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Comparison between Non-linear and ANN Models for Prediction of Corrosion Inhibition Efficiency of Mild Steel

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Abstract: QSAR can assist in the quick and low-cost identification of new corrosion inhibitor compounds. Early research revealed a connection between a molecule's quantum parameters and inhibition efficiency (*IE*). A possible nonlinear equation between experimental inhibition efficiencies (IE_{exp}) of corrosion inhibitors and some quantum parameters was sought for some Triazole derivatives in previous study. This work aims to compare nonlinear model from previous study and artificial neural network (ANN) used in this study to predict inhibition efficiency. The investigation shows that ANN is more efficient and accurate than nonlinear model to predict inhibition efficiencies, where correlation coefficient R (between IE_{exp} and predicted inhibition efficiency (IE_{pred})) increased from 0.95 to 0.99 and mean square error decreased from 4.0×10^{-3} to 6.1×10^{-5}respectively.

Keywords: (QSAR, neural network, corrosion inhibitors, Triazole, modelling, Quantum study)

Introduction

Pipelines are crucial pieces of machinery that are used to move gases and liquids over large distances. In the oil industry, corrosion occurs through procedures including acid cleaning, pickling, and etching, which calls for the use of corrosion inhibitors. The majority of pickling inhibitors are harmful substances. Due to increased global environmental awareness and new environmental protection requirements, these compounds must be replaced with more environmentally acceptable inhibitors. Inhibitors of mild steel corrosion in hydrochloric acid that are non-toxic, like Triazole derivatives, are the focus of this article. Triazole derivatives are among the various heterocyclic chemicals explored as corrosion inhibitors since they are regarded to be environmentally acceptable. Additionally, they are very thermally stable substances that are simple to synthesize, effective at low doses, and inexpensive. For this reason, the main methods for assessing the ability to block and adsorb are electrochemical technique and quantum chemical analysis [1-3].

Numerous approaches, including theoretical and experimental ones, have been used to study the inhibition efficiency of corrosion inhibitors. For instance, the most popular experimental techniques for evaluating the effectiveness of inhibition are electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and weight losses methodology. They are pricy and time-consuming. Theoretical techniques have overcome all of these challenges [1-3]. Most popular technique is QSAR.

Regression models is a set of statistical procedures for estimating the relationships (linear or nonlinear equations) between a dependent variable and one or more independent variables, that are utilized in the fields of chemical engineering and biological sciences are known as quantitative structure–activity relationship models (QSAR) [4].

Artificial neural networks (ANNs) have become effective tools for modeling links between quantum chemical parameters and IE.

It is not always feasible to deal with many corrosion problems by the use of traditional analysis such as nonlinear repression technique. The limitations of traditional methods such multiple linear relationships, partial least squares, and principal component analysis are overcome by the capability of ANN techniques to describe nonlinear relationships [5].

The Triazole compounds that were employed in this work are depicted in Table 1 and Fig. 1 together with their chemical formulas, nomenclature, and structural details. Experimental research has shown these chemicals to be effective in inhibiting corrosion, with efficiencies ranging from 73 to 98.5% [4].

In previous work [4], the nonlinear technique was used to *IE*. Artificial neural networks (ANNs) were used in this study in an effort to forecast *IE*. At the end of this research, a comparison between nonlinear method and the application of ANN for predicting inhibition efficiency was made.

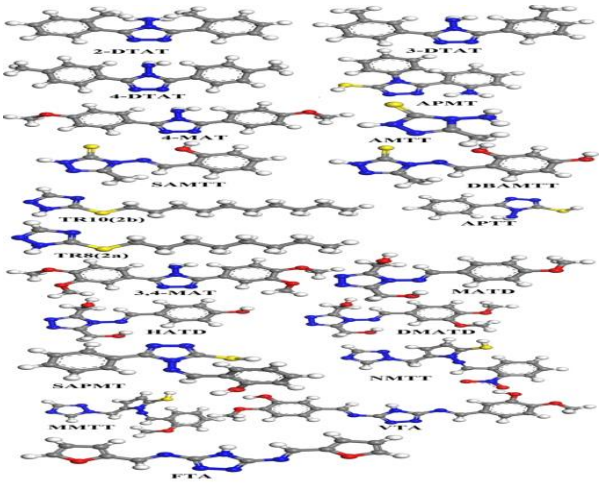

Fig. 1: Chemical structure of Triazole derivatives

Details of calculation methods

Quantum chemical computations were used to examine the molecular structures of the chosen inhibitors. All quantum calculations carried out in the Windows environment with of Material Studio 5.5 using AM1 semi-empirical method. Utilizing the default software parameters, all inhibitors were fully optimized geometrically without any limitations [6].

By the end of the quantum calculations, all calculated quantum parameters are tabulated in Excel file. A table with 20 rows and 10 columns was obtained. Each raw corresponds to a certain inhibitor (from inhbitor1 to inhibitor 20) as shown if Fig.2. The columns correspond to quantum parameters: respectively inhibition efficiency IE, (energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), Total dipole (μ), surface area of molecule (SA), Energy gap (ΔE), Adsorption energy(E_{ads}), temperature (T), inhibitors concentration (C_i), and Log of the partition coefficient (AlogP)) [7]. After organization of quantum parameters in Excel file, these data are easily accessed by Matlab Software.

	A	B	C	D	Insert Function	G	H	I	J
1	IE	HOMO eig	LUMO eig	Total dipo	Molecular	ΔE	Adsorptio	T	Ci	AlogP (Fast
2	0.921	-8.966	-0.414	5.779	306.798	-8.55214	-154.863	30	0.0005	4.856
3	0.883	-9.251	-0.283	5.379	303.578	-8.96852	-151.126	30	0.0005	4.856
4	0.957	-8.846	-0.443	5.511	307.409	-8.40328	-155.334	30	0.0005	4.856
5	0.834	-8.547	-0.432	3.672	278.850	-8.11478	-133.754	25	9.32E-05	3.657
6	0.98	-8.648	-0.388	4.541	324.768	-8.26051	-169.868	30	0.0004	3.416
7	0.73	-8.772	-0.129	3.098	143.402	-8.64292	-62.4055	27	0.0007	0.239
8	0.93	-8.507	-0.490	5.432	246.833	-8.01628	-125.568	27	0.0007	2.513
9	0.94	-8.496	-0.516	4.390	258.299	-7.98041	-127.465	27	0.0007	2.229
10	0.82	-8.692	-0.035	2.648	323.133	-8.65711	-146.651	30	0.000001	4.349
11	0.8	-8.692	-0.036	2.646	279.443	-8.65613	-127.475	30	0.000001	3.556
12	0.9181	-8.605	-0.447	4.423	203.762	-8.15852	-101.817	30	0.0008	2.499
13	0.985	-8.727	-0.580	2.113	384.059	-8.14718	-205.359	35	0.0001	2.910
14	0.9105	-9.259	-0.965	7.183	287.893	-8.29411	-143.797	30	0.001525	2.844
15	0.8824	-9.354	-1.019	6.490	267.400	-8.33546	-132.42	30	0.001611	2.812
16	0.9376	-9.126	-0.984	8.099	319.011	-8.14215	-160.597	30	0.001368	2.591
17	0.956	-8.595	-0.883	3.739	297.219	-7.71214	-159.295	25	0.001687	4.773
18	0.896	-9.094	-1.611	7.807	326.670	-7.48303	-167.276	20	0.001	4.049
19	0.901	-8.700	-0.663	6.853	337.046	-8.03744	-164.211	20	0.001	3.843
20	0.9005	-8.630	-1.321	6.400	278.139	-7.30884	-138.314	28	0.0003	2.982
21	0.93	-8.502	-1.156	1.420	394.798	-7.34609	-201.53	28	0.0003	3.652

Fig. 2: A screenshot of tabulated quantum parameters in Excel file

The excel file was called using xlsread command to load all parameters into Matlab workspace. The quantum parameters table is then presented to artificial neural networks

using nftool command to prepare them for prediction of inhibition efficiency [8].

Table 1: Names, nomenclature and molecular properties of studied trizole derivatives

Full name	Nomenclature	Chemical formula	Net mol. mass
3,5-di(3-tolyl)-4-amino-1,2,4-triazoles	3-DTAT	C16 H16 N4	264.332
3,5-di(2-tolyl)-4-amino-1,2,4-triazoles	2-DTAT	C16 H16 N4	264.332
3,5-di(4-tolyl)-4-amino-1,2,4-triazoles	4-DTAT	C16 H16 N4	264.332
3-aminophenyl-4-phenyl-5-mercapto-1,2,4-triazole	APMT	C14 H12 N4 S	268.338
3,5-bis(4-methoxyphenyl)-4-amino-1,2,4-triazole	4-MAT	C16 H16 N4 O2	296.330
4-amino-5-methyl-4H-1,2,4-triazole-3thiol	AMTT	C3 H6 N4 S	130.169
4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione	SAMTT	C10 H10 N4 O S	234.277
4-(2,4-dihydroxybenzylideneamino)-3-methyl-1H-1,2,4-triazole-5(4H)-thione	DBAMTT	C10 H10 N4 O2 S	250.276
5-decylsulfanyl-1,2,4-triazole	TR10(2b)	C12 H23 N3 S	241.397
5-octylsulfanyl-1,2,4-triazole	TR8(2a)	C10 H19 N3 S	213.343
4-Amino-5-phenyl-4H-1,2,4-triazole-3-thiol	APTT	C8 H8 N4 S	192.240
3,5-bis(3,4-dimethoxyphenyl)-4-amino-1,2,4-triazole	3,4-MAT	C18 H20 N4 O4	356.382
(4-(4-methoxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol	MATD	C12 H14 N4 O3	262.269
(4-(4-hydroxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol	HATD	C11 H12 N4 O3	248.242
(4-(3,4-dimethoxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol	DMATD	C13 H16 N4 O4	292.295
4-salicylideneamino-3-phenyl-5-mercapto-1,2,4-triazole	SAPMT	C15 H12 N4 O S	296.348
1-(2″-nitrobenzyl)methenylideneamino-2-mercapto-5-(1-(1′,2′,4′-triazol)) methenyl-1,3,4-triazole	NMTT	C14 H12 N6 O2 S	328.350
1-(2″-methoxybenzyl)methenylideneamino-2-mercapto-5-(1′-(1′,2′,4′-triazol)) methenyl-1,3,4-triazole	MMTT	C15 H15 N5 O S	313.379
furfuraldine 3,5-diamino-1,2,4-triazole	FTA	C12 H9 N5 O2	255.237
Vanilidine 3,5-diamino-1,2,4-triazole	VTA	C18 H17 N5 O4	367.365

By default, nftool splits the table into three parts: 15% of the data are used for testing, 15% of the data are used for validation, and 70% of the data are used for training as shown in Fig.3. The algorithm modifies the network parameters throughout the course of 1000 epochs during the learning phase. The mean square error between the computed IEcalc and IEexp is calculated during a time. Different training algorithms were tested. The points should ideally go closer to the identify line. The regression factor provides a quantitative evaluation of the overall performance. Also, the number of neurons in the hidden layer is one of ANN's most important characteristics. The network won't be able to model the complex data and the fit won't be good if there aren't enough neurons used.in this work, a small number of hidden layer (10 layer) was employed due to the size of data is large. The Schematically structure of the proposed ANN with 9 inputs (E_{HOMO}, E_{LUM}, μ, SA, ΔE, E_{ads}, T,

Ci, and AlogP) and 1 output IE_{calc} is shown in Fig.4 [9-13].

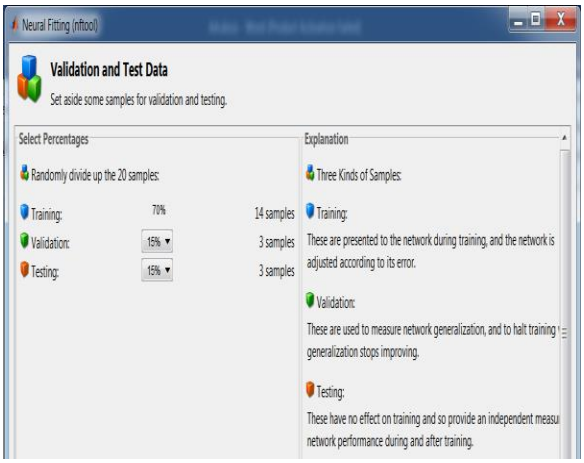

Fig. 3: splitting data into training**,** validation and tested data

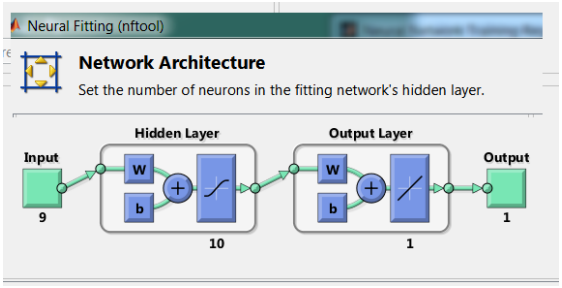

Fig. 4: ANN architecture with 9 input and one output

A statistical relationship between two variables is referred to as a correlation coefficient. There are a number of different kinds of correlation coefficients, but all of them will always fall between -1 and 1, where the strongest possible agreement is very close to 1. The linear relationship's strength and direction are measured by the Pearson product-moment correlation coefficient (R^2). A measure of how well and closely of two variables are related is the correlation coefficient (R) [4].

Results and discussion

The experimental data of inhibition efficacy (Electrochemical impedance spectroscopy (EIS)) were collected from references. This study used AM1 semi-empirical method and QSAR techniques. The compounds in Fig. 1 were subjected to semi-empirical quantum chemical computations, with the results shown in Table 2 [14].

Values for a few quantum chemical characteristics for molecules of Triazole derivatives are listed in Table 2. The HOMO and LUMO energies and how they are distributed across molecules have a crucial role in determining reactivity. The capacity of a molecule to give an electron is often linked to E_{HOMO}, whereas the ability to receive an electron is linked to E_{LUMO}. As a result, the adsorption process is facilitated by larger values of E_{HOMO} and lower values of E_{LUMO}. The results of Table 1 show, the estimated values of E_{HOMO} and E_{LUMO} are not similar to the measured values of IE_{exp}, and the measured quantum chemical parameters altered erratically with IE_{exp} inhibition. This suggested that the inhibitors might not be either the acceptor or the giver of the electrons [15-17].

Additionally, there must be a strong link between quantum parameters and corrosion inhibitor activity in order to derive reliable productivity assumptions. However, none of these parameters and inhibition efficiencies have a clear link. thus the need for new technique is necessary. In previous work, Lukovits non-linear model was employed to perform QSAR. In this study, The QSAR of the studied molecules in Fig. 1 as inhibitors for metal in HCl medium was performed using ANN [19-20].

Between IEexp and IEcalc, a strong correlation coefficient R2 of 0.985 has been obtained. In Table. 3, the calculated IEcalc and R2 values for each approach are provided. In Fig. 4, the values of IEcalc and IEexp for the derivatives of triazoles are plotted. A comparison between calculated and experimental values using nonlinear model and ANN is shown in Figure 4. Figures 5 showed a very high correlation coefficient of ANN than nonlinear model. This

illustrates the close relationship between experimental and predicted values. The suggested ANN model is stable and predicative, as shown by the strong R2 according to statistical parameters [21-23].

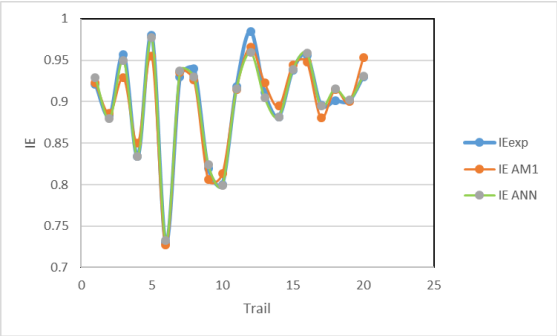

Fig. 5: IE_{calc} obtained by nonlinear method and ANN at different concentrations of compounds Triazole derivatives

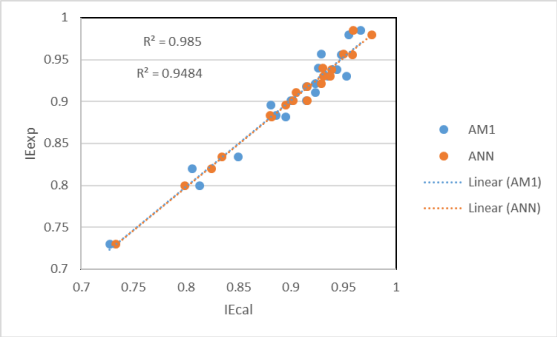

Fig.6: Correlation between IExp and IEcalc using nonlinear method and ANN

Conclusion

After the theoretical tests, it was discovered that the Triazole derivatives' inhibitory efficiency could be predicted using quantum parameters. The investigation shows that ANN is more efficient and accurate than nonlinear model, where correlation coefficient is higher and mean square error is lower. When corrosion measuring devices are not accessible, the ANN might be used to determine predict inhibition efficiency of Triazole derivatives. However, the inhibitory efficiency might be obtained when the quantum parameters are included in the ANN. ANN has higher correlation coefficients than nonlinear model from previous work, which indicate that the model's strength is good and that IE_{calc} and IE_{exp} are extremely close to one another. Following this comparative study, we concluded that ANN is the most appropriate algorithm for this kind of problems.

Table 3. IE_{exp} obtained using EIS of Triazole compounds and IE_{calc} obtained by the proposed equations and ANN method.

				IE_{calc}			
	R			0.974	0.992	Error=(IE_{exp}- IE_{calc})^2	
	R^2			0.949	0.985		
	Compound	Ci (M)	IE_{exp}	AM1	ANN	AM1	ANN
1	3-DTAT	5.00E-04	0.921	0.923	0.929	4.0E-06	6.7E-05
2	2-DTAT	5.00E-04	0.883	0.886	0.880	9.0E-06	1.1E-05
3	4-DTAT	5.00E-04	0.957	0.929	0.950	7.8E-04	4.9E-05
4	APMT	9.32E-05	0.834	0.850	0.834	2.6E-04	7.3E-08
5	4-MAT	4.00E-04	0.980	0.955	0.977	6.3E-04	8.1E-06
6	AMTT	7.00E-04	0.730	0.727	0.733	9.0E-06	7.5E-06
7	SAMTT	7.00E-04	0.930	0.935	0.937	2.5E-05	5.3E-05
8	DBAMTT	7.00E-04	0.940	0.926	0.930	2.0E-04	9.4E-05
9	TR10(2b)	1.00E-06	0.820	0.806	0.824	2.0E-04	1.8E-05
10	TR8(2a)	1.00E-06	0.800	0.813	0.799	1.7E-04	1.0E-06
11	APTT	8.00E-04	0.918	0.915	0.916	9.0E-06	6.2E-06
12	3,4-MAT	1.00E-04	0.985	0.966	0.960	3.6E-04	6.5E-04
13	MATD	1.53E-03	0.911	0.923	0.905	1.4E-04	3.9E-05
14	HATD	1.61E-03	0.882	0.895	0.882	1.7E-04	3.5E-08
15	DMATD	1.37E-03	0.938	0.944	0.939	3.6E-05	5.0E-07
16	SAPMT	1.69E-03	0.956	0.948	0.958	6.4E-05	5.4E-06
17	NMTT	1.00E-03	0.896	0.881	0.895	2.3E-04	8.4E-07
18	MMTT	1.00E-03	0.901	0.915	0.915	2.0E-04	2.1E-04
19	FTA	3.00E-04	0.901	0.900	0.902	1.0E-06	8.6E-07
20	VTA	3.00E-04	0.930	0.953	0.931	5.3E-04	1.3E-06
					mean squared error	4.0E-03	6.1E-05

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