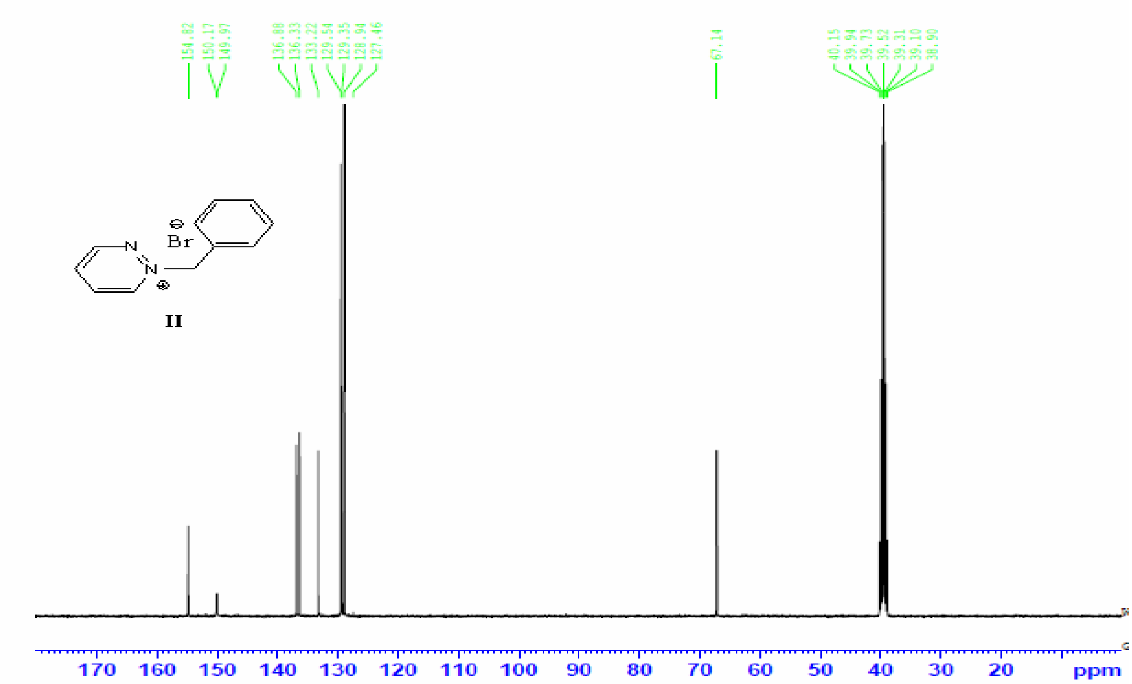


Figure 4. ^{13}C NMR spectrum (DMSO) of 1-benzylpyridazinium bromide (**II**)

*2.1.5. Synthesis of 1-phenethylpyridazinium bromide (**III**)*

Pyridazine (2 g, 0.025 mol), phenetyl bromide (5.06 g, 0.0275 mol) and 10ml of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 80 ºC. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 ºC. Brown crystals, yield 89%, mp 177-179 ºC. ^{1}H NMR (400MHz, DMSO) δ: 3.35 (t, *J* = 7.6, 2H), 5.11 (t, *J* = 7.6, 2H), 7.21-7.27 (m, 5H), 8.60-8.63 (m, 1H), 8.70-7.84 (m, 1H), 9.63-9.65 (m, 1H), 9.95-9.98 (d, *J* = 6 1H). ^{13}C NMR (100MHz, DMSO) δ: 35.3 (CH_2), 65.1 (CH_2), 127.0 (CH), 128.6 (CH), 128.8 (CH), 135.8(CH), 136.1(C), 136.8(CH), 149.9 (CH), 154.5 (CH); LCMS: m/z 264 (M^+).

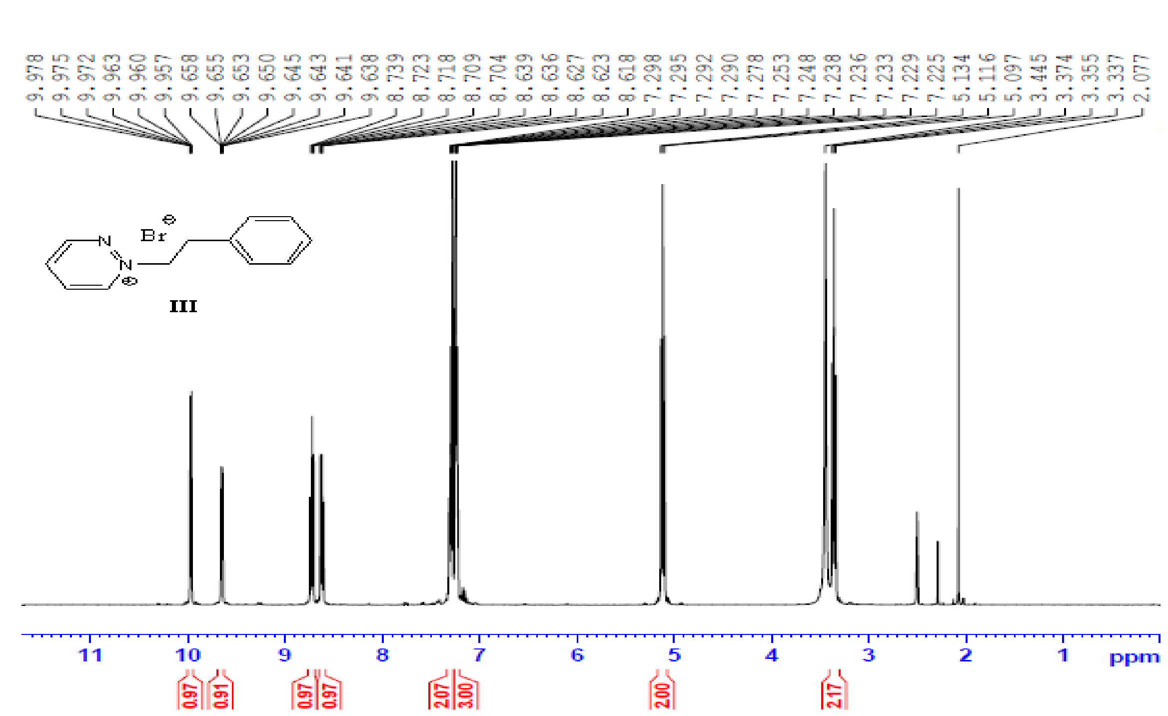


Figure 5. ^{1}H NMR spectrum (DMSO) of 1-phenethylpyridazinium bromide (**III**)

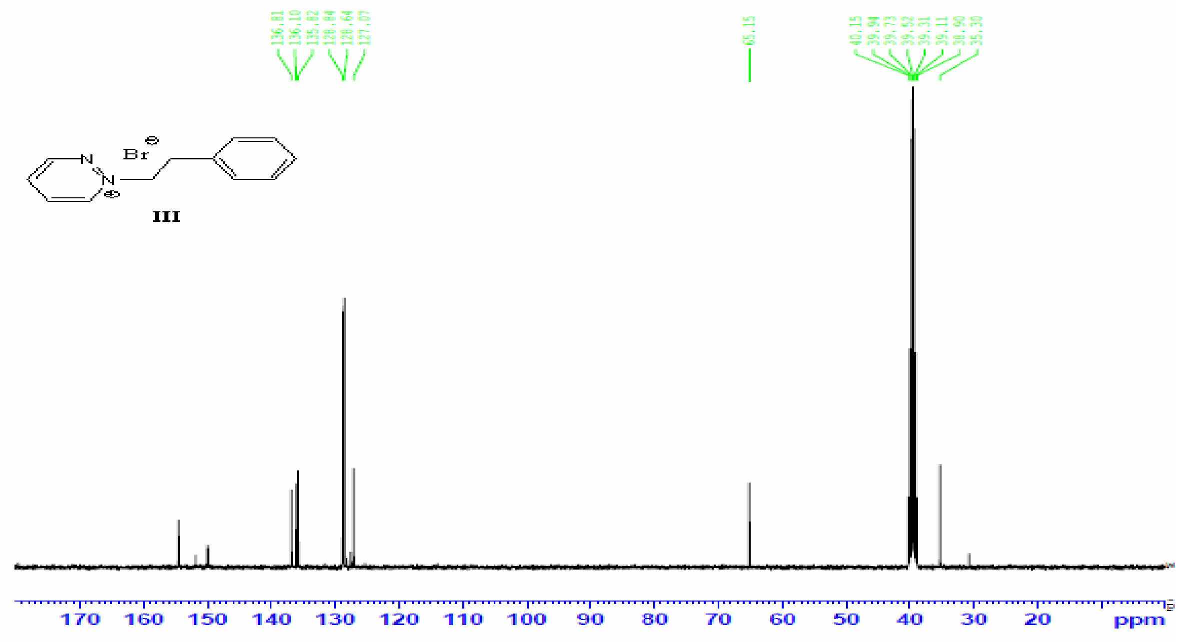


Figure 6. ^{13}C NMR spectrum (DMSO) of 1-phenethylpyridazinium bromide (**III**)

2.1.6. Synthesis of 1-(4-phenoxybutyl)pyridazinium bromide (**IV**)

Pyridazine (2 g, 0.025 mol), (4-bromobutoxy)benzene (6.27 g, 0.0275 mol) and 10ml of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 80 ºC. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 ºC. Brown crystals, yield 85%, mp 127-129 ºC. ^{1}H NMR (400MHz, DMSO) δ: 1.79 (quint, *J* = 7.6, 2H), 2.18 (quint, *J* = 7.6, 2H), 4,01 (t, *J* = 6.2, 2H), 4.92 (t, *J* = 7.4, 2H), 6.89-6.93 (m, 3H), 7.24-7.30 (m, 2H), 8.60-8.64 (m, 1H), 8.74-7.88 (m, 1H), 9.64-9.66 (m, 1H), 10.04-10.06 (d, *J* = 6 1H). ^{13}C NMR (100MHz, DMSO) δ: 25.2 (CH_2), 26.4 (CH_2), 64.2 (CH_2), 66.5 (CH_2), 114.4 (CH), 120.5 (CH), 129.4 (CH), 136.0(CH), 136.6(CH), 149.9(C), 150.0 (CH), 154.5 (CH), 158.4 (CH). LCMS: m/z 308 (M^+).

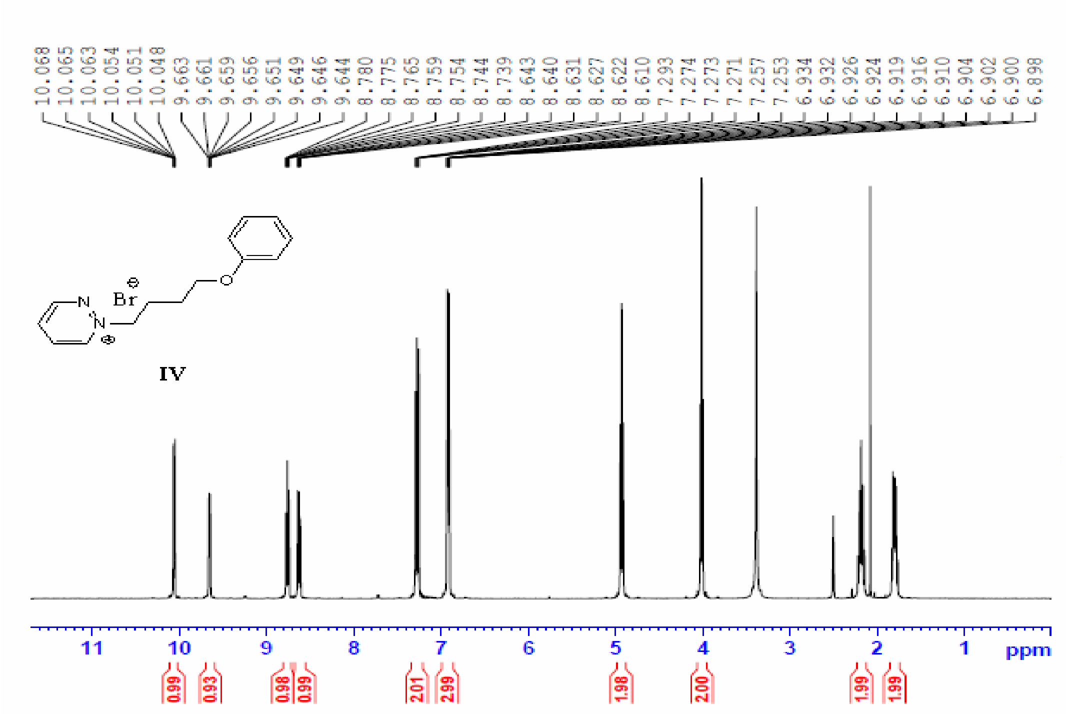


Figure 7. ^{1}H NMR spectrum (DMSO) of 1-(4-phenoxybutyl)pyridazinium bromide (**IV**)

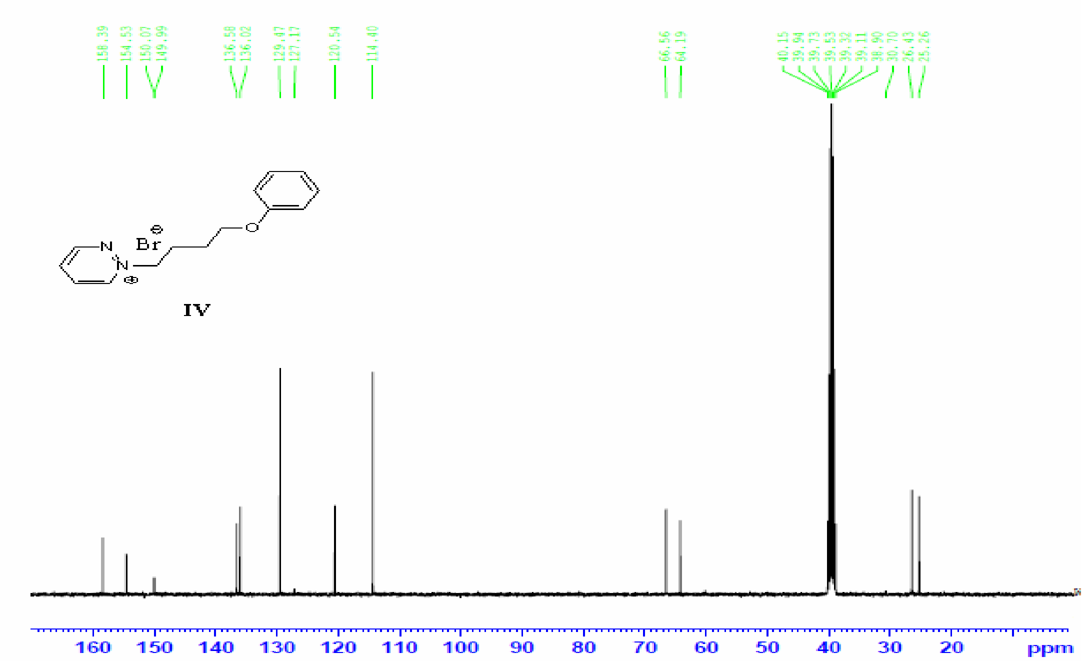


Figure 8. ^{13}C NMR spectrum (DMSO) of 1-(4-phenoxybutyl)pyridazinium bromide (**IV**)

2.2. Electrochemical tests

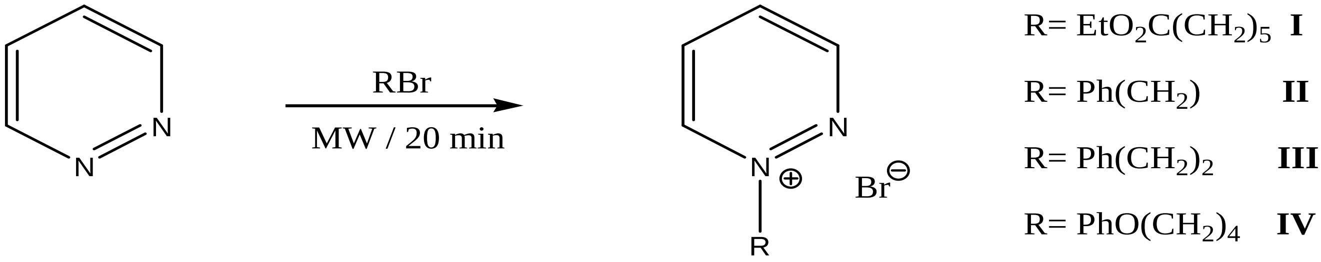
For the weight loss measurements, carbon steel sheets were used of chemical composition (wt%): C = 0.15%, Mn = 0.45%, Si = 0.10, S= 0.05%, P% = 0.03% and the reminder Fe and of size 4 cm^2 were used. The samples were abraded with a series of emery papers, from a coarse grade 500 and proceeding in steps to fine grade 1500, washed thoroughly with doubly distilled water. The cleaned samples were weighed before and after immersion in 1.0 M HCl for 4 hours in the absence and presence of various concentrations of the four ILs inhibitors. The mild steel specimens were rectangular in the form (1.8 cm×1.7 cm × 0.06 cm).

3. Results and Discussion

3.1. Microwave assisted synthesis of new pyradizinium-based ionic liquids

Number of procedures is recommended for Green Chemistry [29] involving: solvent-free reactions, non-classical modes of activation such as ultrasounds or microwaves. The use of MW irradiation leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach. [30-33].

As part of our program aimed, new environmentally friendly pyridazinium-based ionic liquids **(I-IV)** were prepared for the first time by using microwave irradiation in short duration of time with quantitative yields**.**



Scheme 1. N-alkylation of Pyridazine under microwave irradiation (MW).

The nucleophilic alkylation of pyridazine with different functionalized alkyl halides afforded the corresponding pyridazinium halides in 82-89% yield as solids (Table2).

Entry	RX	Yield (%) N-Alkylation
I	$EtO_2C(CH_2)_5Br$	82
II	$Ph(CH_2)Br$	87
III	$Ph(CH_2)_2Br$	89
IV	$PhO(CH_2)_4Br$	85

Table 2. Different entries and reaction yields for the synthesis of pyridazinium-based ionic liquids under microwave irradiation (MW).

Interestingly, the alkylation of pyridazine with different molar rations of alkyl halides afforded only the mono alkylated pyridazium-salts by using both SC and MW methods without any evidence for formation of dialkylated products. These results were supported on the basis of NMR (see the spectroscopic materials in experimental part).

3.2. Inhibitive effect of the new synthesized pyridazinium salts

3.2.1. Gravimetric measurements

The effect of addition of the pyridazinium salts (**I-IV**) at different concentrations on the corrosion of mild steel in 1M HCl solution was studied by weight loss for 4 h at 298 K. Table 3 gatheres the values deduced of W_{corr} and E%. In this case, the inhibition efficiency (E%) is determined by the equation 1:

$$E_w\% = \frac{(W^0_{corr} - W_{corr})}{W^0_{corr}} \times 100 \qquad (1)$$

where W_{corr} and W^o_{corr} are the corrosion rates of steel with and without inhibitor, respectively.

Gravimetric measurement shows that the corrosion decreases in the presence of all novel pyridazinium salts (**I-IV**). The inhibitive action is better expressed by the inhibition efficiency which increases with inhibitor concentration to reach 95.3% for **III** and **IV**, 94.% for **II** and 92.4 % for **I** at 10^{-2}M. Then all the studied inhibitors inhibit the corrosion of steel in 1M HCl, but the inhibitor **III** is found to be more effective even when we used small concentrations 10^{-4}M (Table 3).

Table 3. Gravimetric results of mild steel in 1M HCl without and with addition of inhibitors at 298 K.

Inhibitors	Concentration (M)	W_{corr} (mg.cm^{-2} .h^{-1})	E_W (%)
	Blank	0.424	-
I	10^{-4}	0.2450	42.2
	5.10^{-4}	0.1297	69.5
	10^{-3}	0.0814	80.8
	5.10^{-3}	0.0433	89.8
	10^{-2}	0.0322	92.4
II	10^{-4}	0.1458	65.6
	5.10^{-4}	0.0792	81.3
	10^{-3}	0.0563	86.7
	5.10^{-3}	0.0500	88.2
	10^{-2}	0.0250	94.1
III	10^{-4}	0.0556	86.8
	5.10^{-4}	0.0446	87.7
	10^{-3}	0.0314	92.6
	5.10^{-3}	0.0235	94.4
	10^{-2}	0.0196	95.3
IV	10^{-4}	0.0557	58.1
	5.10^{-4}	0.0510	80.6
	10^{-3}	0.0314	92.6
	5.10^{-3}	0.0235	94.4
	10^{-2}	0.0196	95.3

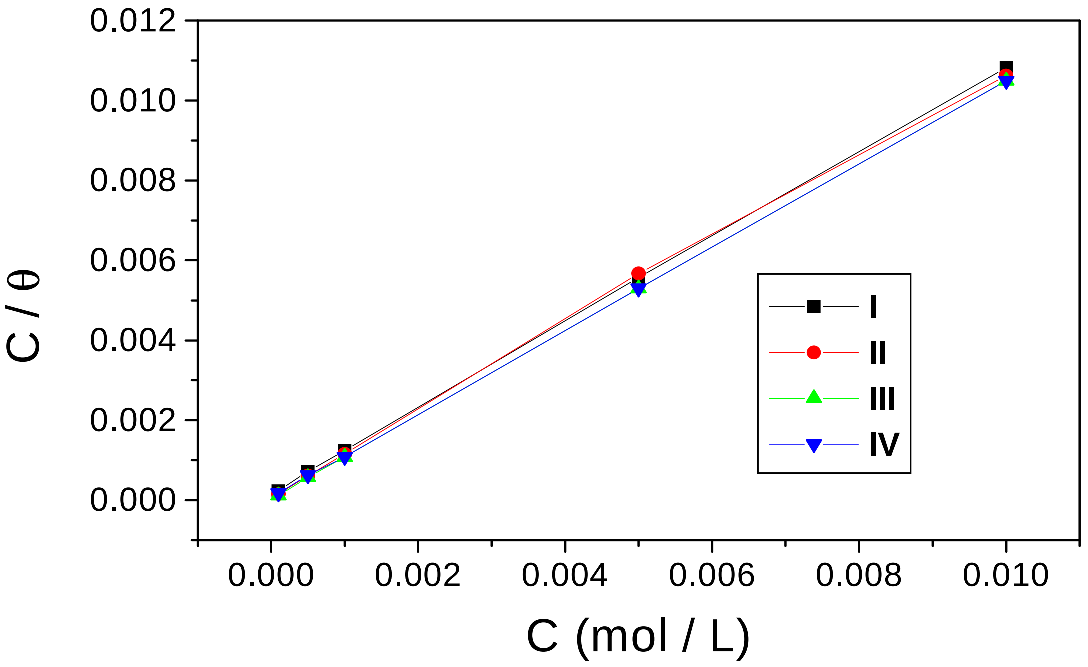
Since 1916, Langmuir adsorption isotherm receives more and more application to explain interaction between organic compound and metal surface in aqueous solution. Its theory is based on the quantitative relation of the covered and uncovered surface in relation with the inhibitor concentration. If θ is the fraction of the surface area covered by adsorbed molecules at any time, the rate of desorption is proportional to θ and equal to k_d θ where k_d is a constant at constant temperature. Similarly the rate of adsorption will be proportional to the area of bare surface and to the rate at which the molecules strike the surface (proportional to the gas pressure P). At equilibrium the rate of desorption equals the rate of adsorption k_a:

$$\mathrm{k_d}\theta = k_d(1-\theta)\,\mathrm{P} \tag{2}$$

The Langmuir isotherm can be written in rearranged form as: [34]

$$\frac{\theta}{C} = \frac{1}{K} + \mathrm{C} \quad \text{with} \quad K = \frac{1}{55.55}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{3}$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage and the standard adsorption free energy (ΔG°_{ads}).



Literature pointed that values of ΔG°_{ads} around -20 $kJ.mol^{-1}$ or lower are related to the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 $kJ.mol^{-1}$ or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [35]. The obtained values of ΔG°_{ads} surrounded -40 $kJ.mol^{-1}$ indicating, that the adsorption mechanism of the ILs tested on mild steel in 1M HCl.solution was typical of physical adsorption (Table 4).

Table 4. Adsorption data of ILs on mild steel in 1M HCl.

	Slope	**R^2**	***k***	**ΔG°_{ads}**
I	1.068	0.9999	5842.5	- 31.44
II	1.063	0.9995	8688.8	- 32.42
III	1.047	0.9999	29325.5	- 35.43
IV	1.043	0.9999	14130.3	- 33.63

3.2.2. Surface morphology study

The surface morphologies of C-steel specimen in 1.0 M HCl solution free or containing some of the ILs inhibitors after 4 h immersion were examined using scanning electron microscopy (SEM) as displayed in Fig. 9a–c. In the absence of inhibitors (Fig. 9a), a very rough surface was observed due to rapid corrosion attack of carbon steel by chloride anions. There are a large number of pits surrounded by iron oxide layer which almost fully covers the carbon steel surface, revealing that pit formation under these conditions occurs continuously during the exposure period while iron oxide builds up over the surface.

It is important to stress out that when ILs inhibitors (**III** and **IV**) are present in the solution (Fg. 9b,c) the morphology of the carbon steel surface are quite different from the previous one and the rough surface (amount of the formed iron oxide and the number of pits) is visibly reduced indicating the formation of a protective film.

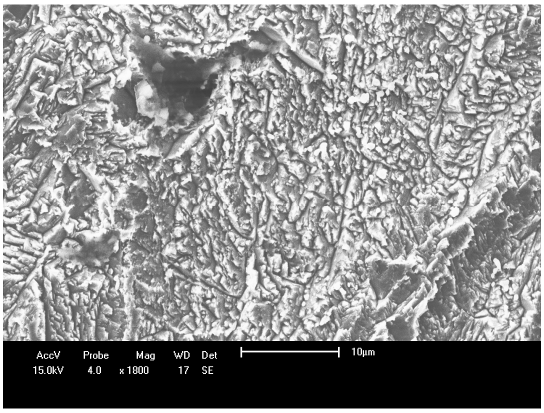


Figure 9a. SEM micrographs of the surface of the C-steel specimens in 1.0 M HCl.

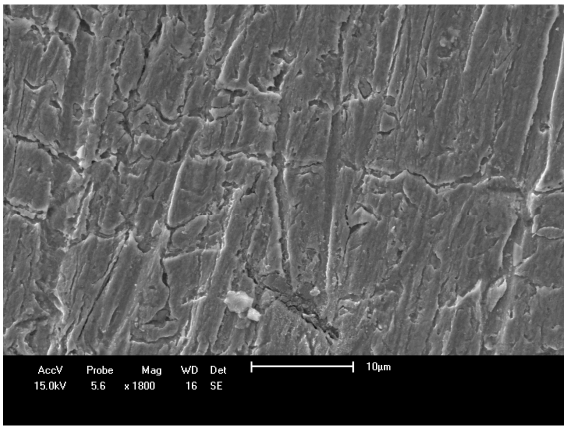


Figure 9b. SEM micrographs of the surface of the C-steel specimens in 1.0 M HCl in absence and in presence of 10^{-3} M of compound **III**.

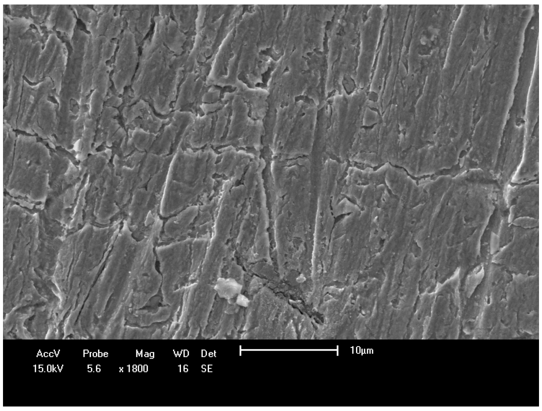


Figure 9c. SEM micrographs of the surface of the C-steel specimens in 1.0 M HCl in absence and in presence of 10^{-3} M of compound **IV**.

Conclusion

From the overall experimental results and discussion the following conclusions can be deduced:

- New environmentally friendly pyridazinium-based ionic liquids were prepared by using microwave irradiation.
- Many advantages for the MW irradiation compared with the standard methods have been recorded.
- The four tested ILs behave as inhibitors for the corrosion of the C-steel in 1 M HCl solution.
- The inhibition efficiency increased with increasing the inhibitor concentration. All of the ILs act as mixed-type inhibitors**.**
- The inhibition is due to the adsorption of the inhibitor molecules on the C-steel surface and the blocking of active sites.
- the adsorption mechanism of the ILs tested on mild steel in 1M HCl solution was typical of physical adsorption.

Acknowledgements

The author gratefully acknowledges the financial support from Taibah University (Grant 430/417), Dr Ziad Moussa for his assistance on the NMR analysis and Dr Saleh Alamry for SEM micrographs.

Refrences

1. Lashkari, M., Arshadi, M.R. *Chemical Physics,* 299 (2004) 131.
2. Sastri, V.S., Corrosion Inhibitors, Principles and Applications, John Wiley & Sons, New York, (1998). p. 25 and 237.
3. Abd El-Maksoud, S.A. and Fouda *Mater. Chem. Phys.* 93 (2005). 84.
4. Srikanth, A.P., Sunitha, T.G., Raman, V., Nanjundan, S. and Rajendran, N. *Mater. Chem. Phys.* 103 (2007) 241.
5. Bouklah, M., Attayibat, A., Hammouti, B., Ramdani, A., Radi, S. and Benkaddour, M. *Appl. Surf. Sci.* 240, (2005) 341.
6. Rogers, R. D.; Seddon, K. R. *Science* 302 (2003) 792-793.
7. Jain, N., Kumar, A., Chauhan, S., Chauhan, S. M. S. *Tetrahedron,* 61 (2005) 1015- 1060.
8. Wilkes, J. S. *Green Chem.* 4 (2002) 73-80.
9. Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim. Acta* 357-358 (2000) 97-102.
10. Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* 35 (1996) 1168-1178.

11. Dieter, K. M.; Dymek, C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc*. 110 (1988) 2722-2726.
12. Forsyth, S.A., Pringle, J.M., MacFarlane, D.R. *Aust. J. Chem*. 57 (2004) 113.
13. Endres, F., El Abedin, S.Z., Matter, S., *Phys. Chem. Chem. Phys*. 8 (2006) 2101.
14. Hagiwara, R.; Ito, Y. *J. Fluorine Chem*. 105 (2000) 221-227.
15. Hua, Z., Xia, S.Q., Ma, P.S. *Chem. Technol. Biotechnol*. 80 (2005) 1089.
16. Abbott, A.P. McKenzie, K.J. *Phys. Chem. Chem. Phys*. 84 (2006) 265.
17. Endres, F. *ChemPhysChem*. 3 (2002) 144.
18. Sato, T., Maruo, T., Marukane, S., Takagi, K. *J. Power Sources* 138 (2004) 253.
19. Ue, M., Takeda, M., Toriumi, A., Kominato, A., Hagiwara, R., Ito, Y. *J. Electrochem. Soc*. 150 (2003) 499.
20. Balducci, A., Bardi, U., Caporali, S., Mastragostino, M., Soavi, F. *Electrochem. Commun*. 6 (2004) 566.
21. Moens, L., Blake, D.M., Rudnicki, D.L., Hale, M.J. *J. Solar Energy Eng*. 125 (2003) 112.
22. Gasparac, R., Martin, C.R. Stupnisek-Lisac, E. *J. Electrochem. Soc*. 147 (2000) 548.
23. Zhang, D.Q., Gao, L.X., Zhu, G.D. *Corros. Sci*. 46 (2004) 3031.
24. Muralidharan, S., Iyer, S.V.K. *Anti-Corros. Met. Mater*. 44 (1997) 100.
25. Shi, S.C., Yi, P.G., Cao, C.Z., Wang, X.Y.*J. Chem. Ind. Eng. Chin*. 56 (2005) 1112.
26. Zhang, Q.B., Hua, Y.X. *Electrochimica Acta* 54 (2009) 1881–1887
27. Likhanova, N.V., Domínguez-Aguilar, M.A., Olivares-Xometl, O., Nava-Entzana, N., Arce, E., Dorantes, H. *Corros. Sci*. 52 (2010) 2088–2097.
28. Quraishi, M.A., Rafiquee, M.Z.A., Khan, S., Saxena, N. *J. Appl. Electrochem*. 37 (2007) 1153.
29. Anastas P. T., Warner J. C., Green Chemistry, Theory and Practice, Oxford University Press, Oxford, UK, (1998).
30. Loupy A. *C. R. Chimie 7* (2004) 103.
31. Aupoix, A., Pegot, B., Vo-Thanh G. *Tetrahedron*, 66 (2010)1352.

32 Yi, F., Peng, Y., Song, G. *Tetrahedron Lett*. 46 (2005) 3931.

33. Singh V.; Kaur S.; Sapehiyia V.; Singh J.; Kad G.L. *Catalysis Comm*. 6 (2005) 57.
34. Shreir, L.L., Jarman, R.A., Burstein, G.T., Corrosion Metal/Environment Reactions, vol. I, third ed., Butterworth–Heinemann, Great Britain, (Vol. 1 & 2), p.2587; 20:23 (1994).
35. M. Benabdellah, A. Tounsi, K.F. Khaled. B. Hammouti, *Arab. J. Chem.*, 4 N°1 (2011) 17-24.

(2011) http://www.jmaterenvironsci.com