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Original Article

Expired naproxen drug as a robust corrosion inhibitor of Al in 3 M hydrochloric acid system

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Abstract

The corrosion inhibition effect of expired naproxen on aluminum (Al) in a 3 M hydrochloric acid (HCl) environment was studied by gasometric, Tafel plot, impedance, quantum chemical, and scanning electron microscopy (SEM) studies. The gasometric results showed that expired naproxen behaves as a corrosion inhibitor for Al in a 3 M HCl medium. The protection efficiency was enhanced and the evolution of hydrogen gas decreased as the concentration of expired naproxen rose. The Tafel plots showed mixed corrosion inhibition properties of expired naproxen. Impedance spectroscopy showed that the expired naproxen inhibited the corrosion of Al by adhering to the surface. Quantum chemical calculations showed that the electron rich elements in the expired naproxen had an interaction capacity with the surface of Al in the 3 M HCl solution medium. SEM photographs showed the corrosion inhibition property of expired naproxen. Due to the presence of electron rich elements in the expired naproxen, the compound is considered to be a superior corrosion inhibitor.

Keywords: expired naproxen**,** aluminum, Tafel plot, impedance, quantum chemical method, gasometric

1. Introduction

The compounds in use to remove impurities and unwanted surface deposits from the surface of metals consist of strong acids. Aluminum (Al) undergoes corrosion when it interacts with hydrochloric acid (HCl) during several cleaning operations. Generally, in chemical and pharmaceutical industries, strong acids are used to eliminate the unnecessary surface deposits and impurities from the surface of Al. Al corrosion is an electrochemical phenomenon which destroys the Al structure. This is a major hitch to be addressed by the educational sectors and industries since it leads to huge economic losses. Among the available techniques, the use of inhibitors is cost effective and the most popular approach for the control of Al corrosion because they are highly efficient, practical, and environmentally safe. Because of the aggressive nature of strong HCl solutions, inhibitors are generally used to inactivate the role of acid on the surface of Al (Diggle, Downie, & Goulding, 1970; Eddy, Odoemelam, & Odiongenyi, 2009; Nathiya, Suresh Perumal, Vajjiravel Murugesan, & Raj, 2018; Pyun & Lee, 2001; Pyun & Moon, 1999).

The species present in the inhibitory molecule creates an insoluble adsorption film on the surface of Al that separates the Al from the HCl solution and prevents the Al disintegration or dissolution process. The high adsorption property of an inhibitor is due to the transfer of electrons from their orbital's to the surface of the Al and a strong bond forms between the inhibitor molecules and surface of the Al. Even though organic compounds that consist of N, O, P, and S elements showed good corrosion inhibition behavior on important industrial metals, not many organic species are used in industry due to the expense, toxicity, and solubility problems. Therefore, the search is for new, inexpensive, and non-toxic corrosion inhibitors. The principle aim of the present research was to develop an inexpensive, non-toxic, and highly soluble corrosion inhibitor for a corrosive solution (Bahrami, Hosseini, & Pilvar, 2010; Baumgaertner & Kaesche, 1990; Binks, Fletcher, & Salama, 2011; Sobhi, Abdallah, & Khairou, 2012; Yazdzad, Shahrabi, & Hosseini, 2008). Drugs are chemical substances that generate several

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biological effects when administered to living organisms. Therefore, the focus of research has shifted to medicinal drugs because they are non-toxic and easily available. For example, naproxen is a medication that is used for pain relief from tendonitis, menstrual cramps, muscle aches, headaches, and dental pain. It also reduces joint stiffness, swelling, and pain. However, naproxen is not suitable for consumers after its expiry date. The use of expired medicinal compounds as corrosion inhibitors may help solve economic and environmental problems and reduce the disposal costs of expired medicinal compounds. Usually, most medicinal compounds are expensive which makes them unsuitable for industry. It is well known that medicinal compounds exhibit 90% of biological activity even after the expiry date (Nestoridia & Pletcher, 2008). However, the use of expired medicinal drugs is restricted because of liability concerns and professional restrictions (Abdallah, 2004; Lee & Pyun, 1995; Mahmoud El-Haddad & Fouda, 2015; Oguzie, 2007). Hence, it is thought worthwhile to examine the inhibition behavior of expired medicinal compounds which are of no use as medical treatments. This investigation selected expired naproxen to examine its corrosion inhibition behavior on Al in a 3 M HCl solution by gasometric, Tafel plot, impedance, quantum chemical, and scanning electron microscopy (SEM) studies.

2. Experimental Part

The elemental composition of the Al metal pieces used in this study was Si (0.3–0.7%), Zn (0.2%), Cr (0.2%), Mn (0.3%), Mg (0.4–0.9%), Ti (0.1%), Cu (0.1%), Fe (0.6%), and the remainder was Al (96.9–97.8%). Expired naproxen was prepared in concentrations of 0.25 g/L, 0.5 g/L, 0.75 g/L, and 1.0 g/L for the aluminum corrosion studies. Dirt on the pieces of Al was removed using emery paper. The emery paper of grades up to 1500 was used to polish the Al metal and finally cleaned with double distilled water. Tafel plot and impedance spectroscopy studies were carried out using the three electrodes of Al (working cell), platinum (counter cell), and calomel (reference cell). The Tafel and impedance spectra were recorded by immersing the Al cell with a surface area of 1 cm^2 in a 3 M HCl solution for about 60–70 min. Potentiodynamic polarization curves (Tafel plots) were recorded in the potential range of ±200 mV at a scan rate of 0.01 V s^{-1}. The measurements of impedance studies were carried out using the AC signals of amplitude 10 mV in a frequency range from 10^5 Hz to 1 Hz. A gasometric apparatus calculates the volume of H_2 gas evolution from the reaction. A quantity of 100 mL of a 3 M HCl solution was added into the reaction vessel which was connected to a burette. The volume of air in the burette was noticed at the contact time of 120 min. Quantum chemical calculations using the PM3 method in ArgusLab software was applied to examine the molecular structure and electronic properties on the protection efficiency of the expired naproxen and to support the Tafel plot, impedance, and gasometric studies. The surface study was carried out by SEM. The aluminum metal was exposed to the 3 M HCl solution without and with 1 g/L of expired naproxen for a 2-h immersion period at room temperature. After this, the aluminum sample was removed from the test solution, dried, and submitted for the SEM analysis.

3. Results and Discussion

3.1 Tafel plot studies

The electrochemical workstation of CH Instruments Inc. was used to perform the Tafel studies. The positive effect of expired naproxen on the polarization property of Al in the 3 M HCl solution was analyzed and the Tafel plots were obtained (Figure 1).

The aluminum corrosion rate (mm/year) can be calculated from the following equation

$$\text{Corrosion rate}\left(\frac{\text{mm}}{\text{year}}\right) = \frac{0.13 \times i_{corr} \times EW}{nd},$$

where, i_{corr}=corrosion current density, d=density of aluminum, EW=equivalent weight of aluminum, n=number of electrons, and 0.13=metric and time conversion factor.

The results obtained from the Tafel plots are shown in Table 1. The Tafel diagrams showed reductions in the corrosion current density values of the cathodic and anodic sections in the presence of the expired naproxen. The introduction of 1.0 g/L of expired naproxen to the 3 M HCl solution (consisting of Al electrode) led to lower corrosion current density values. The anodic plot in the Tafel curves shows the Al oxidation process while the cathodic plot indicates the hydrogen evolution reaction. There is no change in the cathodic and anodic Tafel slope values which suggested the usual blocking effect of the expired naproxen on the Al surface. The expired naproxen inactivated the surface of the Al without changing the aluminum corrosion mechanism. The adsorption of the expired naproxen over the aluminum electrode was responsible for reducing the corrosion current density values by blocking the aluminum surface area.

The results hinted of high coverage on the Al electrode surface of the expired naproxen molecule (1.0 g/L) in the 3 M HCl environment. The nearly unaffected corrosion potential (E_{corr}), cathodic Tafel slope (β_c), and anodic Tafel slope (βa) values showed that the medicinal compound

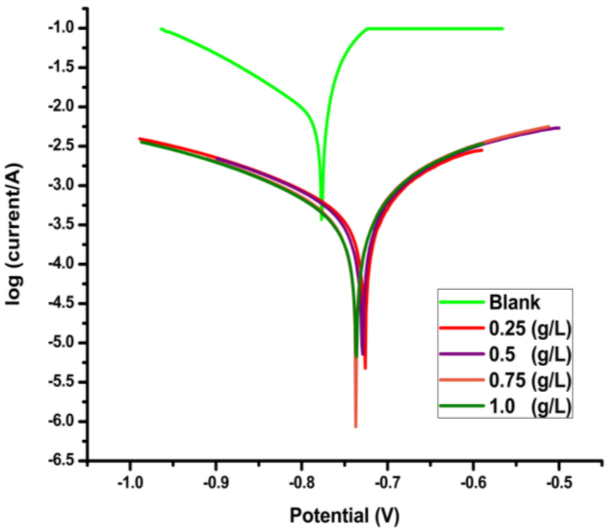

Figure 1. Tafel plots.

Table 1. Tafel results.

C (g/L)	(E_{corr}) (mV)	βa (V/dec)	βc (V/dec)	Corrosion rate (mm/year)	Corrosion current density (A)	Protection efficiency (%)
Blank	−777	0.003	6.392	24120.163	0.05570	
0.25	−726	5.188	4.901	320.441	0.00074	98.663
0.5	−729	5.604	4.963	290.129	0.00067	98.783
0.75	−737	5.883	5.038	242.495	0.00056	98.984
1.0	−736	5.860	5.234	238.165	0.00055	99.002

controlled both the anodic and cathodic processes by simply adsorbing on the Al surface in the 3 M HCl solution. Thus, the electron rich elements in the expired naproxen molecules physically or chemically adsorbed onto the Al electrode surface and blocked the Al corrosion process without altering the reaction mechanism. An increase in the concentration of the expired naproxen generally increased the protection efficiency of the green corrosion inhibitor. As a result of this, the corrosion rate of the Al metal decreased. The maximum shift in the corrosion potential value with respect to the bare solution was 51 mV which was less than 85 mV. Further, both the anodic and cathodic branches shifted towards lower corrosion current density values which indicated mixed type inhibition effects of the expired naproxen on the Al surface in the 3 M HCl system. This observation confirmed that the expired naproxen acted at both the anodic and cathodic domains. Hence, the expired naproxen falls under the category of mixed type.

3.2 Impedance studies

Another important electrochemical technique is AC impedance spectroscopy, which is a non-destructive method to evaluate the corrosion inhibition performance of corrosion inhibitors from the interaction between the aluminum metal and the corrosive environment. The main index expressing the corrosion protection efficiency is the corrosion resistance which is generally measured as the area enclosed by a loop in the impedance plots presented as Nyquist curves. For a good understanding of the phenomenon of corrosion, the mechanism of electrochemical reactions, especially the disintegration aspects taking place on the surface of metal in the electrolyte solution, was comprehensively considered.

Figure 2 shows the Nyquist diagrams of Al in the 3 M HCl solution with and without 0.25 g/L, 0.5 g/L, 0.75 g/L, and 1.0 g/L of expired naproxen. The depressed semicircle of the Al in the 3 M HCl solution was due to the roughness on the Al surface which possibly arose during polishing of the Al electrodes since the polishing was done using emery paper. The charge transfer resistance values had a direct relationship with the expired naproxen concentration. This indicated that adsorption of the inhibitory species was enhanced as the concentration increased. Hence, high charge transfer resistance values and robust corrosion inhibition property were observed at 1.0 g/L of expired naproxen (Table 2).

The equivalent electrical circuit model R(QR)(QR) was used in the present investigation to determine the charge transfer resistance values (Figure 3).

The shape of the Nyquist plots with and without expired naproxen did not change throughout study which showed no variation in the Al corrosion inhibition mechanism due to the presence of expired naproxen to the corrosive solution. The size of the capacitive loop enhances greatly with a rise in the concentration of the expired naproxen. This

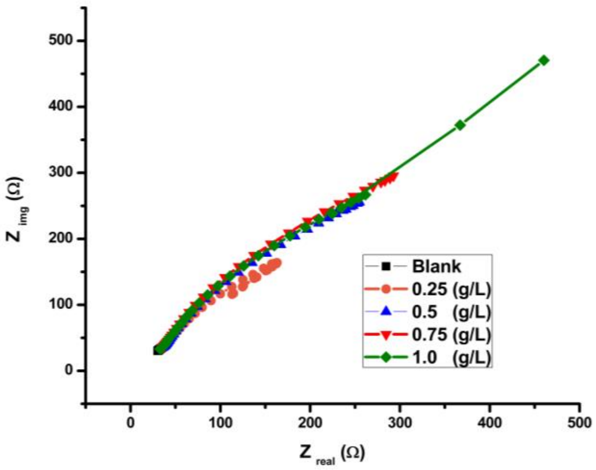

Figure 2. Nyquist plots.

Table 2. Nyquist plot results.

Concentration (g/L)	Charge transfer resistance (Ω)	Protection efficiency (%)
Blank	9.936	
0.25	152.5	93.484
0.5	267.6	96.286
0.75	310.4	96.679
1.0	336.8	97.704

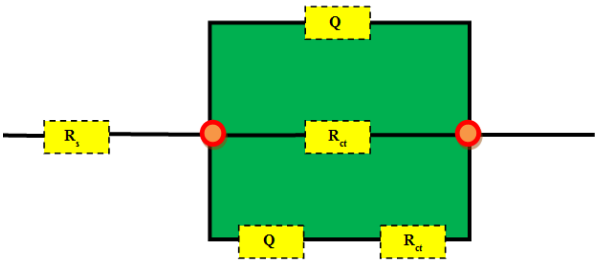

Figure 3. An equivalent electrical circuit model R(QR)(QR) where R_s=resistance of electrolyte in bulk, R_{ct}=charge transfer resistance, and Q=constant phase element.

showed the resistance against corrosion of the Al attack via hindrance of the dissolution reaction due to the adsorption of the expired naproxen molecules. The Nyquist plots were not perfect semicircles because of the roughness of the Al and surface unevenness.

3.3 Gasometric studies

The effect of different amounts of expired naproxen species on the protection efficiency over the Al surface in the 3 M HCl solution was analyzed from gasometric studies. The results of the gasometric technique are presented in Table 3. It was observed that the protection efficiency was enhanced as the concentration of the expired naproxen increased. The increased protection rate was due to the adsorption of expired naproxen molecules on the surface of the Al in the 3 M HCl solution. The Al corrosion inhibition process depended mainly on the ability of the expired naproxen species to settle on the surface of the Al. The Al corrosion inhibition took place via displacement of adsorbed water species on the Al surface.

It was also clear that the amount of evolved hydrogen gas decreased as the concentration of expired naproxen increased. The addition of the expired naproxen to the 3 M HCl solution, which contained the Al electrode, decreased the Al corrosion rate. The maximum protection efficiency and minimum Al corrosion rate were observed at 1.0 g/L of expired naproxen. The addition of expired Naproxen drug to the beaker containing the Al and the 3 M HCl solution greatly reduced the hydrogen evolution process. The gasometric technique results also showed that the protection efficiency was enhanced as the concentration of expired naproxen increased which was very similar to the Tafel plot and impedance spectroscopy results. The protection efficiency obtained from the potentiodynamic polarization, AC impedance spectroscopy, and gasometric techniques are shown in Figure 4.

3.4 Quantum chemical calculations

Theoretical calculations on the expired naproxen were performed using the PM3 method in ArgusLab software to examine the corrosion inhibition property of the expired naproxen.

The ionization potential (I) can be calculated as minus E_{HOMO} where E_{HOMO} is the energy of the highest occupied molecular orbit. Electron affinity (A) can be calculated as minus E_{LUMO} where E_{LUMO} is the energy of the lowest unoccupied molecular orbit. Chemical hardness can be calculated from (η) = $\frac{I-A}{2}$, and chemical softness (σ) can be obtained from σ = $\frac{1}{\eta}$.

The results of quantum chemical calculations are shown in Figure 5 and Table 4. The E_{HOMO} shows the ability of the substance to donate the electron to the Al metal in a 3 M HCl solution whereas E_{LUMO} shows the ability of the substance to accept an electron. A higher value of E_{HOMO} shows a high capability of donating an electron to the metal surface. A lower value of E_{LUMO} shows a great tendency of accepting an electron from another substance. In this investigation, the obtained values showed that the expired naproxen has a greater tendency to donate an electron to the Al surface in the 3 M HCl solution, thus preventing the Al dissolution process. High I values show high stability and inertness of an organic compound and low I values show high reactivity of an organic compound. Softness and hardness are important parameters for measuring the stability and reactivity of an expired drug product. The quantum chemical results fully satisfied the results of the Tafel plot, impedance spectroscopy, and gasometric studies.

Table 3. Gasometric results.

Concentration (g/L)	Volume of hydrogen gas evaluation (mL)	Protection efficiency (%)
Blank	25	
0.25	3.1	87.6
0.50	2.3	90.8
0.75	2.0	92.0
1.00	0.7	97.2

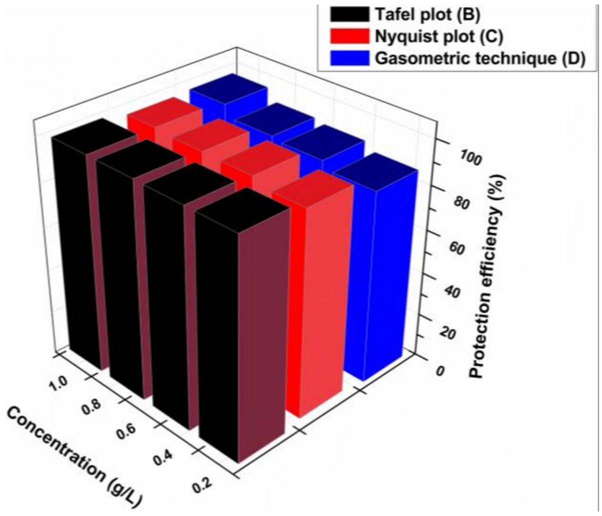

Figure 4. Protection efficiencies obtained from different techniques.

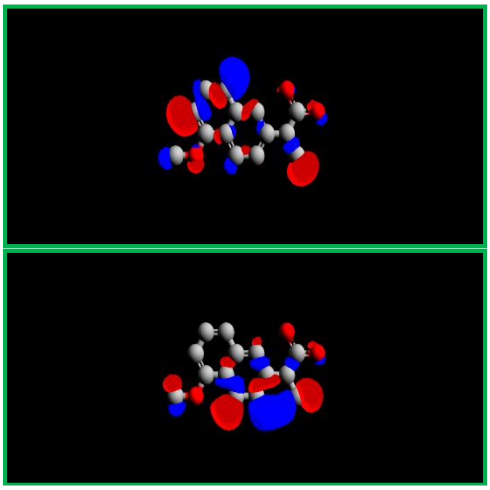

Figure 5. E_{HOMO} and E_{LUMO} of naproxen

Table 4. Quantum chemical parameters using the PM3 method.

$-E_{Homo}$ (eV)	$-E_{LUMO}$ (eV)	Energy gap (eV)	Ionization potential	Electron affinity	Chemical hardness	Chemical softness
10. 338	2.386	7.952	10. 33	2.386	3.97	0.251

3.5 Surface analysis

3.5.1 SEM

The morphology of Al treated with 3 M HCl and Al immersed in 3 M HCl with 1 g/L of expired naproxen were observed by SEM (Figures 6a and 6b**)**. The Al immersed in the 3 M HCl solution showed a rough surface that possessed products of corrosion. Meanwhile, the Al treated with 3 M HCl solution with 1 g/L of expired naproxen showed a smooth surface due to the formation of a protective layer by the expired naproxen molecules on the surface of the Al. This confirmed the corrosion inhibition property of expired naproxen for Al in a 3 M HCl solution.

4. Conclusions

The non-toxic corrosion inhibition of expired naproxen for Al was demonstrated at low amounts of the inhibitor in a 3 M HCl system. The Tafel plots revealed that the expired naproxen exhibited a mixed corrosion property. Impedance spectroscopy results showed that the charge transfer resistance and protection efficiency increased. Furthermore, the Al corrosion rate decreased as the concentrations of the expired naproxen increased. The protection efficiency calculated by the gasometric studies exhibited a protection efficiency of 97.2% at 1 g/L of the expired naproxen. The results of quantum chemical calculations and SEM photographs indicated sole adsorption of the expired naproxen on the electrode surface. The expired naproxen is expected to be a good corrosion inhibitor for Al in several industrial dissolution processes.

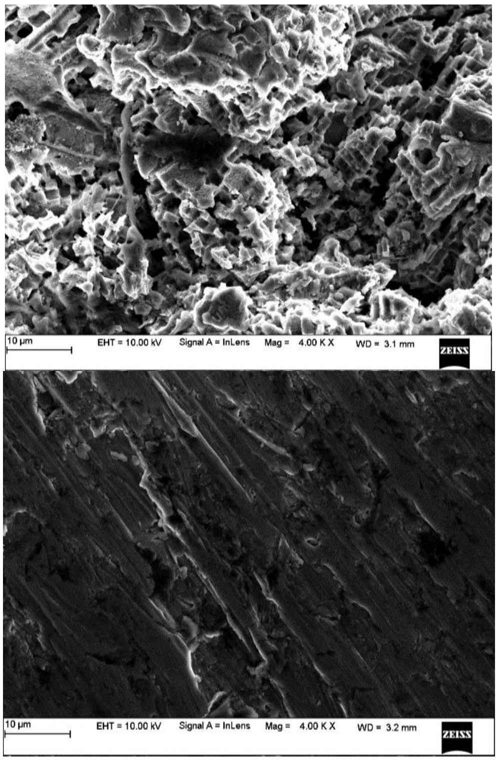

Figure 6. Scanning electron microscopy images: (A) without inhibitor (B) with inhibitor.

References

Abdallah, M. (2004). Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution. *Corrosion Science, 46*, 1981-1996.

Bahrami, M. J., Hosseini, S. M. A., & Pilvar, P. (2010). Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium. *Corrosion Science, 52*, 2793-2803.

Baumgaertner, M., & Kaesche, H. (1990). Aluminum pitting in chloride solutions: morphology and pit growth kinetics. *Corrosion Science*, *31*, 231-236.

Binks, P. B., Fletcher, P. D., & Salama, I. E. (2011). Quantitative prediction of the reduction of corrosion inhibitor effectiveness due to parasitic adsorption onto a competitor surface. *Langmuir, 27*, 469–473.

Diggle, W., Downie, T. C., & Goulding, C. (1970). The dissolution of porous oxide films on aluminium. *Electrochimica Acta*, *15*, 1079-1093.

Eddy, N. O., Odoemelam, S. A., & Odiongenyi, A. O. (2009). Joint effect of halides and ethanol extract of Lasianthera africana on inhibition of corrosion of mild steel in H_2SO_4. *Journal of Applied Electrochemistry, 39*, 849-857.

Lee, E. J., & Pyun, S. J. (1995). The effect of oxide chemistry on the passivity of aluminum surfaces. *Corrosion Science, 37*, 157-168.

Mahmoud El-Haddad, N., & Fouda, A. S. (2015). Electroanalytical, quantum and surface characterization studies on imidazole derivatives as corrosion inhibitors for aluminum in acidic media. *Journal of Molecular Liquids, 209*, 480-486.

Nathiya, R. S., Perumal, S., Murugesan, V., & Raj, V. (2018). Expired drugs: environmentally safe inhibitors for aluminium corrosion in 1 M H_2SO_4. *Journal of Bio- and Tribo-Corrosion*, 4, 4. doi:10.1007/s40735-017-0120-1

Nestoridia, M., & Pletcher, D. (2008). The study of aluminium anodes for high power density Al/air batteries with brine electrolytes. *Journal of Power Sources, 178*, 445–455.

Oguzie, E. E. (2007). Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract. *Corrosion Science, 49*, 1527-1539.

Pyun, S. I., & Lee, W. J. (2001). The effect of prior Cl-ion incorporation into native oxide film on pure aluminium in neutral chloride solution on pit initiation. *Corrosion Science, 43*, 353-363.

Pyun, S. I., & Moon, S. M. (1999). The inhibition mechanism of pitting corrosion of pure aluminum by nitrate and sulfate ions in neutral chloride solution. *Journal of Solid State Electrochemistry, 3*, 331-336.

Sobhi, M., Abdallah, M., & Khairou, K. S. (2012). Sildenafil citrate (Viagra) as a corrosion inhibitor for carbon steel in hydrochloric acid solutions. *Monatshefte für Chemie - Chemical Monthly, 143*, 1379-1387.

Yazdzad, A. R., Shahrabi, T., & Hosseini, M. G. (2008). Inhibition of 3003 aluminum alloy corrosion by propargyl alcohol and tartrate ion and their synergistic effects in 0.5% NaCl solution. *Materials Chemistry and Physics, 109*, 199-205.