DOI: 10.20535/kpisn.2021.3.251475
UDC 620.197.3

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AGRICULTURAL BY-PRODUCT EXTRACTS AS SCALE INHIBITORS OF MILD STEEL IN TAP WATER

Received: 19 Aug. 2021. Accepted: 7 Dec. 2021.

Background. In industrial heating processes, scaling is a major problem especially when natural water is used as heat carrier. The world economic losses due to scaling are estimated to constitute billions of dollars per year, the development of efficient, environmentally friendly and cheap approaches for reduction of scaling is an actual task nowadays. Utilization of agro-food wastes as a renewable source of scale inhibitors for water treatment of cooling water systems is a promising alternative to the existing approaches.

Objective. Three industry by-products, namely rapeseed pomace, sugar beet pulp and fodder radish cake, have been tested as scale inhibitors of mild steel in tap water.

Methods. Ethanol extracts were prepared by maceration and the electrochemical approach to study the scale formation was utilized, based on the measurement of oxygen reduction current during nucleation and formation of calcium carbonate in the presence of extracts. Scaling time, porosity and area density of the scale was determined and used to characterize the inhibition efficiency. Chemical compositions of extracts were analysed by GC-MS analysis (gas chromatography with mass selective detector by mass selective integration).

Results. The rapeseed pomace extract and fodder radish cake extract at the concentration of 10 mL/L appeared to be efficient scaling inhibitors. Sugar beet pulp extract increases the crystallization time, however the amount of deposited scale appeared to be the same as in the tap water.

Conclusions. The scale inhibition is caused mainly by the formation of adsorbed film on the scale nucleus that blocks the surface and prevent further crystal growth. Natural extracts are a promising source of scale inhibitors due to their low price, efficiency and environmental safety.

Keywords: scale inhibitors; mild steel; green inhibitor; scaling time.

Introduction

In industrial heating processes, scaling is a major problem especially when natural water is used as heat carrier. The formation of scale layer leads to the reduction of hydraulic pressure of pipes followed by the increase in heat transfer resistance thus causing extra costs on heating [1], [2]. The world economic losses due to scaling are estimated to constitute billions of dollars per year, the development of efficient, environmentally friendly and cheap approaches for reduction of scaling is an actual task nowadays.

In industry, scaling problem is typically solved by several ways [3], [4]. The simplest technique is regular cleaning of heat exchanging equipment when heat or pressure loses exceed the set value. Scale deposits can be cleaned out either mechanically or chemically. The next approach is based on scaling prevention by removing hardness salts from heated water by using ion exchange resins as well as membrane techniques and reversed osmosis. Despite high efficiency, the utilization of residual salt solutions is an environmental challenge. The most promising approach is reagent water treatment when chemical reagents are added to the water before heating. Added substances form soluble complexes with hardness cations (i.e. Ca^{2+}, Mg^{2+}) that are stable at high temperature, hence preventing the formation of $CaCO_3$. An alternative mechanism includes the formation of

Рекомендуємо цитувати цю статтю так: G.S. Vasyliev, V.I. Vorobyova, Yu.S. Gerasymenko, O.E. Chygyrynets, “Agricultural by-product extracts as scale inhibitors of mild steel in tap water”, *Наукові вісті КПІ*, № 3, с. 74–82, 2021, doi: 10.20535/kpisn.2021.3.251475.

Please cite this article as: G.S. Vasyliev, V.I. Vorobyova, Yu.S. Gerasymenko, and O.E. Chygyrynets, “Agricultural by-product extracts as scale inhibitors of mild steel in tap water”, *KPI Science News*, no. 3, pp. 74–82, 2021. doi: 10.20535/kpisn.2021.3.251475.

adsorbed layer of inhibitor molecules on the surface of $CaCO_3$ nuclei that prevents further crystal growth.

Polyphosphates are the most common inhibitors in industry [5], [6]. The utilization of traditional scale inhibitors is now limited in the agreement with the concept of "green" chemistry in the field of technology, science, and engineering. "12 Principles of green chemistry" have prompted researchers to find out some cheap and effective environmentally friendly scale inhibitors. By-products and waste obtained from food processing (cake and pomace fruits, vegetables and oilseeds) represent a major disposal problem for the food industry. Consequently, the factories are focused on diminishing the environmental impact of the by-products and recovering "green" organic substances from agro-industrial residue and food waste. Besides, food waste valorisation and re-use strategies, rather than conventional food waste processing (i.e. incineration or composting), are becoming more and more popular. There are numerous successful reports about utilizations of various extracts of plant materials in different branches of "green" chemical technology. The food and agricultural products processing industries generate plenty of by-products which contain non-toxic organic substances [7]—[17]. Hence exploitation of agro-food wastes as a renewable source of scale inhibitors for water treatment of cooling water systems is a promising alternative to the existing approaches.

The antiscalant effect of naturally occurring plant extracts (*Azadirachta Indica*, *Bistorta Officinalis*, *Punicagranatum* hull and leaf, palm leaves, seaweeds, Corn stalks, *Aloe Vera*, *Paronychia Argentea*, *Momordica charantia*, *Parietaria Officinalis* and *Spergularia Rubra*) for cooling systems were studied by many proceedings [18]—[23]. It has been suggested that the scale inhibition efficiency of such extracts is caused by involvement of phenolic compounds or polysaccharides. It was shown that some of the organic components of radish and rape cake extract are very promising as individual corrosion and scale inhibitors.

The scale inhibition properties (mechanism) of the green antiscalant agents can be explained by the adsorption process. The adsorption could take place *via* (i) electrostatic attraction between the charged particles and the charged chemical constituents of the extract, (ii) dipole-type interaction between unshared electron pairs in the extracted molecules and growing particles, (iii) π-interaction with particles and surfaces, and (iv) a combination of all the above.

Problem Statement

The aim of the present research is to investigate the natural raw materials from food and agricultural industry as potential sources of scale inhibitors. Three industry by-products, namely rapeseed pomace from the wastes of edible oil production, sugar beet pulp from the wastes of sugar production and fodder radish cake, were chosen for natural inhibitors search.

Experimental section

Extract preparation and composition analyses

The extracts were prepared by maceration the raw material in the ethanol for 24 h. The ethanol and raw material powder were mixed in the weight ratio of 1:10. Then resulted mixtures were filtered with Whatman filter paper to remove their solid contents.

Chemical compositions of extracts were analysed by GC-MS analysis (gas chromatography coupled with mass selective detector by mass selective integration). A gas chromatograph (Shimadzu model GC 17A) equipped with flame ionization detector (FID) was operated in the following conditions: capillary fused silica column (CBP-5) (length, 25 m; internal diameter of 0.25 mm; film thickness of 0.22 μm), temperature of ion source — 280 °C. The GC—MS operated in the electron impact ionization mode (EI) at 70 eV. The oven temperature was programmed as following: the initial temperature of 50 °C was maintained during 2 min, and then increased up to 200 °C with the rate of 10 °C/min and was kept for 5 min. Next, the temperature was raised to 250 °C at the rate of 25 °C/min (for 15 min). Other working conditions included: carrier gas, He (99.99%), inlet pressure 76 kPa, linear velocity of 20 cm/s; temperature of injector 250 °C; temperature of detector 310 °C; split ratio 1:25. The relative contents of the extract components were determined by the method of internal normalization of the peak areas without correcting the sensitivity coefficients. Peak area of each compound was used to determine its percentage and the sum of the areas of all peaks was detected in the total ion current (TIC) trace. The identification and quantification of the compounds were carried out with the use of commercially available databases: Nist 05 (National Institute of Standards and Technology, USA) and Mass Finder3 (Dr. Hochmuth, Scientific Consulting, Germany).

Electrochemical measurements

The tap water from the Kyiv distribution system was utilized in all the experiments. Its composition is presented in Table 1. The measurements were conducted in a 1L glass beaker filled with tap water and thermostated at 25±0.5 °C (Fig. 1). A mild steel cylinder with a diameter of 6 mm and 30 mm length was rotated at 500 rpm and served as a working electrode.

Its surface was prepared by mechanical polishing with P600 emery paper, degreasing, rinsing with distilled water and drying in hot air. The counter electrode was a platinum grid, and a saturated silver chloride electrode (saturated AgCl) was used as a reference one. The working electrode was polarized at –1.1 V (vs. saturated AgCl) for 240 min to induce precipitation of calcium carbonate on its surface. The current-time dependence was registered concurrently. Each test was run for three times to ensure reproducibility.

***Table* 1.** Water chemical composition.

Parameter		Units	Value
pH			7.8–8.0
Dissolved Oxygen	DO	mg/L	6.0
Total Hardness	TH	mmol/L	3.9–4.2
Total Alkalinity	TA	mmol/L	3.9–4.1
Calcium	Ca^{2+}	mmol/L	3.0–3.1
Magnesium	Mg^{2+}	mmol/L	0.9–1.1
Chloride	Cl^-	mg/L	18–25
Sulfate	SO_4^{2-}	mg/L	30–35
Hydrocarbonate	HCO_3^-	mmol/L	3.2–3.5
Total Dissolved Solids	TDS	mg/L	240–260

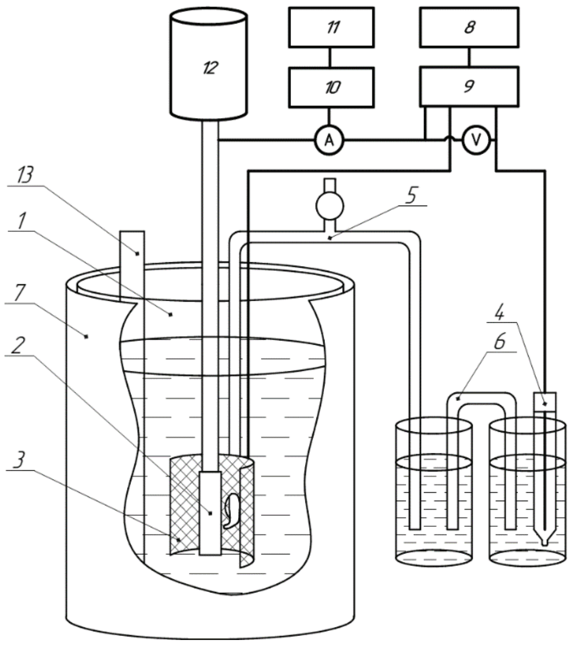


Fig. 1. Polarization apparatus for carbonate electrodeposition in the presence of natural extracts: (*1*) Pyrex vessel, (*2*) working electrode (mild steel cylinder), (*3*) counter electrode (platinum grit), (*4*) reference electrode (saturated silver chloride), (*5*) Luggin capillary, (*6*) salt bridge, (*7*) thermal insulation, (*8*) direct current source, (*9*) potentiostat, (*10*) signal converter, (*11*) computer, (*12*) electric motor, (*13*) regulated water heater.

Scaling investigation

The electrochemical approach for studying of the scale formation is based on the measurement of oxygen reduction current during nucleation and formation of calcium carbonate. The calcium carbonate crystals reduce the electrochemically active surface area of the electrode [24], [25]. Blocking properties of the deposits were evaluated by comparison of electrochemical parameters of the modified and bare electrodes. During the scale formation, the oxygen reduction current, I, is decreased proportionally to the reduction of an electrochemically active surface area. When the surface is free of any deposits (shortly after polarization started) the current reaches its highest value, I_0. After the scaling is finished the lowest oxygen reduction current value, $I_{\min}$, is achieved. In practice, it was measured at the end of the I–t curve (240 min of polarization). When scaling is finished, oxygen reduction can occur on uncovered areas only or through the pores of the scale. Hence, the scale porosity *SP* can be calculated from the values of I_0 and $I_{\min}$ as:

$$SP = \frac{I_{\min}}{I_0} \cdot 100\ \% \qquad (1)$$

The rate of scaling or scaling time, t_s, was found by linear extrapolation of the I–t dependence to zero current. The crystallization kinetics of $CaCO_3$ in the presence of water extracts was characterized by the values of I_0, *SP* and t_s.

To determine the mass of the deposited carbonates the electrodes were weighted before and after electrochemical measurements with 0.0001 g accuracy. The mass of the deposits was used to analyze the results as the area density, mg/cm^2.

Results and Discussion

GC-MS analysis of extracts

The GC-MS analysis results of the radish cake extract (RCE) are given in Table 2. Anthocyanidins including pelargonidin (6.9%) and cyanidin (6.7%), isothiocyanates such as 4-pentenyl isothiocyanate (8.3%), 3-(methylthio)propyl isothiocyanate (iberverin) (4.2%), 3-butenyl isothiocyanate (3.9%), 4-methylpentyl isothiocyanate (3.1%), 4-(methylthio)-3-butenyl isothiocyanate (5,2%), 5-(methylthio)pentyl isothiocyanate (berteroin) (6,9%), 4-(methylthio)butyl isothiocyanate (erucin) (6,4%), and L-sulforaphane (1.1%) were identified in RCE. Other compounds including phenolic derivatives such as eugenol, vanillic acid, pyrogallol, and gallic acid, were also detected together with some fatty acids in substantial amount (8.9 %).

***Table* 2.** Composition of radish cake extract according to GC-MS analysis.

Name of the component	Weight ratio, %
3-(Methylthio)propyl isothiocyanate (Iberverin)	4.2
Benzene-1,2,3-triol (Pyrogallol acid)	2.9
4-pentenyl isothiocyanate	8.3
4-methylpentyl isothiocyanate	3.1
Undecane	1.9
2-Methoxy-4-(prop-2-en-1-yl)phenol (Eugenol)	2.5
4-Hydroxy-3-methoxybenzoic acid (Vanillic acid)	2.8
Dodecanea	1.0
3-Butenyl isothiocyanate	3.9
4-(Methylthio)-3-butenyl isothiocyanate	5.2
4-(Methylthio)butyl isothiocyanate (erucin)	6.4
3,4,5-Trihydroxybenzoic acid (Gallic acid)	2.7
5-(Methylthio)pentyl isothiocyanate (berteroin)	6.9
1-Isothiocyanato-4-methylsulfinylbutane (L-Sulforaphane)	1.1
Detrosex	3.7
Tridecane	1.9
Dodecanoic acid (lauric acid)	0.8
2-(3,4-Dihydroxyphenyl)chromenylium-3,5,7-triol (Cyanidin)	6.7
Hexadecanoic acid (palmitic acid)	2.2
2-(4-Hydroxyphenyl)chromenylium-3,5,7-triol (Pelargonidin)	6.9
Octadecanoic aced	5.9
Methyl linoleate	5.1
Sophorose	7.1

The main compounds extracted from rape cake are given in Table 3. A series of 18 compounds were found, including aldehydes, saturated and unsaturated fatty acids, terpenes, ketones, and glycosides. The major phytocompounds identified in the rape pomace extract are 4-hydroxy-3,5-dimethoxybenzaldehyde (20.5 %), 3′,5′-dimethoxyacetophenone (28.3 %), and (9Z)-octadec-9-enoic acid (12.2 %). Other 39.7 % of the total compounds were present by 15 individual compounds.

The GC-MS analysis of sugar beet pulp extract showed the presence of 6 compounds (Table 4). The maximum amount of the component present in sugar beet pulp extract are sophorose (11.2 %) and sugar acid ((2S,3R,4S,5R)-2,3,4,5-tetrahydroxy-6-oxo-hexanoic acid) (36.9 %). These compounds constitute over 48 % of the total amount of extract compounds.

***Table* 3.** Composition of the rape cake extract according to GC-MS analysis

Name of the component	Weight ratio, %
Guanosine	10.4
Sucrose	1.2
Xanthosine	4.3
3’,5’-Dimethoxyacetophenone	28.3
4-Hydroxy-3,5-dimethoxybenzaldehyde	20.5
Acetic acid	1.6
n-Cyclohexyl-4-hydroxybytyramide	1.6
(9Z,12Z)-9,12-Octadecadienoic acid (Linoleic acid)	4.8
Hexadecanoic acid (Palmitic acid)	4.1
(9Z)-Octadec-9-enoicacid (Oleic acid)	12.2
Octadecanoic acid	2.0
Pyrrolidine, 1-(1-oxo-7,10-hexadecadienyl)	0.9
Ethanamine, 2,2’-oxybis[N,N-dimethyl]	0.9
7-Dehydrodiosgenin	2.1
Campesterol	1.1
γ-Sitosterol	1.2
β-Sitosterol	1.1
Ergosta-5,22-dien-3-ol	2.4

***Table* 4.** Composition of the sugar beet pulp extract according to GC-MS analysis

Name of the component	Weight ratio, %
1-Methyl-4-(prop-1-en-2-yl)cyclohex-1-ene	3.7
(2S,3R,4S,5R)-2,3,4,5-Tetrahydroxy-6-oxo-hexanoic acid (L-Iduronic acid)	36.9
(E)-3-(4-Hydroxy-3-methoxy-phenyl)prop-2-enoic acid	4.4
Sophorose	11.2

Electrochemical scaling test

The normalized chronoamperometric curves obtained for the rape grist extract, radish cake extract and sugar beet pulp extract in concentrations of 1 and 10 mL/L are given at Fig. 2.

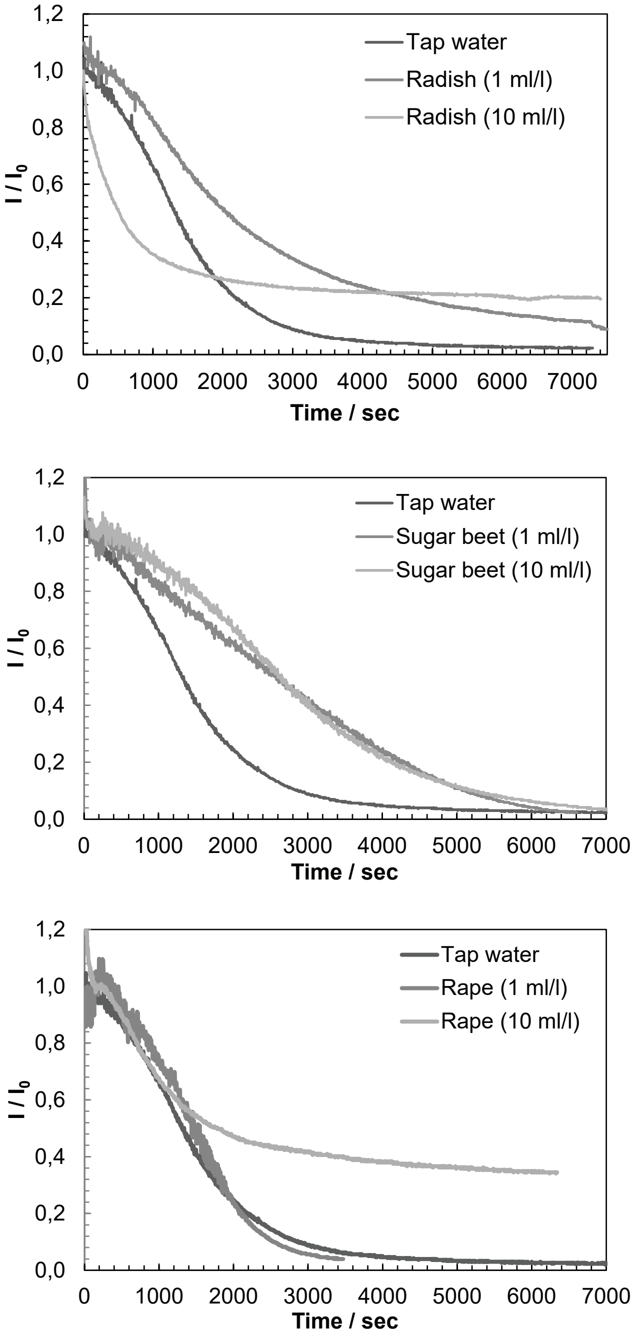


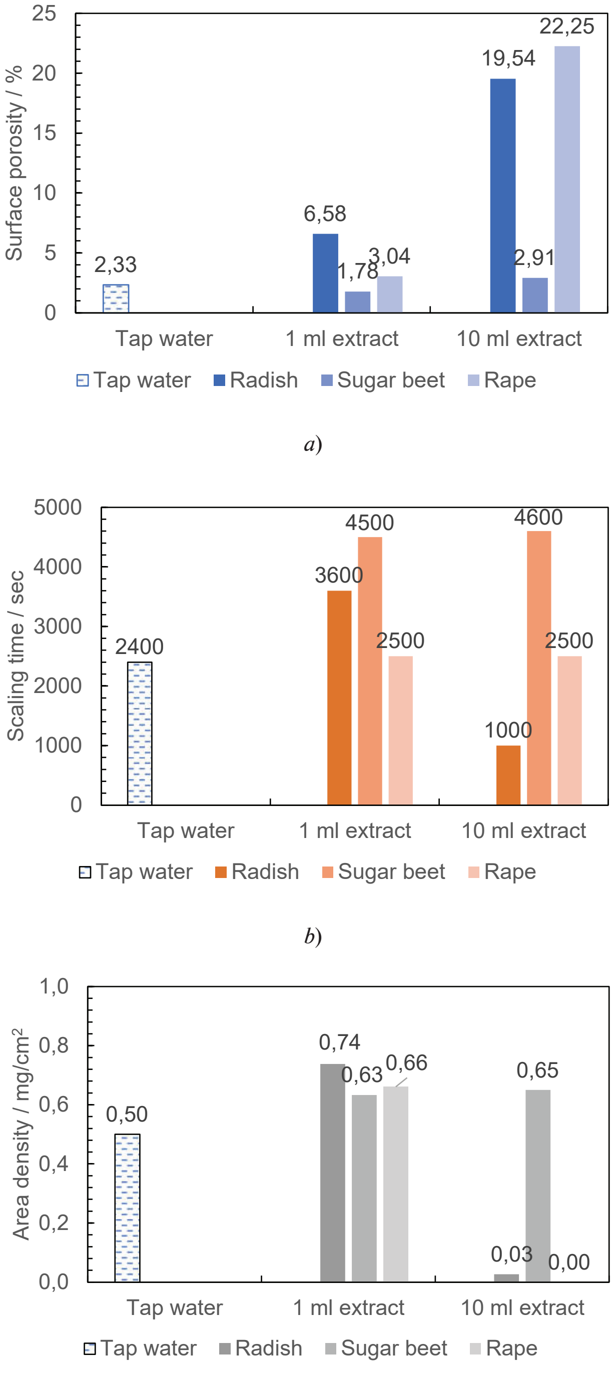
Fig. 2. Normalized chronoamperometric curves with the extract concentration as a parameter.

All the curves show a similar trend of the current reduction due to carbonates crystallization on the steel surface, however the current/time dependences are different depending on the extract nature and its concentration. The radish cake extract of 1 mL/L concentration slows down the crystallization, and at 10 mL/L the residual current is high. At the same time, when sugar beet pulp extract is added to the water at both tested concentrations, the current reduction occurs more slowly, however the residual current is nearly the same as in tap water. The rape grist extract at the concentration of 1 mL/L does not change the chronoamperometric curve, obtained in tap water. At higher concentration of 10 mL/L, the current remains high throughout the test meaning the crystallization is inhibited.

The values of surface porosity *SP*, scaling time t_s and area density for all the tested extracts are collected in Fig. 3. The area density values show that all the tested extracts at 1 mL/L concentration do not reduce the mass of scale deposited on the surface. The mass of the deposits is even slightly higher compared to tap water as a result of inhibitor attachment to the surface. At 10 mL/L concentration radish cake extract and rape grist extract prevent the crystallization as practically no changes in the electrode weight were detected after the test. In contrary, sugar beet pulp extract at 10 mL/L concentration does not prevent scaling and the area density is the same as in tap water.

Scale porosity values are in a good agreement with the area density. In 1 mL/L concentration the porosity values remain close to those obtained in tap water despite radish cake extract, where *SP* is above 6 %. At 10 mL/L concentration the *SP* in both radish cake extract and rape grist extract is around 20 % meaning weak blocking abilities of the scale layer. In the presence of sugar beet pulp extract, the porosity remains the same as in tap water, meaning this reagent does not inhibit the scale formation.

Scaling time is another important parameter to characterize the crystallization process. Sugar beet pulp extract nearly doubles scaling time compared to tap water, however, it does not influence the amount of the deposited scale. Rape grist extract does not change the scaling time comparing to tap water, but significantly inhibits the deposition process. Radish cake extract in 1 mL/L concentration increases t_s to 3600 sec, but at higher concentration of 10 mL/L t_s is reduced to 1000 sec.



a)

b)

c)

Fig. 3. Influence of the extract concentration on scale crystallization parameters: (a) scale porosity, (b) scaling time, (c) deposited mass.

The reduction of t_s and the absence of scale layer on the electrode surface means that the extracts form a barrier layer on the steel surface. The layer blocks the surface from the supply of calcium carbonate as well as reduces oxygen supply. Thus, the reduction of t_s in conditions when no calcium was deposited is attributed to the formation of a barrier layer from extract compounds.

The by-products extracts are composed of numerous naturally occurring organic compounds. Owing to the complex chemical composition of these extracts, it is rather difficult to assign the scale inhibitive effective to a particular constituent. The difference in scale inhibition efficiency between these three extracts is due to their different phytochemical composition. These compounds contain lone pairs of electrons and conjugated π-type bond system which may be responsible for the adsorption process (coordination) on the growth sites on the surface and preventing scale formation. The increase in the number of functional groups contained in molecules of the main extracts improves their surface-binding capacity and respectively inhibitory effect of the corresponding extract.

The analyses of the scientific and technical literature suggests that the scale inhibition action performed by the radish cake extract is mainly due to the presence of polysaccharides and phenolic derivatives. Also, it is generally recognized that the inhibitory effect of polysaccharides and phenolic compounds on calcium carbonate crystal formation is influenced by both the location of the adsorbed inhibitor molecules at the crystals surface and the extent of chemical bonding with the surface. The radish cake extract contains organic components characterized by branched structures and presence of heteroatoms like oxygen, sulfur and aromatic rings with a high electron density. This high electron density can facilitate better coordination interaction, and stronger bonding between the metal surface and radish cake extract molecules. According to the previous research [22], the polysaccharides and phenolic compounds [23] act by surface adsorption, blocking the active growth of sites on the surface, therefore preventing the scale formation. Also, the radish cake extract contains organic molecules such as isothiocyanates. The major phytocompounds identified in the sugar beet pulp and rape cake extracts are sugar acid, fatty acids, aldehydes, ketones. However, they contain a low amount of polysaccharides, isothiocyanates or phenolic compounds.

Conclusions

The water/ethanol extracts of the rapeseed pomace, sugar beet pulp and fodder radish cake were prepared and tested as scale inhibitors of mild steel in tap water. The main constituents of extracts were identified by GC-MS methods. Analysis of the radish cake extract showed that anthocyanins, phenolic compounds and polysaccharides are the main classes among the present compounds. A high concentration of fatty acids, aldehydes, ketones were detected in rapeseed pomace extract. The GC-MS analysis of the sugar beet pulp extract revealed the presence of sugar acids and sophorose.

Electrochemical scaling test showed different scaling inhibition efficiency of the tested extracts. The rapeseed pomace extract and fodder radish cake extract at the concentration of 10 mL/L appeared to be efficient scaling inhibitors. The cathodic current remains high meaning surface of the electrode being not blocked with scale crystals and practically no scale detected on the electrode surface after the test. Sugar beet pulp extract increases the crystallization time, however the amount of deposited scale appeared to be the same as in the tap water. The scale inhibition is caused mainly by the formation of adsorbed film on the scale nucleus that blocks the surface and prevents further crystal growth.

Natural extracts are a promising source of scale inhibitors due to their low price, efficiency and environmental safety.

Acknowledgements

This work was supported by the Ministry of education and science of Ukraine [grant number 2403, 2021].

References

[1] E. F. C. Somerscales, “Fundamentals of corrosion fouling”, *Exp. Therm. Fluid Sci.*, vol. 14, no 4, pp. 335–355. May 1997. doi: 10.1016/s0894-1777(96)00136-7.

[2] M. Chaussemier *et al.*, “State of art of natural inhibitors of calcium carbonate scaling. A review article”, *Desalination*, vol. 356, pp. 47–55. Jan. 2015. doi: 10.1016/j.desal.2014.10.014.

[3] G. S. Vasyliev and S. M. Vasylieva, “The Influence of Ultrasound on the Carbonate Cathodic Crystallization in Artificial Potable Water”, *J. Electrochem. Soc.*, vol. 164, no 4, pp. H250–H256, Mar. 2017. doi: 10.1149/2.0301706jes.

[4] G. Vasyliev, S. Vasylieva, A. Novosad and Y. Gerasymenko, “Ultrasonic modification of carbonate scale electrochemically deposited in tap water”, *Ultrasonics Sonochemistry*, vol. 48, pp. 57–63. Nov. 2018. doi: 10.1016/j.ultsonch.2018.05.026.

[5] Chen Wang, Deyi Zhu and Xikui Wang, “Low-phosphorus maleic acid and sodium ρ-styrenesulfonate copolymer as calcium carbonate scale inhibitor”, *J. Appl. Polym. Sci.*, vol. 115, no. 4, pp. 2149–2155, Oct. 2009. doi: 10.1002/app.31300.

[6] A. L. Kavitha, T. Vasudevan and H. G. Prabu, “Evaluation of synthesized antiscalants for cooling water system application”, *Desalination*, vol. 268, no. 1–3, pp. 38–45. Mar. 2011. doi: 10.1016/j.desal.2010.09.047.

[7] V. Vorobyova, O. Chygyrynetś, M. Skiba, I. Kurmakova and O. Bondar, “Self-assembled monoterpenoid phenol as vapor phase atmospheric corrosion inhibitor of carbon steel”, *Int. J. Corros. Scale Inhib.*, vol. 6, no. 4, pp. 485–503, Nov. 2017. doi:10.17675/2305-6894-2017-6-4-8.

[8] O. E. Chygyrynets’, V. I. Vorobyova, G. Y. Galchenko and I. G. Roslik, “Investigation of the efficiency of inhibitors of atmospheric corrosion”, *Metall. Min. Ind.*, vol. 4, no. 2, pp. 100–106, 2012.

[9] O. E. Chyhyrynets’ and V. I. Vorob’iova, “Anticorrosion Properties of the Extract of Rapeseed Oil Cake as a Volatile Inhibitor of the Atmospheric Corrosion of Steel”, *Mater. Sci.*, vol. 49, no. 3, pp. 318–325, Nov. 2013. doi: 10.1007/s11003-013-9617-z.

[10] V. I. Vorob’iova, O. E. Chyhyrynets and O.I. Vasyl’kevych, “Mechanism of Formation of the Protective Films on Steel by Volatile Compounds of Rapeseed Cake”, *Mater. Sci.*, vol. 50, no. 5, pp. 726–735, Mar. 2015. doi:10.1007/s11003-015-9778-z.

[11] E. Chygyrynets’ and V. Vorobyova, “A study of rape-cake extract as eco-friendly vapor phase corrosion inhibitor”, *Chem. Chem. Technol.*, vol. 8, no. 2, pp. 235–242. Jun. 2014. doi: 10.23939/chcht08.02.235.

[12] V. Vorobyova and M. Skiba, “Apricot cake extract as corrosion inhibitor of steel: chemical composition and anti-corrosion properties”, *Chem. J. Mold.*, vol. 14, no. 1, pp. 77–87. May 2019. doi: 10.19261/cjm.2018.525.

[13] V. Vorobyova, O. Chygyrynets’, M. Skiba, I. Trus and S. Frolenkova, “Grape pomace extract as green vapor phase corrosion inhibitor”, *Chem. Chem. Technol.*, vol. 12, no. 3, pp. 410–418, Sep. 2018. doi: 10.23939/chcht12.03.410.

[14] V. Vorobyova, M. Skiba and O. Chygyrynets’, “A novel eco-friendly vapor phase corrosion inhibitor of mild steel”, *Pigment & Resin Technology*, vol. 48, no. 2, pp. 137–147. Feb. 2019. doi: 10.1108/PRT-03-2018-0025.

[15] V. I. Vorobyova, M. I. Skiba, A. S. Shakun and S. V. Nahirniak, “Relationship between the inhibition and antioxidant properties of the plant and biomass wastes extracts – A Review”, *Int. J. Corros. Scale Inhib.* vol. 8, no. 2, pp. 150–178. May 2019. doi: 10.17675/2305-6894-2019-8-2-1.

[16] V. Vorobyova, O. Chygyrynets and M. Skiba, “4-hydroxy-3-methoxybenzaldehyde as a volatile inhibitor on the atmospheric corrosion of carbon steel”, *J. Chem. Technol. Metall.*, vol. 53, no. 2, pp. 336–345, 2017.

[17] V. Vorobyova, O. Chygyrynetsґ M. Skiba, T. Zhuk, I. Kurmakova and O. Bondar, “A comprehensive study of grape pomace

extract and its active components as effective vapour phase corrosion inhibitor of mild steel", Int. J. Corros. Scale Inhib., vol. 7, no. 2, pp. 185–202, Jul. 2018. doi: 10.17675/2305-6894-2018-7-2-6.

[18] Z. Mohammadi and M. Rahsepar, "The use of green *Bistorta Officinalis* extract for effective inhibition of corrosion and scale formation problems in cooling water system", *J. Alloys Compd.*, vol. 770, pp. 669–678, Jan. 2019. doi: 10.1016/j.jallcom.2018.08.198.

[19] Z. Belarbi, B. Sotta, L. Makhloufi, B. Tribollet and J. Gamby, "Modelling of delay effect of calcium carbonate deposition kinetics on rotating disk electrode in the presence of green inhibitor", *Electrochim. Acta*, vol. 189, pp. 118–127, Jan. 2016. doi: 10.1016/j.electacta.2015.12.089.

[20] H. Cheap-Charpentier *et al.*, "Antiscalant properties of Spergularia rubra and Parietaria officinalis aqueous solutions", *J. Cryst. Growth*, vol. 443, pp. 43–49. Jun. 2016. doi: 10.1016/j.jcrysgro.2016.03.020.

[21] D. E. Abd-El-Khalek, B. A. Abd-El-Nabey, M. A. Abdel-kawi and S. R. Ramadan, "Investigation of a novel environmentally friendly inhibitor for calcium carbonate scaling in cooling water", *Desalination and Water Treat.*, vol. 57, no. 7, pp. 2870–2876, Feb. 2016. doi:10.1080/19443994.2014.987174.

[22] M. Chaussemier *et al.*, "State of art of natural inhibitors of calcium carbonate scaling. A review article", *Desalination,* vol. 356, pp. 47–55, Jan. 2015. doi: 10.1016/j.desal.2014.10.014.

[23] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, E. Khamis and D. E. Abd-El-Khalek, "A natural extract as scale and corrosion inhibitor for steel surface in brine solution", *Desalination*, vol. 278, no. 1–3, pp. 337–342, Sep. 2011. doi: 10.1016/j.desal.2011.05.048.

[24] C. Deslouis, D. Festy, O. Gil, G. Rius, S. Touzain and B. Tribollet, "Characterization of calcareous deposits in artificial sea water by impedance techniques – I. Deposit of $CaCO_3$ without $Mg(OH)_2$", *Electrochim. Acta*, vol. 43, no. 12–13, pp. 1891–1901, May 1998. doi: 10.1016/s0013-4686(97)00303-4.

[25] A. Neville, T. Hodgkiess and A. P. Morizot, "Electrochemical assessment of calcium carbonate deposition using a rotating disc electrode (RDE)", *J. Appl. Electrochem.*, vol. 29, pp. 455–462, Apr. 1999.

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ЕКСТРАКТИ ВІДХОДІВ ХАРЧОВОЇ ПРОМИСЛОВОСТІ ЯК ІНГІБІТОРИ НАКИПОУТВОРЕННЯ НА ПОВЕРХНІ МАЛОВУГЛЕЦЕВОЇ СТАЛІ У ВОДОПРОВІДНІЙ ВОДИ

Проблематика. У промислових процесах нагрівання серйозною проблемою є накипоутворення, особливо у випадку використання як теплоносія води природного походження. Втрати світової економіки через утворення накипу оцінюються в мільярди доларів на рік. Тому розробка ефективних інгібіторів накипоутворення є актуальною задачею. Перспективним джерелом екологічно чистих та дешевих інгібіторів утворення накипу можуть стати відходи харчової промисловості.

Мета дослідження. Випробувати як інгібітори утворення накипу на поверхні маловуглецевої сталі у водопровідній воді екстракти трьох побічних продуктів харчової промислові: шроту ріпаку, жому цукрового буряку та макухи з кормової редьки.

Методика реалізації. Досліджувані речовини додавали до води у вигляді етанольних екстрактів, які готували методом мацерації. Для вивчення процесу утворення накипу використовували електрохімічний підхід, суть якого полягає у реєстрації зміни величини струму відновлення кисню в часі в процесі зародження та росту шару карбонату кальцію на поверхні сталі в присутності екстрактів. Для оцінки ефективності інгібування визначали час накипоутворення, пористість та питому масу накипу. Хімічний склад екстрактів визначали методом газової хроматографії з масоселективним детектором шляхом масоселективного інтегрування.

Результати дослідження. Ефективними інгібіторами накипоутворення виявилися екстракти шроту ріпаку та екстракт макухи редьки в концентрації 10 мл/л. Екстракт жому цукрового буряку збільшує час кристалізації, але не впливає на кількість осаду накипу.

Висновки. Інгібування накипоутворення викликано головним чином утворенням адсорбованої плівки на зародках накипу, яка блокує поверхню і перешкоджає подальшому росту кристалів. Відходи харчової промисловості є перспективним джерелом інгібіторів накипу через їх низьку ціну та екологічну безпеку.

Ключові слова: інгібітори накипоутворення; маловуглецева сталь; зелений інгібітор; час накипоутворення.

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ЭКСТРАКТЫ ОТХОДОВ ПИЩЕВОЙ ПРОМЫШЛЕННОСТИ КАК ИНГИБИТОРЫ НАКИПЕОБРАЗОВАНИЯ НА ПОВЕРХНОСТИ МАЛОУГЛЕРОДИСТОЙ СТАЛИ В ВОДОПРОВОДНОЙ ВОДЕ

Проблематика. В промышленных процессах нагрева накипеобразование является существенной проблемой, особенно в случае использования в качестве теплоносителя воды природного происхождения. Потери мировой экономики из-за образования накипи оцениваются в миллиарды долларов в год. Поэтому разработка эффективных ингибиторов накипеобразования является актуальной задачей. Перспективным источником экологически чистых и дешевых ингибиторов образования накипи могут стать отходы пищевой промышленности.

Цель исследования. Испытать в качестве ингибиторов образования накипи на поверхности малоуглеродистой стали в водопроводной воде экстракты трех побочных продуктов пищевой промышленности: шрота рапса, жома сахарной свеклы и жмыха кормовой редьки.

Методика реализации. Исследуемые вещества добавляли к воде в виде этанольных экстрактов, которые готовили методом мацерации. Для изучения процесса образования накипи использовали электрохимический подход, суть которого заключается в регистрации изменения величины тока восстановления кислорода во времени в процессе зарождения и роста слоя карбоната кальция на поверхности стали в присутствии экстрактов. Для оценки эффективности ингибирования определяли время напипеобразования, пористость и удельную массу накипи. Химический состав экстрактов определяли методом газовой хроматографии с массоселективным детектором путем массоселективного интегрирования.

Результаты исследования. Эффективными ингибиторами накипеобразования оказались экстракты шрота рапса и жмыха редьки в концентрации 10 мл / л. Экстракт жома сахарной свеклы увеличивает время кристаллизации, однако не влияет на количество осадка накипи.

Выводы. Ингибирования накипеобразования вызвано, главным образом, образованием адсорбированной пленки органических веществ на зародышах накипи, которая блокирует поверхность и препятствует дальнейшему росту кристаллов. Отходы пищевой промышленности являются перспективным источником ингибиторов накипи вследствие их низкой цены и экологической безопасности.

Ключевые слова: ингибиторы накипеобразования; малоуглеродистая сталь; зеленый ингибитор; время накипеобразования.

Рекомендована Радою
хіміко-технологічного факультету
КПІ ім. Ігоря Сікорського

Надійшла до редакції
19 серпня 2021 року

Прийнята до публікації
7 грудня 2021 року