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Review

Copper Corrosion Inhibitors. Period 2008-2014. A Review

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This review is a result of the literature survey concerning the possibility of copper corrosion prevention. Focus is on the efficiency obtained using various organic compounds as corrosion inhibitors in numerous conditions. Several groups of compounds are found to be particularly important such as: azoles, purine and derivatives and amino acids. On the other hand plant extracts and natural products also have prominent positions in these studies. There are some new methods of inhibitor application and new investigating techniques as well as the novel research approaches developed recently.

Keywords: copper, corrosion, inhibition, inhibitor

1. INTRODUCTION

Copper corrosion and the possibility to inhibit that process have been topics of interest of wide scientific society for quite some time now. This is obvious from the great number of studies conducted and published so far and that will be at least partially analysed in the following text. The main aim of this review is to summarize the results and knowledge regarding copper corrosion inhibition, gathered and published in papers from the time our previous review [1, 2] was published onward. Specifically this refers to a part dealing with azole group compounds since they were the main topic of mentioned reviews. Besides, some of the topics, i.e. analysis of the behaviour of certain groups of inhibitors, covers longer period of time since they were not previously considered.

Several groups of inhibitors were subject of this literature survey and those are: azole compounds, still the most often used and studied to the very least detail; followed by inhibitors known as non-toxic and environmentally friendly such as purine and derivatives, amino acids, plant extracts and natural products, pharmaceutical compounds; and also carboxylic acids, ionic liquids and some other compounds.

2. AZOLE COMPOUNDS

Azole compounds are well known copper corrosion inhibitors as can be concluded from numerous papers published so far, whereas some of the results are summarized in reviews we previously published [1, 2]. However, the research dealing with these inhibitors is still in progress. It is important to mention some of the other reviews such as the one published by Finšgar and Milošev [3] dealing especially with the most often mentioned copper corrosion inhibitor, namely benzotriazole (BTAH). Besides, there are other papers presenting the possibility of BTAH application alone [4-12] or together with some other compounds such as potassium sorbate [13], polypyrrole [14], Na_3PO_4 [15] or triton X-100 [11] in order to obtain improved inhibition efficiency. The derivatives of benzotriazole, namely 5-pentyl-BTA and 5-chloro-BTA [7], N-[benzotriazol-1-yl-(phenyl)-methylene]-N-phenyl-hydrazine and N-[benzotriazol-1-yl-(4-methoxy-phenyl)-methylene]-N-phenyl-hydrazine [8], N-(2-thiazolyl)-1H-benzotriazole-1-carbothioamide [16, 17], N-(furan-2-ylmethyl)-1H-benzotriazole-1-carbothioamide and N-benzyl-1H-benzotriazole-1-carbothioamide [17], 1-(2-thienyl carbonyl)-benzotriazole and 1-(2-pyrrole carbonyl)-benzotriazole [11] are also investigated as copper corrosion inhibitors and the results indicate that they provide better quality and efficiency of protection.

Other azole compounds are studied as copper corrosion inhibitors as well. Some of them are 1,2,4-triazole [4, 18] and derivatives: 3-amino-1,2,4-triazole [7, 18], 4-amino-1,2,4-triazole [7], 4-amino-4H-1,2,4-triazole-3thiol, 4-amino-5-methyl-4H-1,2,4-triazole-3thiol and 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol [19], 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole [20], bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)-butane [21]; 2-mercaptobenzoxazole [22], 5-(4'-dimetylaminobenzylidene)-2,4-dioxotetrahydro-1,3-thiazole [23], benzothiazole [5], 2-mercaptobenzothiazole [9, 24], 2-(octadecylthio)benzothiazole [25]; imidazole [26] and derivatives: 2-mercapto-1-methylimidazole [27], 4-methyl-1-(p-tolyl)-imidazole and 4-methyl-1-phenyl imidazole [28, 29], 4-methyl-1-(o-tolyl)-imidazole [28], benzimidazole [9] and 2-mercaptobenzimidazole [9, 30-32], 2-thiobenzylbenzimidazole [30, 33], 2-thiomethylbenzimidazole [30], 5-methoxy-2-(octadecylthio)benzimidazole [34]; thiadiazole [9] and derivatives: 2,5-dimercapto-1,3,4-thiadiazole [35], 5-phenyl-1,3,4-thiadiazole-2-thiol and 2-(5-mercapto-1,3,4-thiadiazole-2-yl)-phenol [36], 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium [37], 5-phenyl-2-amino-1,3,4-thiadiazole, 5-(4-methoxyphenyl)-2-amino-1,3,4-thiadiazole, 5-(4-nitrophenyl)-2-amino-1,3,4-thiadiazole [38], 5-methyl-[1,3,4]thiadiazol-2-ylsulfanyl)-acetic acid(4-dimethylamino-benzylidene)-hydrazid [39], 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole [40]; methyl 3-((2-mercaptophenyl)imino)butanoate [41], 5-phenyl-1-H-tetrazole [42], 1,2-dihydro-3-(octadecylthio)benzotriazine [43], 2,4,6-trimercapto-1,3,5-triazine [44]. From this list it is obvious that the possibilities for derivatives formation are numerous and widely exploited.

The study performed by Otmacic Curkovic and coworkers [28] using different imidazole derivatives showed that even insignificant changes in structure can lead to significant changes in inhibiting properties and mechanism.

Several studies dealt with improved inhibition effects noticed in the presence of combination of compounds; such as sodium dodecylbenzenesulphonate and 2-mercaptobenzoimidazole in sulphuric acid solution [32] as well as polyaspartic acid and imidazole in aminosulfonic acid [26].

New research results lead to the already known conclusions that the mode of action of azole inhibitors includes adsorption [7, 11, 16, 17, 19, 22-24, 27, 36, 37, 44] of organic molecules on the surface of copper that may be of physical [10, 20, 32, 38] or chemical nature [5, 9, 17, 25, 39, 42, 43] or even the combination of both [5, 19, 30, 33, 36]. In some cases the formation of complexes involving inhibitor and copper is confirmed [4, 6, 21, 22, 25, 34, 36, 41, 43]. The interaction between inhibitor molecule and copper is enabled due to the presence of heteroatoms, mostly N and S, or π electrons in organic compound molecule [6, 9, 16, 17, 22, 24, 25, 27, 35, 37, 40, 43, 45]. Finšgar [45] showed that even the inhibitor film growth kinetics can be important for inhibition efficiency as can be seen using 1,2,4-triazole and 3-amino-1,2,4-triazole as an example. It is shown that slower and logarithmic growth of 3-amino-1,2,4-triazole layer leads to the formation of compact, dense and more protective layer in comparison with the layer of 1,2,4-triazole that is characterized by faster and linear growth.

Most of azoles act as mixed-type inhibitors [6, 10, 17, 20-24, 36, 37, 44], whereas in some cases more pronounced effect on cathodic [19, 36, 44] or anodic [5, 6, 24, 37] process can be noticed.

The values of obtained inhibition efficiency are summarized in Table 1. and they increase with concentration and time of immersion [9, 10, 17, 21, 28, 32, 44] and decrease with temperature increase [19, 20, 25, 34, 41, 43], time of exposure to aggressive media [25, 34, 43] and in the presence of thiosulfate or sulfide ions [42]. The effect of medium pH is also studied and the conclusion is that increase of pH leads to the inhibition efficiency increase [9, 29]. The analysis of the data presented in Table 1 indicates that some of the azole compounds can be excellent copper corrosion inhibitors under certain conditions with inhibition efficiency exceeding 99%.

Table 1a. The efficiency of copper corrosion inhibition obtained in the presence of azole compounds

Inhibitor	Concentration	Medium	IE%			Reference
Benzotriazole (BTAH)	600ppm	1.0M H_2SO_4	87^{pp}	90^{EIS}	92^{Rn}	5
Benzothiazole (BNS)			95	96	97	
Benzotriazole (BTAH)	1×10^{-2}M	0.1M H_2SO_4 283-298K 100-400rpm	98^{pp}			46
Methyl 3-((2-mercaptophenyl) imino) butanoate (MMPB)	1×10^{-2}M	0.1M HCl	99.30^{Rp}			41
2,4,6-Trimercapto-1,3,5-triazine (TMTA) SAM	1×10^{-4}M 180min	0.5M NaCl	92.4^{pp}			44
	1×10^{-4}M 80min		93.9^{EIS}			
Methimazole (MMI) SAM	3h	0.1M KCl	91.2^{pp}	93.8^{EIS}		27
2-Amino-5-(4-pyridinyl)-1,3,4-thiadiazole (4-APTD) SAM	1×10^{-4}M 3h	0.1M KCl	90.4^{pp}	86.7^{EIS}		40
Benzotriazole (BTAH)	5.0g 24h	8.4mg/cm^2 NaCl ATEL 90% RH 50˚C	95.2^{pp}	99.6^{EIS}		6
Polyaspartic acid (PASP)	1g/l	3% aminosulfonic acid solution	89.8^{pp}			26
PASP+ imidazole (IM)	0.5g/l+0.5g/l		95.4^{pp}			
2-Thiobenzylbenzimidazole (TBBI)	1×10^{-3}M	1M HNO_3 1h 25˚C	90.04^{wl}			30

2-Thiomethylbenzimidazole (TMBI)			88.75[wl]			
2-Mercaptobenzimidazole (MBI)			87.65[wl]			
2-Thiobenzylbenzimidazole (TBBI)	1×10^{-3}M	1M HNO_3	90.02[wl]		89.10[calc]	33
Polypyrrole-oxalic acid-benzotriazole (PPy-Ox-BTA)	0.5M – 0.1M – 0.01M	3.5wt.% NaCl 480h	80*			14
PPy-Ox	0.5M – 0.1M		51*			
4-Amino-4H-1,2,4-triazole-3thiol (ATT)	2.58×10^{-3}M	0.5M HCl 303K	92.05[pp]	98.64[EIS]	87.50[wl]	19
4-Amino-5-methyl-4H-1,2,4-triazole-3thiol (AMTT)			95.78	98.99	92.50	
4-Amino-5-ethyl-4H-1,2,4-triazole-3thiol (AETT)			96.09	99.04	95.00	
Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT))	1×10^{-2}M	2M HNO_3 303 K	94.7[pp]	92.8[EIS]	91.7[wl]	20
Benzotriazole (BTAH)	vacuum pyrolysis 0.3g 200°C 30min 1.33Pa	3.5%mass NaCl + 0.001M/0.01M sulfide ions	99.991/79.351[pp]			8
N-[Benzotriazol-1-yl- (phenyl)-methylene]-N-phenyl-hydrazine			100.00/99.997			
N-[Benzotriazol-1-yl-(4-methoxy-phenyl)-methylene]-N-phenyl-hydrazine			100.00/99.994			
5-Phenyl-1,3,4-thiadiazole-2-thiol (PTT)	100mg/l	3.5% NaCl	97.5[pp]	96.6[EIS]	98.2[wl]	36
2-(5-Mercapto-1,3,4-thiadiazole-2-yl)-phenol (MTP)			97.1	94.8	97.7	
5-Mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium (MPTT) SAM	2×10^{-2}M 8h assembly 25˚C	0.5M NaCl	92.2[pp]		90.1[EIS]	6
	2×10^{-2}M 24h 25˚C		93.7		93.5	
	2×10^{-2}M 8h 55 ˚C		93.8		94.4	

Table 1b. The efficiency of copper corrosion inhibition obtained in the presence of azole compounds

Inhibitor	Concentration	Medium		IE%			Reference
5-(4'- Dimetyl amino benzylidene)-2,4- dioxotetrahydro-1,3-thiazole (DABDT)	1×10^{-2}M	0.1 M Na_2SO_4 pH 3		90[pp]		91[wl]	23
2-(Octadecylthio) benzothiazole (2-OTBT) SAM	2×10^{-2}M in ethyl acetate 24h	0.02M NaCl 0.5h 30°C		93.5[pp]		98.9[EIS]	25
		0.2M NaCl 0.5h 30°C		86.4		97.7	
5-Methoxy-2-(octadecylthio) benzimidazole (MOTBI) SAM	1×10^{-2}M in methanol 24h	0.02M NaCl 0.5h 30°C		99.91[pp]		99.3[EIS]	34
		0.2M NaCl 0.5h 30°C		93.82		98.4	
1,2-Dihydro-3-(octadecylthio) benzotriazine (DOTBT) SAM	2.5×10^{-3}M in methanol 24h 30°C	0.02M NaCl 0.5h 30°C		99.7[pp]		99.4[EIS]	43
		0.2M NaCl 0.5h 30°C		93.3		96.2	
Benzotriazole (BTAH)	0.3×10^{-3}M	Borate buffer	pH 10.4	0.86**	85[pp]	85[EIS]	9
			pH 8.4	0.91			
			pH 6.4	0.87			
Mercaptobenzothiazole (MBT)			pH 10.4	0.96	95	94	
			pH 8.4	0.99			

			pH 6.4	0.98		
Benzimidazole (BIMD)			pH 10.4	0.89	88	90
			pH 8.4	0.94		
			pH 6.4	0.92		
Mercaptobenzimidazole (MBIMD)			pH 10.4	0.91	89	90
			pH 8.4	0.94		
			pH 6.4	0.91		
Thiadiazole (TDA)			pH 10.4	0.94	92	93
			pH 8.4	0.96		
			pH 6.4	0.95		
5-Methyl-[1, 3, 4] thiadiazol-2-ylsulfanyl)-acetic acid(4-dimethylamino-benzylidene)-hydrazid (MTYDBH)	100mg/l	3.5% NaCl 298K (wl 7days)	pH 7.5	98.48^{pp}	99.37^{EIS}	99.07^{wl}	39
	50mg/l		pH 9.5	99.00^{pp}	99.88^{EIS}		
			pH 7.5	98.20	99.33		
			pH 5.5	88.95	96.46		
2-Mercaptobenzimidazole (MBIH)	1×10^{-3}M	3wt% NaCl pH 5.5 180 days		87.5^{wl}			18
N-(2-thiazolyl)-1H-benzotriazole-1-carbothioamide (TBC)	5×10^{-2}M	0.5M HCl		93.92^{pp}	97.0^{EIS}	96.36^{wl}	16
N-(2-thiazolyl)-1H-benzotriazole-1-carbothioamide (TBC)	5×10^{-3}M	1M HNO_3		93.08^{pp}	98.10^{EIS}	97.4^{wl}	17
N-(furan-2-ylmethyl)-1H-benzotriazole-1-carbothioamide (FBC)				89.32	92.29	90.6	
N-benzyl-1H-benzotriazole-1-carbothioamide (BBC)				85.31	90.20	89.7	
Diniconazole ((E)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazole-1-yl)-1-pentenyl-3-ol)	100mg/l	3.5% NaCl		98.1^{pp}	99.2^{EIS}	96.6^{wl}	47
Triadimefon (1-(4-chlorophenoxy-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone))				95.3	97.3	96.5	

Table 1c. The efficiency of copper corrosion inhibition obtained in the presence of azole compounds

Inhibitor	Concentration	Medium	IE%			Reference
Benzotriazole (BTAH)	0.14×10^{-3}M	Ground water	61.37^{pp}	57.83^{EIS}	57.77^{wl}	11
1-(2-Thienyl carbonyl)-benzotriazole (TCBT)	0.12×10^{-3}M		56.67	70.81	69.97	
1-(2-Pyrrole carbonyl)-benzotriazole (PCBT)	0.095×10^{-3}M		69.36	72.84	73.92	
Triton X-100 (TX-100)	0.16×10^{-3}M		72.86	61.64	62.79	
BTAH + TX-100	$0.14+0.16\times10^{-3}$M		80.64	81.62	81.81	
TCBT + TX-100	$0.12+0.16\times10^{-3}$M		88.38	89.04	89.11	
PCBT + TX-100	$0.095+0.16\times10^{-3}$M		91.34	92.07	91.74	
Dodecylbenzenesulphonate (SDBS)	1×10^{-4}M	0.5M H_2SO_4	63^{pp}	75.16^{EIS}		32
2-Mercaptobenzoimidazole (2-MBI)	1×10^{-4}M		82^{pp}	96.40^{EIS}		
	5×10^{-4}M		93^{pp}	96.77^{EIS}		
SDBS + 2-MBI	$(1+1)\times10^{-4}$M		96^{pp}	96.80^{EIS}		
Benzotriazole (BTAH)	6g/l	17wt% (0.534M) tetra-n-butylammonium	93.8^{pp}	95.9^{EIS}	94.2^{wl}	10
	2g/l		88.9	94.8	90.0	
Benzotriazole (BTAH)	2g/l				90.0^{wl}	15

Benzotriazole (BTAH) + Na_3PO_4 (SP)	2+1g/l	bromide (TBAB)	98.3^{pp}	96.4^{EIS}	96.3	
5-(3-Aminophenyl)-tetrazole (APT)	5×10^{-3}M 1h	0.5M HCl	87.4^{pp}	86.1^{EIS}		48
	5×10^{-3}M 24h		84.9	82.1		
	5×10^{-3}M 72h				~90^{wl}	
3-Amino-5-mercapto-1,2,4-triazole (AMTA)	1×10^{-3}M	3.5% NaCl	81.7^{pp}	90^{wl}		49
5-(3-Aminophenyl)-tetrazole (APTA)			88.3^{pp}	95^{wl}		
3-Amino-1,2,4-triazole (ATA)	5×10^{-3}M	0.5M HCl	93.8^{pp}	72^{wl}		50
3-Amino-5-mercapto-1,2,4-triazole (AMTA)			84.8^{pp}	83^{wl}		
5-Phenyl-1-H tetrazole (PTAH)	1×10^{-2}M	0.6M NaCl	99.41^{pp}			42
2,5-Dimercapto-1,3,4-thiadiazole (DMTD) SAM	7.5×10^{-3}M in ethanol 10h	0.5M HCl	90.7^{pp}	84.2^{EIS}		35
5-Phenyl-2-amino-1,3,4-thiadiazole (APT)	6×10^{-3}M	0.5M H_2SO_4	87.1^{pp}	74.3^{EIS}		38
5-(4-Methoxyphenyl)-2-amino-1,3,4-thiadiazole (AMPT)			90.0	86.7		
5-(4-Nitrophenyl)-2-amino-1,3,4-thiadiazole (ANPT)			73.4	63.3		
4-Methyl-1-phenyl imidazole (PMI)	5×10^{-3}M	0.5M HCl pH~0.3	19^{pp}			29
		0.5M NaCl pH=5.6	93			
4-Methyl-1-(p-tolyl) imidazole (TMI)	1×10^{-3}M	0.5M HCl	37			
		0.5M NaCl	92			

Values of inhibition efficiency are calculated based on the data obtained using: pp – polarization measurements; EIS – EIS measurements; Rn – Noise resistance; Rp – polarization resistance; ATEL – adsorbed thin electrolyte layers; wl – weight loss; * – the average dissolution rate was estimated from the amount of copper ions dissolved was determined by ICP-AES; ** – surface coverage obtained using anodic current density; rpm – Rotation per minute; calc – density functional theory (DFT) methods using the Gaussian 03 W suite of programs

The experimental data are often complemented by computer simulations and calculations [9, 16, 19, 30, 33, 35, 37, 38] indicating new trend in research approach.

Hence, nowadays more attention is devoted to the understanding of the molecular level occurrences involved in corrosion [51] and corrosion inhibition, namely the modes of adsorption of inhibitors on metal surface. Grillo and associates [52, 53] studied the adsorption of benzotriazole on Cu(111) surface. Kokalj and Peljhan [54] included also 3-amino-1,2,4-triazole and 1-hydroxybenzotriazole adsorption on perfect Cu(111) surface in their studies. Awad and coworkers [55] applied computational simulation by molecular dynamic model as a tool for the study of adsorption of some triazole (5-amino 1,2,4 triazole, 5-amino-3-mercapto 1,2,4 triazole, 5-amino-3-methyl thio 1,2,4 triazole, 1-amino-3-methyl thio 1,2,4 triazole) molecules on copper surface. After providing the evidence that 2-mercaptobenzimidazole is a very efficient copper corrosion inhibitor in NaCl solutions, by performing long term weight loss and electrochemical measurements [18], Finšgar continued with the detailed study of its adsorption on copper surface [56]. The adsorption of 2-mercaptobenzimidazole

was also studied by Obot et al. [57] by density functional theory (DFT) and molecular dynamics simulations.

However, even though the results obtained by computer simulation of inhibitor molecule electronic properties are sometimes in accordance with experimental findings it can't be taken as a rule, as it is presented by Kokalj [58]. He studied the molecular electronic properties of three corrosion inhibitors for copper: 3-amino-1,2,4-triazole (ATA), benzotriazole (BTAH), and 1-hydroxybenzotriazole (BTAOH); and it is shown that the trend of copper corrosion inhibition performance in near-neutral chloride solution is BTAH > ATA >> BTAOH, whereas calculations based simply on electronic properties of molecules indicate that the expected performance should be ATA ≠ BTAH ≈ BTAOH. Having that in mind Kokalj and coworkers [59] emphasize the importance of a complex approach with rigorous modelling taking into account numerous factors involved in the corrosion inhibition mechanism: interaction of neutral and deprotonated inhibitor molecules with the surface; role of intermolecular association of inhibitors on the surface; solvation effects; double-layer electric field effects on the molecule-surface bonding; and comparison of inhibitors-surface bonding to that of aggressive chloride anions. Besides, the characteristics of the media, such as pH and the presence of reactive species in solution, as well as the electrode potential and the chemical and physical properties of the metal must be considered.

The research group that includes Peljhan, Koller and Kokalj studied the effect of copper surface geometry on the adsorption of benzotriazole and chloride ions [60] and also on the dehydrogenation of benzotriazole [61]. The results imply that all the investigated species i.e. benzotriazole, dehydrogenated benzotriazole ($BTA^{\odot}$) and Cl, adsorb stronger on surfaces with lower coordination numbers; the exception is H, a side-product of BTAH dehydrogenation, which is rather insensitive to surface geometry. As for the energy of adsorption it can be said that it follows the trend Cl > $BTA^{\odot}$ >> BTAH. On the other hand, the enhanced bonding of $BTA^{\odot}$ on the reduced coordination Cu surface sites is responsible for it being able to passivate the reactive under-coordinated (defective) surface sites as well as for the formation of organometallic complexes on flat facets, such as the BTA-Cu-BTA complex or $[BTA\text{-}Cu]_n$ polymer. These observations don't take into acount the effect of a solvent, however it is significant factor and in the studied case for the aqueous-phase adsorption energy is reversed and the adsorption of deprotonated BTA^{-} is more exothermic than that of Cl^{-}, i.e., magnitudes follow the (111) ≳ (100) > (110) sequence. From these observations it is clear why the dehydrogenation of BTAH is important i.e. only in that form it binds to copper strong enough to compete with corrosive species. The activation energy depends on copper plane and the presence of solvent. It is concluded that dehydrogenation of BTAH can be feasible at room temperature on more open or defective copper surfaces, whereas, on densely packed Cu(111), it is hindered, because there the desorption energy is considerably smaller. However, on many investigated surface geometries, the desorption of BTAH is estimated to be more probable than the dehydrogenation, implying that dehydrogenation would be achievable by continually populating the adsorption state. As for the solvent effect it is concluded that water molecules may aid the dehydrogenation by reducing the activation energy. Kovačević and Kokalj [62] studied the mode of adsorption and bonding of benzotriazole and benzimidazole on copper and also came to the conclusion that azole type inhibitors in dehydrogenated (deprotonated) forms interact much stronger with metal surfaces than molecules in

neutral and protonated forms. Besides, it is noticed that the adsorbed protonated forms are prone to deprotonation and transition from neutral to deprotonated form is more likely on more reactive metals. They also studied the adsorption of azole molecules: imidazole, triazole, tetrazole and pentazole; in protonated ($MolH_2^+$), neutral (MolH), and deprotonated (Mol^-) forms on Cu(111) in gas and aqueous phase [63]. The results showed that chemisorptive bonding is the strongest in the case of deprotonated forms of inhibitors. The only exception is the behaviour of imidazole. In fact, the free energy of neutral molecule adsorption from the aqueous-phase is comparable to that of deprotonated form, so the neutral imidazole molecule is considered as the active specie. This is explained by the more basic nature of imidazole which deprotonated form would be important only at high pH values. On the other hand, the deprotonated forms of triazole and tetrazole are the active species for inhibiting corrosion. The importance of solvent is also highlighted by the fact that the gas-phase adsorption energy on Cu(111) follows the Mol^- > $MolH_2^+$ > MolH trend, while in aqueous-phase the trend changes to Mol^- > MolH > $MolH_2^+$ and also the adsorption energy is reduced. This behaviour can be explained knowing that aqueous-phase adsorption can be seen as a substitution reaction influenced by the competitive molecule-surface and molecule-water interactions. The role of nitrogen atoms in azole molecules and the relation between adsorption bonding and copper corrosion inhibition was studied as well [62-64]. It is concluded that the unsaturated N atoms are responsible for bonding and that the adsorption energy decreases with increasing the number of nitrogen atoms in azole ring i.e. imidazole > triazole > tetrazole > pentazole.

In the recent years new methodologies for inhibitors application are developed, such as formation of sol-gel coatings, the method reviewed in detail by Wang and Bierwagen [65], or metallic glass coatings [66] and vacuum pyrolysis of the inhibitor in the presence of copper specimens [8].

Novel techniques for corrosion inhibition studies are also emerging, such as alternating current scanning electrochemical microscopy [67, 68] or a technique that combines the scanning vibrating electrode technique (SVET) and dual potentiometric/amperometric operation in scanning electrochemical microscopy (SECM) [31, 69]. In situ monitoring of corrosion processes is very interesting option and it is shown by Wang and He [70] that in the case some light-absorbing ions are involved the combination of cyclic voltammetry and cyclic voltabsorptometry can be very useful technique. Since the mode of azole action includes adsorption on copper surface it is of interest to study the kinetics of that process and Simbeck et al. [71, 72] introduced fast impedance scanning quartz microbalance (FIS-QCM) as a means to perform those studies.

Obviously, the progress in corrosion studies leads to the broadening of the research approaches so Luciano and co-workers [73] introduced the possibility of use of chemometric tools in their review.

3. PURINE AND DERIVATIVES

Purine and adenine are structural derivatives of imidazole, containing the additional pyrimidine ring and in the case of adenine the amino group. It was previously reported that purine can effectively inhibit corrosion of copper in chloride media [1, 74]. However, the interest in these compounds is progressively growing in the past few years as it can be seen in the increasing number of published

papers. The results of the studies are summarized in the Table 2. It can be concluded that adenine is more efficient and both inhibitors exhibit the best performance in neutral media, although they can be used with satisfactory results in acid [75, 76] and alkaline media [77]. The mode of their action includes adsorption on copper surface that can be best fitted to Langmuir adsorption isotherm and the formation of protective layer containing Cu(I)-inhibitor complex [75-80]. Purine and its derivatives are considered environmentally friendly corrosion inhibitors since they are non-toxic and biodegradable. This particular quality makes them possibly suitable for medicinal application. Alvarez et al. [81] studied the effect of purine pre-treatment of the intrauterine device (IUD) on copper "burst release" in simulated uterine fluid (SUF). The pre-treatment was performed in 5g dm^{-3} NaCl solution containing different concentrations of purine and for various time intervals and the resulting inhibition efficiencies are presented in Table 2. It is concluded that it can be efectively used for this purpose also and the advantage is the ease of application and control of the desired copper release. The results obtained by Levin and associates [82] showed that purine and adenine can also be used as copper corrosion inhibitors in hydrocarbon media.

Table 2. The efficiency of copper corrosion inhibition obtained in the presence of purine and adenine

Inhibitor	Concentration	Medium	Surface coverage degree	Reference
Adenine	1×10^{-2}M	1M NaCl	0.92^{pp}	79
Purine	1×10^{-2}M	0.5M $NaNO_3$	0.90^{pp}	76
Adenine			0.91^{pp}	
Purine	1×10^{-2}M	0.5M Na_2SO_4 pH 6.8	0.91^{wl}	75
Adenine			0.94^{wl}	
Purine		0.5M Na_2SO_4 pH 1.0	0.79^{wl}	
Adenine			0.88^{wl}	
Purine	1×10^{-2}M	0.5M Na_2SO_4 pH 6.8	0.76^{pp}	78
Adenine			0.91^{pp}	
Purine	1×10^{-2}M	0.5M Na_2SO_4 pH 7.0	0.91^{pp}	77
		0.5M Na_2SO_4 pH 9.0	0.89^{pp}	
			IE% at -0.1 V vs. SCE	
Purine	1×10^{-3}M 1h	SUF	61.20^{pp}	81
	1×10^{-3}M 3h		98.61^{pp}	
	1×10^{-2}M 1h		98.10^{pp}	
	1×10^{-2}M 3h		99.18^{pp}	

Values of surface coverage degree are calculated based on the data obtained using: pp – potentiodynamic polarization curves, wl – weight los

The compound with very similar structure that is also proved corrosion inhibitor [1, 83] is caffeine. Recently caffeine and two similar compounds, namely theobromine and theophylline, are evaluated as inhibitors of copper corrosion in 0.1mol dm^{-3} H_2SO_4 [84]. However, despite the similarity regarding molecule structure, only caffeine of all the studied compounds acts as corrosion inhibitor. The mode of caffeine action includes the adsorption on copper surface to form a protective hydrophobic layer and hence the displacement of water and oxygen from it. As a result, corrosion reactions are retarded. Caffeine influences cathodic reaction by simple adsorption on cathodic sites and

is regarded mainly as cathodic inhibitor. On the other hand when anodic reaction is examined, copper-caffeine complex formation and its adsorption have to be considered, with characteristic isosbestic point at potential of +0.035V vs. SCE. The complex is defined as Cu(II)-caffeine complex. The adsorption process can be most accurately fitted to Temkin isotherm, whereas it is considered a mix of physical and chemical adsorption with ΔG of -31.1kJ mol^{-1}. Inhibition efficiency value in the presence of 10×10^{-3}mol dm^{-3} caffeine calculated from potentiodynamic polarization curves is 71%. From impedance measurements surface coverage of 0.72 is obtained in the presence of the same concentration of caffeine. Caffeine is also proved to inhibit copper corrosion to some extent in NaCl and HCl solutions [85]. In the presence of 3g dm^{-3} caffeine the inhibition efficiency obtained by weight loss measurements is 43.14% in 3% NaCl and in the presence of 2g dm^{-3} in 4% HCl it reaches 52.63%.

4. AMINO ACIDS

Table 3. The efficiency of copper corrosion inhibition obtained in the presence of cysteine

Inhibitor		Concentration	Medium	IE %			Reference
Cys	/	16×10^{-3}M	0.6M NaCl	76.55^{pp}			103
	/	18×10^{-3}M	1M HCl	84.13^{pp}			
	Cu^{2+}	$(18+0.1)\times10^{-3}$M		89.52^{pp}			
Cys		1×10^{-2}M	3.5% NaCl	97.080/96.574^{EIS}			110
		1×10^{-2}M+3.5% NaCl	pH 8.5 298K/328K	84.699/94.869^{EIS}			
Cys		1×10^{-3}M	3.5% NaCl	26.30^{pp}			115
N-acetylcys				44.90^{pp}			
Cys	AA	1×10^{-4}M+1×10^{-5}M	3% NaCl	76.40^{pp}	66.40^{EIS}		113
SAM		(1h)					
	N_2	1×10^{-4}M+30min (1h)		82.50^{pp}	78.00^{EIS}		
	Air	1×10^{-4}M+30min (1h)		86.30^{pp}	86.90^{EIS}		
	$KMnO_4$	1×10^{-4}M+1×10^{-5}M (1h)		91.20^{pp}	90.40^{EIS}		
DL-cys		1×10^{-5}M	0.5M HCl	58.70^{wl}			92
Cys	/	1×10^{-3}M 12h	0.5M HCl	59.60^{pp}	45.60^{EIS}		111
SAM	DAC	1×10^{-3}M+1×10^{-2}M		80.00^{pp}	73.50^{EIS}		
	DAM	1×10^{-3}M+1×10^{-2}M		90.10^{pp}	80.50^{EIS}		
Cys	/	15×10^{-3}M	0.5M HCl	92.90^{EIS}			112
	Gly+Glu	$(5+5+5)\times10^{-3}$M		90.70^{EIS}			
Glutathione		10×10^{-3}M		96.40^{EIS}			
Cys		10×10^{-3}M	0.5M HCl	52.00^{pp}			114
Cys		1×10^{-2}M	0.5M Na_2SO_4 pH~7	75.68^{pp}			107
			0.5M Na_2SO_4 pH~9	88.16^{pp}			
Cys		1×10^{-2}M	0.5M Na_2SO_4 pH~2	82.73^{pp}			108
L-cys		150ppm	0.5M H_2SO_4	303K	303K	24h	106
				55.30^{pp}	55.65^{EIS}	17.72^{wl}	
Cys		1×10^{-3}M	1M HNO_3	58.00^{pp}		61.00^{wl}	90
Cys		1×10^{-3}M	8M H_3PO_4	52.17^{pp}			98

Values of inhibition efficiency are calculated using data gathered from: pp – potentiodynamic curves; EIS – EIS measurements; wl – weight loss; Cys – cysteine; AA – ascorbic acid; DAC – dodecylacid; DAM – dodecylamine; Gly – glycine; Glu – glutamic acid

Amino acids are known as one of the environmentally friendly and non-toxic classes of corrosion inhibitors. The possibility of their use is mentioned also in the previous review of copper corrosion inhibitors [1] based on the results of the studies on cysteine [86] and tryptophan [87]. However, from that time onward the number of studies dealing with amino acids as copper corrosion inhibitors is increasing rapidly. The data published in literature so far are summed up in the Tables 3-6, presented in the following material. They can be cathodic [88-91], anodic [92] and mixed-type [93, 94] inhibitors. The mode of inhibitive action includes adsorption on copper surface which is favoured by the presence of heteroatoms, aromatic ring or large molecular surface [89-101]. Especially the amino acids containing sulfur atoms proved to be very efficient corrosion inhibitors due to their ability to be adsorbed as bidentate ligands with coordination taking place through amino or carboxyl group and –SH group [90, 102-105].

Cysteine is one of the amino acids containing –SH group and probably the most studied amino acid in terms of corrosion inhibition. After it was proved inhibitor of copper anodic dissolution in sulfuric acid [86, 106], it was used in further studies in various media. According to our findings it can be used efficiently in sulfate solutions in broad pH region [107-109], as well as in, as other authors presented, chloride solutions [92, 103, 110-115], nitric [90] and phosphoric acid [98]. Cysteine is often considered cathodic type inhibitor [103, 115], however, the behavior exhibited during anodic polarization is influenced as well [86, 92, 107, 108, 110], or in some cases it is considered mixed-type inhibitor [106]. Inhibition effect is observed within the potential region where $Cu(I)_{ads}$ is the dominant copper specie so the protective layer is assumed to be Cu(I)-cys. Dursun and Nişli [116] found that cysteine forms a complex with Cu(I) rather than with Cu(II), so that at higher potentials corresponding to Cu(II) formation, cysteine exhibits lower inhibition efficiency. The resulting complex has high stability constant value [117, 118] hence it provides good corrosion inhibition. Besides already mentioned effect, Cu(II) also influences oxidation of the Cu(I)-cys complex [119].

The adsorption is important part of inhibition mechanism and it can be usually most acurately fitted to Langmuir adsorption isotherm [106-108]. Gibbs free energy of adsorption corresponds to physical [107, 110] or chemical [108] adsorption, depending on the conditions. However, according to some authors [98] the mode of adsorption, which is of physical nature according to ΔG, fits Temkin and kinetic-thermodynamic model.

According to the data presented in the Table 3, some conclusions can be made regarding cysteine application efficiency in media of different pH values. If the values of IE in sulfate solutions of various pH are analyzed [107, 108] it is obvious that in neutral media IE is minimal whereas it increases in acid and alkaline solutions. This conclusion is in agreement with already known facts [120] that the inhibition effect is minimal at pH close to the isoelectric point, whereas as pH moves towards acid or alkaline medium the dipole moment is greater and hence the inhibition is stronger. As for cysteine, the zwitterion structure is dominant in the pH range from 1.91 to 8.16, whereas above and below these values cation and anion forms are dominant, respectively [86, 121]. Sinergystic effect is

observed in the presence of chloride ions as well as in the presence of Cu(II) ions in 1.0mol dm^{-3} HCl [103].

Cysteine can be used as efficient copper corrosion inhibitor in the form of self-assembled membrane (SAM) on copper surface, as well [111, 113]. The conditions used for the assembly have an influence on the subsequent inhibition efficiency provided by the SAM. According to Zhang and coworkers [113] Cys adsorbs onto Cu and Cu_2O surface to form a protective film, however, the mode of attachment is different. The interaction with Cu occurs via N atom, while in the case of Cu_2O it occurs via S atom and with higher energy of adsorption. This can be a reason for the improvement of protective characteristics in the presence of dissolved oxygen or oxidizing agent like $KMnO_4$, which can be seen in Table 3. It is also possible to improve protective effect of Cys SAM by modification with dodecylacid (DAC) or dodecylamine (DAM) [111], whereas DAM/Cys SAM is more efficient.

There are attempts to correlate the inhibition efficiency of organic molecules and molecule energy. Quantum studies performed by Abdel Rahman et al. [98] showed that the inhibitors with higher inhibition efficiency have larger number of adsorption centers in the molecule, in the case of cysteine four (two oxygen, nitrogen and sulfur atoms). Also there is an agreement between quantum chemical parameters related to the electronic structure of the investigated compounds (E_{HOMO}, ΔE, E_t, σ, η, TNC, MV) and their ability to inhibit the corrosion process. The computation of the energies of the molecules, E_{HOMO}, E_{LUMO} and energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) was performed in several other cases [90, 98, 112, 114] and the results indicated that Cys molecule has a low value of energy gap which is shown to be in correlation with high inhibition efficiency. The important contribution to efficiency is provided by the presence of S atom and adsorption through thiol group. These calculations can be of use in the estimation of the possible effect of joined use of a group of amino acids, as well as that of their product [112]. It is shown that due to the repulsive forces glycine, glutamic acid and cysteine together have a small improving effect on copper corrosion inhibition. However, the improvement is significant when they are linked via –CONH– bond to form a tripeptide (glutathione) compound. This effect is attributed to the presence of many hetero-atoms which are potential adsorption centers and its lower E_{LUMO} energy level.

Compound of similar structure to cysteine, cysteamine (CA), has been studied from the point of application like copper corrosion inhibitor and the adsorption on copper surface [122]. The conclusion was that the optimal conditions for the formation of SAM that provides the highest inhibition efficiency are 5h of immersion and pH of the 1×10^{-2}mol dm^{-3} CA aqueous solution 2.85. The monolayer formed under those conditions provided corrosion inhibition efficiency in 3wt% NaCl of 90% or 88.66% based on polarization or impedance parameters, respectively. Surface-enhanced Raman scattering (SERS) spectra of CA combined with the electrochemical measurements showed that trans-conformer exhibited better inhibition ability.

Methionine (MET) is another amino acid that contains S atom in its molecule. It is classified as an essential amino acid, which is aliphatic, non-polar and neutral [114]. Methionine received substantial attention as copper corrosion inhibitor [95, 97, 114, 115, 123-126]. The results as presented in Table 4.

According to some authors [97, 123] the mode of methionine action is inhibition of the oxidation of Cu(I) to soluble Cu(II). The inhibition mechanism includes adsorption of methionine

molecule on copper surface. In comparison with other studied amino acids (i.e. alanine, aspartic acid, leucine, glutamic acid, glutamine, asparagine, threonine) [95] smaller energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) indicates stronger adsorption of methionine on the surface of copper. This can be ascribed to the presence of -OH and $-S-CH_3$ groups in the molecule of methionine, which leads to the occurrence of synergistic intramolecular effect. Synergistic effect is noticed in several cases due to the formation of more resistant film, in comparison to methionine alone, which acts as chatodic reaction inhibitor. Namely, Zhang et al. [97] observed that in the presence of Zn^{2+} ions inhibition efficiency increases due to the formation and adsorption of more compact layer that contains complex of zinc and methionine. Zhang et al. [123] found that cetrimonium bromid (CTAB) or cetilpiridinum bromid (CPB) have a similar influence, whereas, the combination of MET/CTAB has a better protective effect compared with MET/CPB. This is explained by the stronger electrostatic interaction between MET and CTAB.

Table 4. The efficiency of copper corrosion inhibition obtained in the presence of methionine

Inhibitor		Concentration	Medium	IE %			Reference
Methionine		1×10^{-2}M	3.5% NaCl	$51.05/64.52^{EIS}$			126
		1×10^{-2}M+3.5% NaCl	pH 8.5 298K/328K	$39.75/62.01^{EIS}$			
Methionine		1×10^{-3}M	3.5% NaCl	82.00^{pp}			115
Methionine	/	12×10^{-3}M	0.5M HCl	84.15^{pp}	76.71^{EIS}		97
	Zn^{2+}	$(12+0.5)\times10^{-3}$M		91.96^{pp}	87.07^{EIS}		
Methionine	/	0.05M	0.5M HCl	72.70^{pp}			123
	CTAB	0.05M+0.01M	1h	85.20^{pp}			
	CPB	0.05M+0.005M		81.20^{pp}			
Methionine		10×10^{-3}M	0.5M HCl	$\sim10.00^{pp}$			114
L-methionine		5×10^{-3}M	1.0M HNO_3	81.60^{pp}	88.00^{EIS}	87.60^{wl}	125
L-methionine sulfoxide				87.50^{pp}	90.20^{EIS}	91.20^{wl}	
L-methionine sulfone				90.70^{pp}	93.50^{EIS}	94.10^{wl}	
Methionine		1×10^{-3}M	1.0M HNO_3	80.38^{pp}	93.98^{wl}		95

Values of inhibition efficiency are calculated using data gathered from: pp – potentiodynamic curves; EIS – EIS measurements; wl – weight loss; CTAB – cetrimonium bromid; CPB – cetilpiridinum bromid

Khaled [125] studied the inhibition performance of L-methionine, and its derivatives: L-methionine sulfoxide and L-methionine sulfone. The results show that they act as mixed-type inhibitors, whereas the inhibition mechanism includes adsorption and hydrogen bond formation. The most efficient inhibitor is L-methionine sulfone that has more susceptible sites for the adsorption on the copper surface. The quantum mechanical approach is shown to be useful for the estimation of inhibitor effectiveness as it is demonstrated that the inhibition efficiency increases with increase in E_{HOMO} and decrease in E_{LUMO}, dipole moment μ and energy gap ΔE.

Numerous other amino acids are studied as copper corrosion inhibitors [89-96, 98, 112, 114, 124, 127]. All of the research was focused on their effect in acidic media and the results obtained in hydrochloric acid are presented in Table 5, and in other acids in Table 6. The most often studied media

is hydrochloric acid and as it can be concluded from Table 5, α-alanine and glutamic acid provided corrosion protection with the efficiency of over 90%. It is also interesting and important to mention that some other amino acids can be efficient copper corrosion inhibitors when they are used in the combination with some other compounds as it can be seen in the following examples: SAMs formed from arginine, glutamine or histidine and KI; L-phenylalanine with Ce(IV). In these cases well known synergistic effect becomes relevant.

Table 5. The efficiency of copper corrosion inhibition in hydrochloric acid obtained in the presence of amino acids

Inhibitor		Concentration	Medium	IE %		Reference
Arginine SAM	/	1×10^{-3}M 6h	0.5M HCl	62.00^{pp}	63.00^{EIS}	127
	KI	$5/5\times10^{-3}$M 2h		85.00^{pp}	87.00^{EIS}	
Glycine		15×10^{-3}M	0.5M HCl	60.00^{EIS}		112
Glutamic acid		15×10^{-3}M		61.60^{EIS}		
Glycine			0.5M HCl	45.40^{pp}		91
Threonine				40.10^{pp}		
Phenylalanine				19.40^{pp}		
Glutamic acid				53.60^{pp}		
DL-alanine		1×10^{-5}M	0.5M HCl	42.70^{wl}		92
α-alanine		1×10^{-3}M	1M HCl 25°C	94.00^{pp}		128
Aspartic acid				52.00^{pp}		
L-glutamine				55.00^{pp}		
L-lysine		1×10^{-5}M		74.00^{pp}		
Serine		1×10^{-3}M 1h	0.5M HCl	54.70^{pp}	83.10^{EIS}	89
Threonine				83.40^{pp}	87.70^{EIS}	
Glutamic acid				90.40^{pp}	94.50^{EIS}	
Aspartic acid		0.1M	0.5M HCl	56.88^{EIS}		93
Glutamic acid				59.70^{EIS}		
Asparagine				65.26^{EIS}		
Glutamine	/			73.50^{EIS}		
	KI	$(10+5)\times10^{-3}$M		93.74^{EIS}		
Alanine		10×10^{-3}M	0.5M HCl	-12.00^{a}		114
Leucine				-02.00^{a}		
Asparagine				/		
Glycine				$\sim$02.00-03.00^{a}		
Tyrosine				12.00^{a}		
Threonine				12.00^{a}		
Tryptophan				12.00^{a}		
Arginine				25.00^{a}		
Histidine				27.00^{a}		
L-phenylalanine	/	7×10^{-3}M	0.5M HCl	29.60^{pp}	29.50^{EIS}	88
	Ce(IV)	$(5+2)\times10^{-3}$M		71.80^{pp}	82.70^{EIS}	
$Ce(SO_4)_2$		7×10^{-3}M		-64.90^{a}	-62.70^{EIS}	
Histidine SAM	pH 2	10×10^{-3}M	0.5M HCl		17^{EIS}	129
	pH 10			75^{pp}	74	
	pH 13				51	
	pH 10 KI	$(10+5)\times10^{-3}$M		84	89	

Values of inhibition efficiency are calculated using data gathered from: pp – potentiodynamic curves; EIS – EIS measurements; wl – weight loss

According to the data presented in Table 6 it can be said that tyrosine provides the best inhibition effect in nitric and sulfuric acid among all the tested amino acids. Histidine on the other hand was the most efficient in phosphoric acid.

Table 6. The efficiency of copper corrosion inhibition in various media obtained in the presence of amino acids

Inhibitor	Concentration	Medium	IE %		Reference
Proline	1×10^{-3}M	8M H_3PO_4	39.60^{pp}		98
Phenylalanine			47.82^{pp}		
Alanine			36.00^{pp}		
Histidine			54.34^{pp}		
Glycine			32.90^{pp}		
Valine	50×10^{-3}M	0.5M H_2SO_4	74.10^{pp}	72.00^{EIS}	94
Alanine			74.90^{pp}	73.00^{EIS}	
Glycine			90.90^{pp}	92.00^{EIS}	
Tyrosine			97.90^{pp}	96.80^{EIS}	
Valine	1×10^{-3}M	1M HNO_3	-20.00^{pp}	-15.00^{wl}	90
Glycine			-01.00^{pp}	-04.00^{wl}	
Arginine			46.00^{pp}	38.00^{wl}	
Lysine			56.00^{pp}	54.00^{wl}	
Aspartic acid	1×10^{-3}M	1.0M HNO_3	28.07^{pp}	31.48^{wl}	95
Glutamic acid			37.55^{pp}	37.04^{wl}	
Alanine			24.51^{pp}	18.56^{wl}	
Asparagine			45.01^{pp}	42.59^{wl}	
Glutamine			40.20^{pp}	40.74^{wl}	
Leucine			33.84^{pp}	35.18^{wl}	
Threonine			50.41^{pp}	48.15^{wl}	
Proline	1×10^{-3}M	1.0M HNO_3	29.70^{pp}	33.30^{wl}	96
Phenylalanine			36.00^{pp}	38.90^{wl}	
Tyrosine			81.90^{pp}	70.40^{wl}	
Tryptophan			67.20^{pp}	82.70^{wl}	

Values of inhibition efficiency are calculated using data gathered from: pp – potentiodynamic curves; EIS – EIS measurements; wl – weight loss

5. PLANT EXTRACTS AND NATURAL PRODUCTS

Plant extracts have been of interest as corrosion inhibitors for a relatively long period of time as can be seen from the data presented in the review papers published by several authors [130-133]. However, the number of research dealing with this topic increases progressively in the past few years. Some of the results obtained by various research groups are presented in Table 7. The main characteristics that make them one of the classes of favourite new corrosion inhibitors are their non-toxicity, environmentally friendly behaviour, and in the addition the facts that they are cheap and renewable. Nevertheless, the most important parameter for the evaluation of the possibility to use such material as corrosion inhibitor is the degree to which corrosion rate is diminished. As it can be seen from the Table 7, the inhibition efficiency values are over 90% in significant number of studies indicating that some plant extracts can be applied as efficient copper corrosion inhibitors. One of the

mentioned studies includes *Azadirachta indica* extracts studied as copper corrosion inhibitors in acid media. It is shown that leaves extract can provide very efficient protection against corrosion in 0.5mol dm^{-3} sulphuric acid [134] whereas seed extract can be applied in nitric acid [135].

The mode of action of plant extract is the adsorption of its constituents on the metal surface. Taking into account the phytochemical composition, presented in Table 8, the adsorption occurs due to the presence of oxygen active centres. The adsorption is described as chemisorption in accordance with Frumkin adsorption isotherm [134, 135]. Copper corrosion in sulfuric acid can also be efficiently inhibited by *Cannabis* extract [136] due to the presence of oxygen, nitrogen atoms and π-electrons in extract constituents, named in Table 8, that are known for enabling interaction with copper. It is found that the extract adsorption can be described using Langmuir, Flory-Huggins isotherms and kinetic-thermodynamic model. The effect of HCl on copper can be diminished by the addition of *Tecomella Undulata* seeds extract [137] and also by the addition of *Zenthoxylum alatum* [138]. *Zenthoxylum alatum* is surfactant that can get adsorbed on copper surface since it contains nitrogen and carbonyl group. The adsorption takes place on both anodic and cathodic sites according to the Langmuir isotherm.

Table 7. The efficiency of copper corrosion inhibition in the presence of plant extract

Inhibitor	Form	Concentration	Medium	IE %	Reference
Azadirachta Indica	Commercial leaves extract powder	$1g/dm^3$	0.5M H_2SO_4	86.40^{pp}	134
	Acid extract of dry seed	1%	1.0N HNO_3 3h	95.69^{wl}	135
Cannabis	Extract of the flowering tops of plants	10ppm 10ppm 10ppm 25ppm 25ppm	0.5M H_2SO_4	86.00^{pp} 83.00^{EIS} 84.40^{wl} 96.00^{pp} 91.00^{EIS}	136
Tecomella undulata	Root extract Branches extract Leaves extract Seeds extract	5%	1N HCl 72h	86.72^{wl} 89.27^{wl} 86.13^{wl} 93.84^{wl}	137
Zenthoxylum alatum	Commercial non-ionic surfactant plant	800ppm	0.1M HCl 2h 30-40˚C	95.80^{pp} 98.28^{wl}	138
Artemisia herbaalba	Extract Artemisia oil	$6g/dm^3$	2M H_3PO_4 + 0.3M NaCl	89.00^{pp} 87.00^{EIS} 87.00^{wl}	139
Cassia Siamea Lam.	Root extract	$10mg/dm^3$	0.5M NaOH	78.30^{adt}	140
Gnetum africana *Musa acuminate* peel	Extract in HNO_3	$3mg/dm^3$	2.5M HNO_3 303K	80.50^{wl} 76.10^{wl}	141
Varthemia Iphionoides	Apigenin Luteolin-3'-methyl ether Quercetin-3,3'-dimethylether Jeceidine	1×10^{-4}M	2M HNO_3 4h 25˚C	78.30^{wl} 85.10^{wl} 89.30^{wl} 91.60^{wl}	142
Emblica officinalis	Leaves extract – 150g in ethanole	1000ppm	Natural sea water, 30˚C	79.99^{wl}	143

Allium Cepa	Water extract of the outer layer	0.6 g/dm^3	Industrial chill wastewater systems 24h, 39.5˚C	46.00^{wl}	144
Rhizopora apiculata	Tannin extracted from the mangrove bark	3g/dm^3	0.5M HCl	82.40^{pp} 87.60^{EIS} 72.80^{wl}	145
			1.0M HCl	68.80^{pp} 71.40^{wl}	146
Vitis vinifera	Seed and skin extract 150g in ethanole	1000ppm	Natural sea water 24h , Room temperature	76.08^{wl}	147
Lawsonia inermis *Phoenix dactyligera* *Zea mays*	Water-extracts from the dry leaves	5g/dm^3	0.2M HCl 24h 25±0.2˚C	31.80^{wl} 21.70^{wl} 17.20^{wl}	148
Ziziphus mauritiana	Plant extract in ethanol	1.288g/dm^3	0.5N HCl 72h 30˚C	88.52^{wl}	149

Values of inhibition efficiency are calculated based on the data obtained using: pp – potentiodynamic polarisation curves; EIS – EIS measurements; wl – weight loss; adt – absorbance difference technique

Number of other plant extracts also enables inhibition of copper corrosion to some degree, as it can be seen in Table 7. Generally, it can be said that organic compounds containing heteroatoms or π-electrons, present in their extracts, enable the adsorption on copper surface and hence inhibition of corrosion. The most common heteroatom present in phytochemical constituents of studied extracts is oxygen so it is the most probable active centre involved in interaction with copper [144, 147, 149]. The adsorption that presents the mode of extracts action is most often physical by nature and described by Langmuir adsorption isotherm [140, 141, 143, 147, 149], but also in some cases by Temkin isotherm [143, 147].

There are several factors that are known to have an effect on the inhibition efficiency values obtained. Usually the increase of the temperature leads to the decrease of the possible inhibition efficiency [140-143, 147]. On the other hand the increase of concentration leads to the increase of inhibition efficiency [141, 143, 146, 147, 149]. Regarding the time of exposure it can be concluded that usually the effect of time increase is negative [141, 143, 147], but nevertheless in some research the data state opposite [149].

Most of the studies are done using extracts of complex composition. In those cases the appearance of compounds interaction and possible synergistic effect should also be taken in consideration [149]. Nevertheless some of the researchers decided to use specific compounds isolated from extracts such as tannins or flavonoids. Tannins are polyphenols of vegetal origin. The basic components of tannins are sugars, gallic acid, ellagic acid, and flavonoids. Shah and co-authors [145, 146] studied tannins isolated from *Mangrove* as potential copper corrosion inhibitors in HCl and concluded that IE over 80% can be obtained. The mode of action is inhibition of cathodic reaction that takes place due to physical adsorption via oxygen active centres of the flavonoid monomers of tannin on the metal surface. The appropriate adsorption isotherm is found to be Langmuir isotherm. Al-Qudah [142] used substituted flavonoids, named in Table 7, isolated from *Varthemia iphionoides* as copper

corrosion inhibitors. The increase of concentration induces the inhibition effect increase. However, at some point limiting value is achieved due to the formation of an adsorbed monolayer film. The adsorption occurs via carbonyl and hydroxyl group of the flavonoid molecule and follows Langmuir adsorption isotherm. The most efficient of the studied compounds is jeceidine, showing that the addition of electron donating methoxy group (OCH_3) improves inhibitory action.

According to the data presented in Table 8 regarding the phytochemical composition of studied plant extracts, it can be concluded that most of them contain tannins, flavonoids and phenolic compounds among others. The proposition that they are compounds most probably responsible for inhibitory characteristics is also supported by the results of studies of isolated tannins and flavonoids as corrosion inhibitors.

One of the naturally occurring products, phytic acid (PA) that can be found in beans, brown rice, corn, sesame seeds, and wheat bran, is studied as potential copper corrosion inhibitor [150]. The benefits of its application would include its non-toxic and environmentally friendly nature. According to the results the efficiency of copper corrosion inhibition in 3wt% NaCl reached 87.4% when film was formed in 0.11×10^{-3}mol dm^{-3} PA solution for 6h. The salt of phytic acid Na phytate ($NaIP_6$) was found to be very efficient copper corrosion inhibitor in 0.1mol dm^{-3} NaOH solution, specifically, in concentration range 0.01 and 0.1mol dm^{-3} it provides inhibition efficiency about 90% [70].

Table 8. Constituents of plant extracts

Plant / Compound	Saponin	Phlobatanin	Tannin	Anthraquinone	Glycosides	Flavonoid	Terpene	Steroids	Alkaloid	Phenols	Sugars	Organic acids	Camphor	α-thuyone	β-thuyone	Camphene	1,8-cineole	Emblica A and B	Phyllanthin	Punigluconin	Pedunculagin	Cannabidiol CBD	Cannabinol	Anandamide (AEA)	2- Arachidonoyl glycerol (2-AG)	Reference
Azadirachta indica seed	+++ ++	++ +	+++ +++	+ -	+++ +++	+ +	+++ +++		+++ ++																	135
Cassia siamea Lam.	*		*	*	*			*	*	*																140
Rhizopora apiculata			*																							145, 146
Ziziphus mauritiana			*			*				*	*	*														149
Artemisia herbaalba													46%	33.2%	9.0%	8.5%	6.4%									139
Varthemia iphionoides						*																				142
Vitis vinifera										*																147
Allium cepa						*																				144
Emblica officinalis																		*	*	*	*					143
Gnetuma africana	++	++	++	++	+++	-	+++	+++																		141
Musa acuminate peel	+++	++	+++	++	+++	++	+++	+++																		
Cannabis																						*	*	*	*	136

Indicators present in Table have the following meaning: - absent; + present in trace quantity; ++ moderately present; +++ present in large quantity; * present but in unknown quantity

6. PHARMACEUTICAL COMPOUNDS, IONIC LIQUIDS, CARBOXYLIC ACIDS AND OTHER COMPOUNDS

Vitamin C is well known supplement in human diet, which makes it favorable as non-toxic and also environmentally acceptable potential corrosion inhibitor. The possibility of its application in this manner is studied in solutions of NaCl and HCl [85]. Abiola and coworkers [151] studied the possibility to use 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride, shorter thiamine hydrochloride or vitamin B_1 hydrochloride as copper corrosion inhibitor in 2.5mol dm^{-3} HNO_3. This compound is also studied due to the fact it is potential non-toxic corrosion inhibitor. The results are presented in Table 9.

Potassium folate, another non-toxic environmentally friendly compound used in pharmaceutical fields, is studied as copper corrosion inhibitor [152]. According to the results presented in Table 9, potassium folate acts as inhibitor of copper corrosion and this effect is due to the physisorption of the organic compound on surface of copper that obeys Flory–Huggins isotherm and kinetic–thermodynamic model. Folate acts as an anodic-type inhibitor, whereas the inhibition efficiency increases with concentration and time of immersion and decreases with increasing the Na_2SO_4 concentration and temperature.

Some other pharmaceutical compounds are studied as non-toxic and inexpensive copper corrosion inhibitors as well [153]. Namely, 6-chloro-1,1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulphonamide (compound I), 1-((s)-3-mercapto-2-methyl propanoyl) pyrrolidine-2-carboxylic acid (compound II) and 3-(2-methoxy phenoxy) propane 1,2-diol (compound III). The values of inhibition efficiency are presented in Table 9. The mode of action includes adsorption on copper surface that can be best fitted to Temkin adsorption isotherm and Gibbs free energy of adsorption of approximately -60kJ mol^{-1} indicates strong spontaneous adsorption. It is obvious from IE values that compound I is the best corrosion inhibitor among studied compounds and it can be attributed to molecular size as well as to the large number of centres of adsorption (4-O, 2-S and 3-N atoms) and increased electron density.

Table 9. The efficiency of copper corrosion inhibition in the presence of pharmaceutical compounds

Inhibitor	Concentration	Medium	IE %				Reference
Vitamin C	3g/dm^3	4% HCl	61.93[wl]				85
		3% NaCl	66.01[wl]				
Thiamine hydrochloride	2×10^{-3}M	30min 30°C 2.5M HNO_3	69.9[wl]				151
Potassium folate	10×10^{-3}M	1M Na_2SO_4 15°C	73.9[pp]				152
	6×10^{-3}M		60.9[pp]		63.57[EIS]		
I	1.1×10^{-5}M	2M HNO_3	82.6[wl]	89.7[pp]	60.5[EIS]	80.6[EFM]	153
II			79.4	85.6	43.5	67.1	
III			75.9	64.8	32.2	63.9	

Values of inhibition efficiency are calculated based on the data obtained using: wl – weight loss; pp – potentiodynamic polarization; EIS – electrochemical impedance spectroscopy; EFM – electrical frequency modulation

Scendo and Uznanska [154, 155] studied the effect of some ionic liquids (ILs) on corrosion of copper. Ionic liquids are in essence molten salts containing organic cations and with low melting points. They have an amphiphilic group with a long chain, hydrophobic tail, and a hydrophilic polar head in their structure. Central atoms of cations are usually nitrogen, sulphur and phosphorus. The attractive possibility is to introduce various functional groups into cations, which enables the change of the physicochemical properties of ILs and various applications of ILs. The studies included 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-butyl-3-methylimidazolium bromide (BMIMBr) [154] and 1-butyl-4-methylpyridinium tetrafluoroborate (4MBPBF$_4$) [155], results are presented in Table 10. In all the studied cases the inhibition efficiency increased with inhibitor concentration. The inhibitors acted as mixed-type inhibitors which inhibitive effect is due to the blocking of the reaction sites on copper surface, without affecting the cathodic and anodic reaction mechanism. The adsorption occurring on copper surface can be described by Langmuir adsorption isotherm. Calculated values of ΔG_{ads} indicate that BMIMCl and BMIMBr are chemically adsorbed on copper in 1.0mol dm^{-3} Cl^- solutions of pH 1.0 [154], whereas 4MBPBF$_4$ is physically adsorbed on the copper surface in phosphate solution [155]. Authors propose that the adsorption of BMIMCl and BMIMBr molecules occurs through the formation of copper-nitrogen coordinate bond or the interaction between the aromatic ring π-electrons and copper. Regarding the effect of pH and temperature, based on the results obtained using 4MBPBF$_4$ it can be concluded that IE is higher in less acidic media and it decreases at higher temperature.

Table 10. The efficiency of copper corrosion inhibition in the presence of ionic liquids

Inhibitor	Concentration	Medium		IE %	Reference
1-Butyl-3-methylimidazolium chloride (BMIMCl)	50×10^{-3}M	1.0M Cl^- pH 1.0 (NaCl+HCl)		96^{pp}	154
1-Butyl-3-methylimidazolium bromide (BMIMBr)				83	
1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF$_4$)	50×10^{-3}M	0.5M PO_4^{3-}	pH 2	92^{pp}	155
			pH 4	94	

Values of inhibition efficiency are calculated based on the data obtained using: pp – potentiodynamic polarization

Carboxylic acid behavior as copper corrosion inhibitor was studied by Quartarone and associates [156] using indole-3-carboxylic acid added to sulphuric acid solution, as a representative. Some results are presented in Table 11 and it is also interesting to notice that with the increase of temperature from 25 to 35˚C inhibition efficiency and adsorption energy decrease, whereas with

further temperature increase to 55˚C both values increase. The adsorption followed the Langmuir's isotherm, with contribution of both physisorption and chemisorption.

Table 11. The efficiency of copper corrosion inhibition in the presence of carboxylic acids

Inhibitor	Concentration	Medium	IE %	Reference
Myristic acid (MA)	Grinding followed by etching in 10% HNO_3 for 30s 0.05M in ethanol 20min	0.2g/l Na_2SO_4, 0.2g/l $NaHCO_3$, 0.2g/l $NaNO_3$ pH 5 (adjusted with 10% H_2SO_4)	>95	158
Decanoic acid (DA)			>80	
Hexanoic acid (HA)			34	
Stearic acid (SA)			98.5^{pp}	
Stearic acid (SA)	Grinding, 0.05M in ethanol 20min		96	
Copper decanoate (CuC_{10})	Deposition in sodium carboxylate solution 0.025M. The modification of the copper electrode was performed by 100 successive cyclic voltammetric scans in a potential window from −1.1 to 0.6V vs SCE with a scan rate of 50mV/s.	0.1M Na_2SO_4	21	157
Copper dodecanoate (CuC_{12})			41	
Indole-3-carboxylic acid (ICA)	2×10^{-3}M	0.5M H_2SO_4 25˚C	81^{pp} 89^{EIS}	156

Values of inhibition efficiency are calculated based on the data obtained using: pp – potentiodynamic polarization; EIS – electrochemical impedance spectroscopy

Several other compounds are investigated as potential inhibitors of copper corrosion in various media. The results are presented in Table 12. It can be seen that in a few cases inhibition efficiency exceeded 90% indicating that those compounds can effectively inhibit corrosion of copper for example N-1-naphthylethylenediamine dihydrochloride monomethanolate and (E)-3-(4-methoxyphenyl)-1-phenyl prop-2-en-1-one in HNO_3; 2-mercapto-4-amino-5-nitroso-6-hydroxy pyrimidine or sodium diethyldithiocarbamate in NaCl and cobalt(II) 5,10,15,20-tetrakis(2-aminophenyl)-porphyrin (Co(II)(T(o-NH2)PP) in Na_2SO_4.

Table 12. The efficiency of various compounds as copper corrosion inhibitors

Inhibitor	Concentration	Medium	IE %				Reference
N-1-naphthylethylenediamine dihydrochloride monomethanolate (N-NEDHME)	1×10^{-3}M	2M HNO_3	93.53^{pp}	92.38^{EIS}		95.26^{wl}	159
2-Mercapto-4-amino-5-nitroso-6-hydroxy pyrimidine (MAP)	1×10^{-3}M	3.5% NaCl	88.9^{pp}	90.7^{EIS}	91.6^{wl}	92.2^{EFM}	160
(E)-3-(4-methoxyphenyl)-1-phenyl prop-2-en-1-one	1.5×10^{-5}M	1M HNO_3	89.3^{pp}	91.4^{EIS}	80.2^{wl}	88.13^{EFM}	161
(E)-3-(4-methylphenyl) -1-phenyl prop-2-en-1-one			85.7	89.5	75.0	85.3	
(E)-3-(phenyl)-1-phenyl prop-2-en-1-one			76.97	78.9	70.8	78.91	
(E)-3-(4-choloro phenyl)-1-phenyl prop-2-en-1-one			58.2	78.9	58.3	44.68	
Cobalt (II) 5,10,15,20-tetrakis(2-aminophenyl)-	1×10^{-3}M 24h	0.1M Na_2SO_4	97.94^{EIS}				162

porphyrin (Co(II)(T(o-NH_2)PP) SAM				
2-(Pyridin-2-yliminomethyl)-phenol (HL) SAM	1×10^{-3}M in ethanol 120min	0.1M NaCl	82.30[pp]	163
Poly(m-phenylenediamine) (PMPD) film	0.15M MPD 0.2M sodium oxalate electrochemical synthesis	0.1M H_2SO_4 0h	71.67[EIS]	164
		24h	90.69	
Polyaniline (PANI)	Electrochemical polymerization aqueous solution of 0.3M sodium benzoate and 0.2M aniline	0.5M NaCl	96[pp]	165
Sodium diethyldithiocarbamate (DDTC) SAM	1×10^{-3}M 16h	3% NaCl	99.3[EIS]	166

Values of inhibition efficiency are calculated based on the data obtained using: wl – weight loss; pp – potentiodynamic polarization; EIS – electrochemical impedance spectroscopy; EFM – electrical frequency modulation

7. CONCLUSIONS

According to the data presented in the text above several conclusions can be made.

- First of all there are numerous compounds tested as copper corrosion inhibitors in various media and several groups of compounds stand out both due to the provided protection degree and the quantity of literature dedicated to them. They are in the first place: azoles and amino acids. Nevertheless, the interest in purine and derivatives, plant extracts, natural products and pharmaceutical compounds is increasing over the past years.
- The focus turns to environmental impact of corrosion inhibitors, hence non-toxic environmentally friendly and biodegradable compounds are favoured.
- More attention is devoted to the understanding of the molecular level processes taking place at the surface of copper involving inhibitor molecules and metal.
- There are novel research approaches and techniques, as well as the new methods for the application of inhibitors.

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