

Solvent Effect on Scale inhibition Performance of *Sargassum latifolium* in Industrial Water Systems

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Abstract: Scale deposition is a major concern in industry. In this work, phytochemicals extracted from *Sargassum latifolium* by two different solvents were investigated as eco-friendly antiscalants which can be considered alternative to synthesized antiscalants. *Sargassum* has high content of allginic acid, which has the ability to bind calcium ions. Aqueous (EE) and ethanol (AE) extracts of *Sargassum latifolium* were characterized by FT-IR and UV spectroscopy. Antiscaling performance of *Sargassum latifolium* was studied using chronoamperometry and electrochemical impedance spectroscopy. In addition, Scanning electron microscope was used to examine CaCO₃ crystals. The results showed that the efficiency of ethanol extract of *S. latifolium* is lower than aqueous extract however characterization data of the two extracts displayed that ethanol extract is rich in many functional groups than aqueous extract. In order to avoid the effect of ethanol, phytochemicals extracted by ethanol were dissolved in water (AEE) which duplicated their efficiency. Moreover, preserving these phytochemicals in solid form controls the biodegradation of the extract and prolongs its shelf time.

Keywords: Green scale inhibitor; natural extract, chronoamperometry, EIS, extraction methods.

1. Introduction

Scaling phenomenon is a major concern in many industries (Legrand & Leroy, 1990). It can cause numerous technical problems like partial obstruction of pipes followed by decrease in flow rate, reduced heat transfer, increase of energy consumption and clogging of membrane filters which can strongly affect desalination process (Horner et al., 2017). Commercial antiscalants including phosphonate and sulfonate formulations (Jafar Mazumder, 2020 ; Abd-El-Khalek & Abd-El-Nabey, 2013) which are often used to control scale deposition and may have harmful effect on the environment. These hazardous effects of most synthetic scale inhibitors are the motivation for developing new green products such as maleic acid, aspartic acid, and carboxylic acid – based

polymers (Zhou et al., 2021; Martinod et al., 2008; Martinod et al., 2009; Li et al., 2006; Amjad, 2012; Wang et al., 2015) and biodegradable biopolymers (Husna et al., 2021; Khamis et al., 2021). Because of the low cost, renewable nature, biodegradability and ease of application, several plant extracts have been used earlier as green scale inhibitors and for other water treatment applications (Verma et al., 2018, C. Bouyahia et al., 2022). Also, seaweed extracts were employed as inhibitor for scale deposition (Khamis et al., 2016; Khamis et al., 2020). Sargassum is important seaweed that is widely distributed in Mediterranean and red seas in Egypt. Sargassum species are used in many folk applications in human nutrition and are considered a rich source of vitamins, carotenoids, proteins, and minerals (Rushdi et al., 2020), more over Sargassum has high content of alginic acid (Shevchenko et al., 2007; Obluchinskaia, 2008; Manev et al., 2013), which has the ability to bind calcium ions. In fact, choice of the suitable solvents for extraction of plant (M. El batrioui, 2022) and seaweeds is very important for effective extraction. Previous studies reveal that water is the best solvent because of its simplicity, availability, non-hazardous nature, non-flammable, uniquely redox-stable, inexpensive properties (Sharghi 2009, Bose et al., 2003, Varma, 2016, Duan, 2015). However, some phytochemicals require organic solvents like ethanol and methanol to be extracted (Verma et al., 2018). Red and green seaweeds was extracted using methanol as solvent (Khamis et al., 2016) with scale inhibition efficiency reached 61.3 and 63 %, respectively, however environmental limitation of methanol. On other hand, the efficiency of aqueous extract of brown seaweeds (*Sargassum muticum*) as scale inhibitor were investigated which reached 80% (Khamis et al., 2020). Our work aims to investigate scale inhibition performance of the phytochemicals extracted from brown algae (*Sargassum latifolium*) in water and ethanol as a comparative study. Effect of extraction method on antiscaling properties of *S. latifolium* extract towards CaCO_3 formation was examined using chronoamperometry and electrochemical impedance spectroscopy.

2. Methodology

2.1. Materials:

Double distilled water and analytical reagent-grade NaCl, NaHCO_3 , Na_2SO_4 and CaCl_2 (Al-Gomhorya Chemicals CO., Egypt) were used for preparing solutions. Brown algae (*Sargassum latifolium*) were collected from Red sea (Hurdaga city, Egypt).

2.2. Preparation of *S. latifolium* extracts:

Sargassum latifolium algae were dried for two hours in oven at 70°C and grinding to powdery form. Stock solution of algae extract was obtained by the following methods:

a. Preparation of aqueous and ethanolic extracts of *S. latifolium* :

As shown in Figure 1, 5 g sample of the powder was refluxed in 100 mL ethanol and deionized water for one hour at 100°C to obtain ethanolic (EE) and aqueous (AE) extracts, respectively. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was expressed in terms of grams per liter. The extracts were protected from the light in an amber bottle and placed under refrigeration.

b. Preparation of aqueous solution of ethanolic extract of *S. latifolium* (AEE) :

In this method, Compounds of lower polarity was extracted by ethanol, then ethanolic extract of *S. latifolium* was dried to evaporate ethanol from the solution. Dried extract was solubilized in distilled water to prepare stock aqueous solution.



Figure 1. Flow chart representative of the extraction procedure for *S. latifolium*.

2.3. Characterization of extracts:

a. UV–Visible analysis :

The EE, AE, and AEE extracts of *S. latifolium* were characterized by UV–vis as basic analytical methods and to assessment if they are various mixtures of secondary metabolites; UV–Vis spectra were recorded by Thermo Evolution Array UV–Visible spectrophotometer VWR-1600PC in the range from 200 to 800 nm at room temperature. Distilled water and ethanol were used also as blank in the UV–vis spectroscopy.

b. FTIR analysis :

The chemical composition of the prepared extracts was studied by using FT-IR spectrometer (perkin-Elmer LS-55- Luminescence spectrometer). The solutions were dried and the dried powders were characterized in the range 4000–500 cm⁻¹ using KBr pellet method.

2.4. Electrochemical measurements for CaCO₃ Scaling:

The electrochemical measurements were carried out in a cell with three-electrode mode (Abd-El-Khalek & Abd-El-Nabey, 2013); platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was steel that had the following chemical composition (wt. %): C, 0.21; S, 0.04; Mn, 2.5; P, 0.04; Si, 0.35; balance Fe. Chronoamperometry and electrochemical impedance measurements were performed using Gamery instrument G300™ Potentiostat/ Galvanostat/ ZRA. Chronoamperometry curves were carried out by polarizing the steel electrode to –1 V (vs. SCE) for 3 h in brine solution in the absence and presence of prepared extracts. Thus, the current passing through the steel electrode, during calcareous deposits, is recorded with respect to time. EIS measurements were done after scale deposition process. The frequency range for EIS measurements was 0.1 to 1×10⁴ Hz with applied potential signal amplitude of 10 mV. All the measurements were done at 40.0 ± 0.1°C. To test the reliability and reproducibility of the measurements, triplicate experiments were performed in each case at the same conditions.

3.5. Microscopic Examination:

The morphology and crystal lattices of scale were observed with Scanning electron microscope, SEM, (JEOL-5300 Scanning microscope). Prior to SEM examination, scale crystals were sputter-coated with a thin film of gold under vacuum.

2. Results and discussion:

3.1.Characterization of extracts

UV–vis spectra

Figure 2 shows the UV–vis absorption spectra of *S. latifolium* seaweed extract by ethanol (EE) and water (AE). It can be observed that each extract contains quinones which are evidenced by absorption peak at 418 nm (Bunghez et al., 2013). Moreover, ethanolic extract characterized by phenolic acids and its derivatives (flavones, flavonols, phenylpropenes and quinones) at absorption range 220-280 nm and 330-420 nm, respectively(Bunghez et al., 2013). Also, ethanol extract was characterized by chlorophyll with absorption peak at 661 nm (Lai et al., 2008). On other hand, phenolic derivatives were detected in aqueous extract at absorption spectrum at 350nm. It is clear that different phytochemicals were obtained by using extraction solvents with slight polarity differences (Pontaza-Liconaa et al., 2019) where ethanol extract was rich in phenolic acids and chlorophyll (Figure 3).

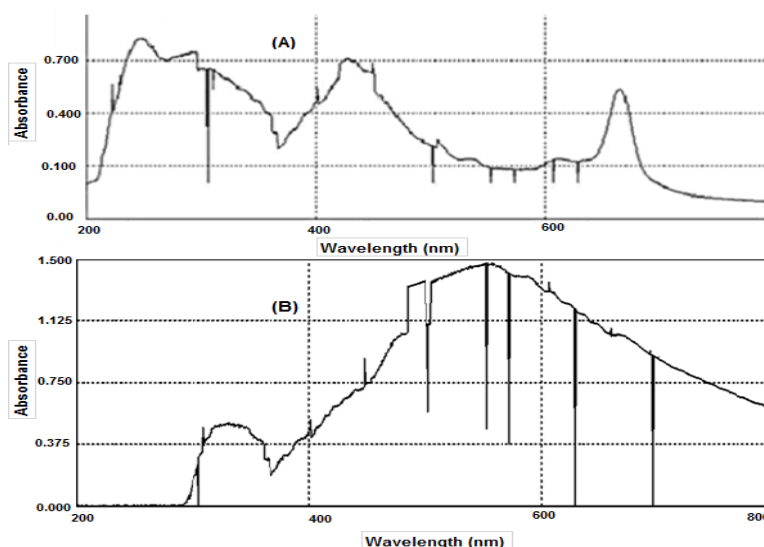


Figure 2. UV-Visible spectrum of *S. latifolium* extracts obtained with ethanol extract (A) and aqueous extract (B).

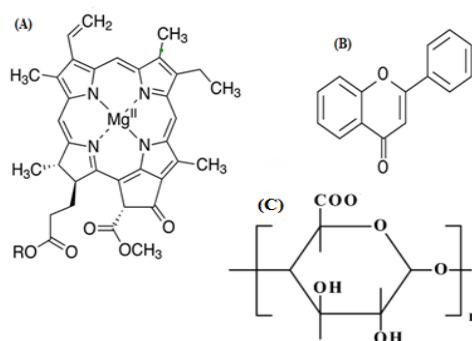


Figure 3. Structural data of chlorophylls (A) flavonoids (B) and alginate (C).

FT-IR analysis

An additional studies can be identification of specific chemical functional groups existing in the two extracts. Figure 4 shows FTIR spectra in the range 500 to 4000 cm^{-1} for extraction of *S. latifolium* using water and ethanol as solvents. As presented in Table 1, in both extracts, the bands observed in the studied range displayed five fingerprints around the following absorption regions: 3,400–3,500, 1,637, 1,500–1,400, 1,100–1300 cm^{-1} and 1000–1,100 cm^{-1} (Figure 4). The broadband in the first region is probably due to for O-H stretch and H-bonded of alcohol, phenols and carboxylic acids as found in alginates (Figure 3), pectin, cellulose, and lignin (Saeed et al., 2010). The band at 1637 cm^{-1} could be related to C=C stretching vibration of aromatic rings (Edison & Franca et al., 2014, Sethuraman, 2013, Nunes et al. 2016) and to the vibration of N-H of amines, C=O of amides and carboxylic groups Özcan et al., 2012, which could be related to flavonoids (Figure 3B) and amino acids, The vibration bands in the region of 1,500–1,400 cm^{-1} corresponds to stretching vibration of aromatic C=C. A vibration in the regions 1,100–1300 cm^{-1} , which is a result of C–O stretching (Hssaini et al., 2022, Vongsvivut et al., 2013). Finally, the vibrations in the regions 1000–1,100 cm^{-1} marks a very strong and sharp peak, which is probably assigned to C–OH group as well as the stretches C–C and C–O in the carbohydrate structure and C–O in the phenol.

On other hand, additional bands are observed in ethanol extract. These absorption bands include, a vibration around 1,387 and 1314 cm^{-1} that are most likely assigned to carbohydrates, fatty acids, or amino acids side chain (Vongsvivut et al., 2013), where the 1,314 cm^{-1} vibration is associated with CH_2 rocking (Schwanninger et al., 2004). Also, the absorbance at the region 3,000–2,800 cm^{-1} may be related to C-H stretching vibration of methyl and methoxy groups (Venkateswarlu et al., 2014, Vardin et al., 2008) and to stretching vibration of $-\text{CH}_3$ or $-\text{CH}_2$ groups in carboxylic acid (Hssaini et al., 2022).

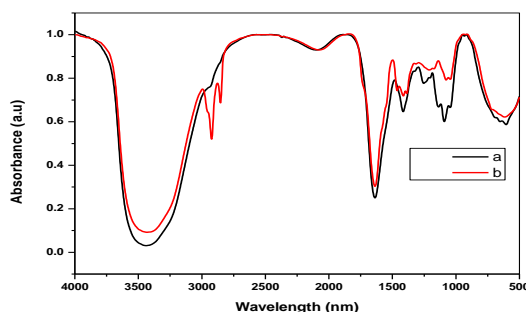


Figure 4. FT-IR analysis of *S. latifolium* extracts obtained with aqueous extract (a) and ethanol extract (b).

3.2. Evaluation of anti-scaling performance of *S. latifolium*

Figure 5 displayed the chronoamperometry curves of polarized steel in brine solution in the absence and presence of aqueous extract of *S. latifolium*. As seen, in the absence of the extract, the current density decreased linearly due to growth of calcium carbonate crystals that occupied steel surface. After growth stage, the current decreased slowly and reached to limited current at which steel surface was covered by insulating layer of calcite crystals and the recorded residual current was 73 μA . While, addition of aqueous and ethanolic extracts to the solution decreased the rate of crystal growth and the value of the residual current density increased to 101 and 88 μA due to absence of the insulating CaCO_3 scale layer. This results clarify that aqueous extract reduces scaling growth rate

than ethanolic extract however the high content of functional groups in ethanolic extract as illustrated in IR results.

Table 1. FTIR peak value of *S. latifolium* extracts.

Peak Value		Spectroscopic Assignments	Functional Groups
EE	AE		
3432.77	3439.74	H-bonded, O–H stretch	Alcohols, Phenols
2923.38	--	C–H stretch	Alkanes
2853.65	--	ν C-H stretch	Alkanes
2076.51	2101.23	C \equiv C stretch	Alkynes
1637.31	1637.46	C–C stretch or C=O of carboxylic group or C=C and C=N stretch	Aromatics
1462.82 1414.04	1415.43	C=C stretch	aromatic
1387.28 1314.77	--	C–C stretch	in-ring
1209.93 1173.02	1253.80 1136.29	C-O	acyl and phenol stretch
1077.45 1044.48	1091.81 1045.01	C-C stretching; C-O	alcohol or alkoxy groups; (C-O) related to carbohydrates and polysaccharides

Chronoamperometry curves in figure 6 support this behavior where increasing the concentration of ethanolic extract to 350 ppm increasing scaling growth rate and consequently decreased the residual current to 61.3 μ A compared with 100 ppm of the extract. While increasing the concentration of aqueous extract increased the residual current to 123 μ A. In fact, Alcohol has been proposed to increase the SI upon addition (Chen et al., 2006) and accelerate the supersaturation in the solution and increase CaCO_3 precipitation rate (Chen et al., 2006; Sand et al., 2012). The significant increase in the precipitation rate was explained by (Konopacka-lyskawa et al., 2020), where the rate of nucleation depends mainly on supersaturation, crystal surface energy and temperature. The presence of alcohol as extract solvent increased supersaturation by reducing the solubility of calcium carbonate and reducing the surface energy of the formed crystals. Figure 7 displayed SEM images of CaCO_3 crystals after direct precipitation. As seen, normal rhomboidal cubic calcium carbonate crystals are observed in the absence of *S. latifolium* extracts and no notable crystals modification was observed in presence of aqueous extract. On other hand, presence of ethanolic extract of the algae modifies the cubic shape of CaCO_3 crystals into spherical -grained morphologies. It is reported that presence of ethanol as an additive in an aqueous solution during a CaCO_3 precipitation process, stabilizes vaterite type of CaCO_3 crystals (Manoli and Dalas, 2000 ; Seo et al., 2005). It was proposed that during the incubation period, the interaction of organic solvent with the surface of the vaterite

and calcite played a major role, and slowed down the transformation of vaterite into calcite (Konopacka-lyskawa et al. ,2020)

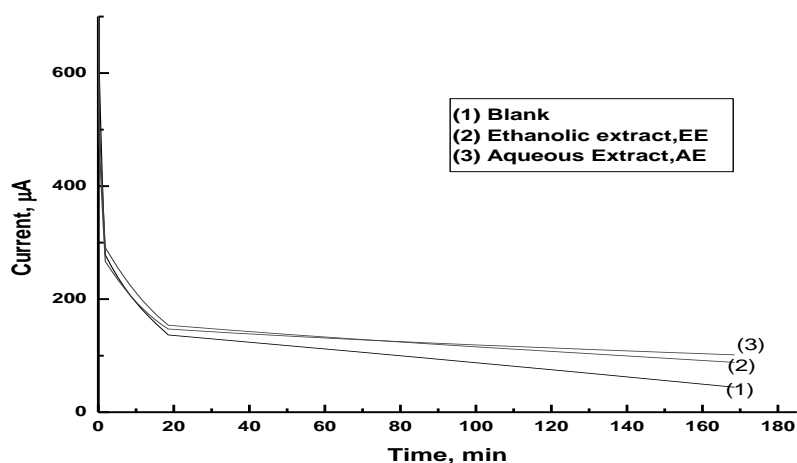


Figure 5. Chronoamperometry curves for polarized steel electrode in CaCl_2 brine solution in the absence and presence of different concentrations of *S. latifolium* at -1 V vs SCE and 40°C .

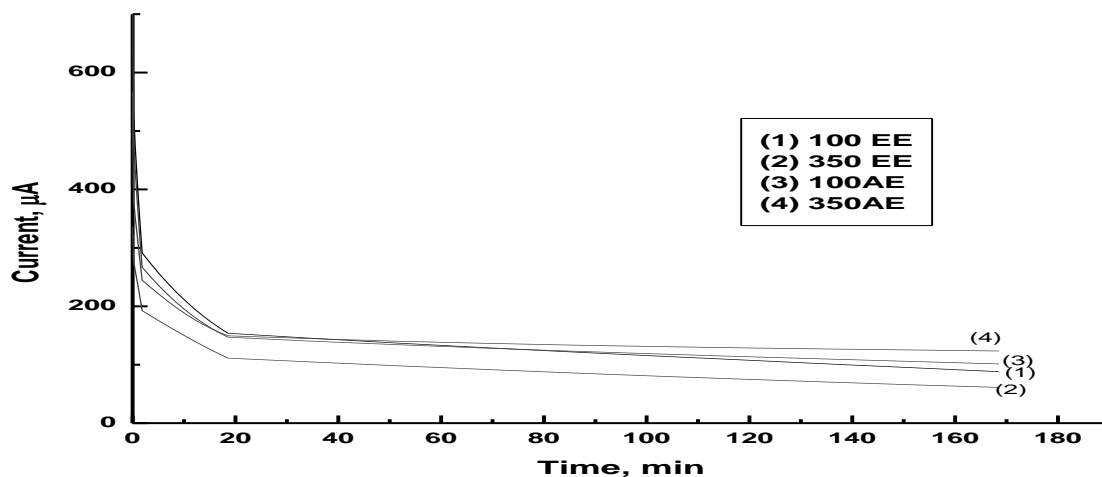
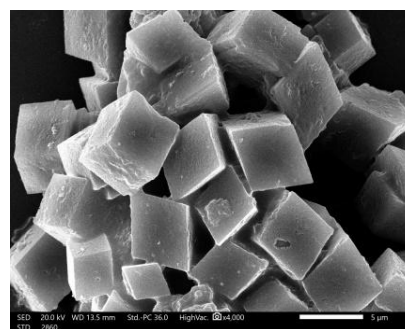
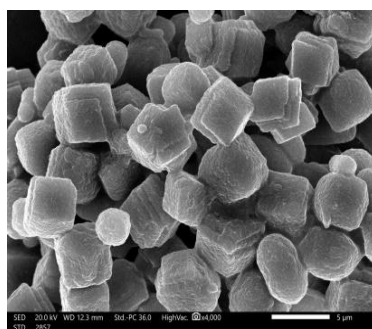
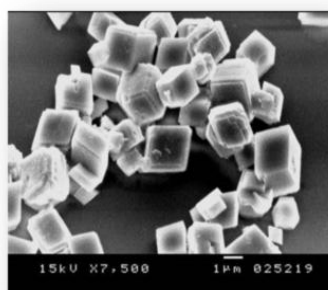


Figure 6. Chronoamperometry curves for polarized steel electrode in CaCl_2 brine solution in presence of different concentrations of ethanolic (EE) and aqueous (AE) extracts of *S. latifolium* at -1 V vs SCE and 40°C .



Blank

Ethanolic extract

Water extract

Figure 7. SEM images of CaCO_3 crystals in the absence, and in presence of ethanolic or aqueous extracts.

Impedance spectroscopy:

Impedance technique will be used to improve the understanding of the electrochemical scaling process and determine the efficiency of different extracts of *S. latifolium*. In this section, the efficiency of aqueous solution of the ethanolic extract (AEE) is discussed compared with aqueous and ethanolic extracts of the algae.

Figure 8 represents Nyquist plots for steel after cathodic polarization in brine solution in the absence and presence of different extracts of *S. latifolium*. The figure displayed the typical feature of depressed semi-circles of impedance spectra which their sizes decrease according to the following order; Blank > EE > AE > AEE. This order displayed that presence of low polarity phytochemicals extracted by ethanol (EEA) highly reduced the insulation caused by CaCO_3 layer where the size of the semi-circles of impedance spectrum is directly proportional with amount and compactness of CaCO_3 scale formed on the steel surface.

The equivalent circuit that used to fit the experimental data of impedance curves after scale formation processes in brine solution was illustrated in Figure 9.

Table 2 shows Computer fit results of the impedance spectra obtained for the steel electrode in brine solution containing 100 ppm of *S. latifolium* extract using different methods of extraction. The percentage of scale inhibition could be determined from the following equation (Abdel-Gaber et al., 2008):

$$\% \text{ Scale Inhibition } (\%Is) = \frac{[(R_{ct})_o - (R_{ct})_i]}{(R_{ct})_o} \times 100 \quad (1)$$

where $(R_{ct})_o$ and $(R_{ct})_i$ are charge transfer resistances after polarizing the steel electrode at -1 V (vs. SCE) in scaling environment for 3 h in the absence and the presence of the scale inhibitor, respectively. The results indicated that the presence of the extracts decreases the charge transfer resistance R_{ct} , which is directly proportional to the formation of scale. Also, presence of the aqueous extract increased the non-ideal film capacitance values, Q , due to the formation of the double layer which reduce the formation of the insulating layer on the metal surface (Khamis et al., 2016). While presence of ethanolic extract decreases the non-ideal film capacitance as a result of an increase in the thickness of the electrical double layer associated to presence of alcohol molecules which increase charge density near metal surface. Also, the table illustrated that aqueous extract (AE) of *S. latifolium* is more efficient than ethanolic extract (AE) and the percent of scale inhibition ($\%Is$) was duplicated in presence of aqueous solution of lower polarity phytochemicals that extracted by ethanol (AEE). These phytochemicals contain some compounds with carboxylic or hydroxyl groups which might be involved in the inhibition mechanism (Horner et al., 2017).

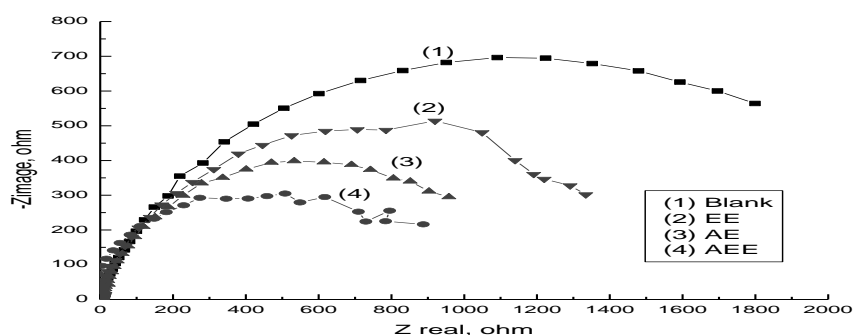


Figure 8. Impedance spectra of polarized steel in brine solution in the absence and the presence of 100 ppm of *S. latifolium* extracts after 3 hours at 40 °C.

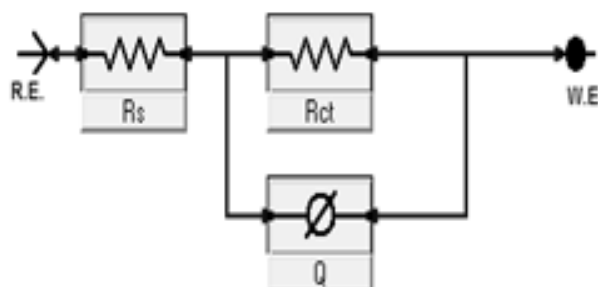


Figure 9. Schematic for the equivalent circuit models used to determine the impedance parameters for scale process in the CaCl_2 brine solution . (R_s : the solution resistance, R_{ct} : the charge transfer resistance. Q : is associated to the double-layer capacitance).

Table 2: Computer fit results of the impedance spectra obtained for the steel electrode that was cathodically polarized in CaCl_2 brine solution containing 100 ppm of *S. latifolium* extracts after 3 hours

Antiscalant	Conc., ppm	R_s ohm.cm ²	Q μF	n	R_{ct} Ohm.cm ²	% I_s
Stage 1	0	0.07 ± 0.04	230.7 ± 1.13	0.75	2147 ± 26.0	-----
	AE	048 ± 0.026	525 ± 1.2	0.76	1198 ± 13.1	44.2 %
	EE	6.13 ± 0.05	96.3 ± 0.56	0.80	1480 ± 12.5	30.9 %
Stage 2	EEW	0.11 ± 0.02	382.4 ± 2.7	0.90	756.8 ± 16.8	64.7 %

Conclusion

In this study, the antiscaling properties of *Sargassum latifolium* extract were investigated using different extraction methods. FT-IR and UV spectra revealed that ethanol extract of *S. latifolium* contains more functional groups than aqueous extract, however scale inhibition performance of the aqueous extract is the best. To avoid the effect of ethanol which act as accelerator for CaCO_3 precipitation, aqueous solution of low polarity phytochemicals that extracted by ethanol were prepared. This method of extraction duplicates the efficiency of the extract. The ethanolic extract of *S. latifolium* may contain some compounds with carboxylic or hydroxyl groups which might be involved in the inhibition mechanism. It can be concluded that better inhibition efficiency towards CaCO_3 precipitation was achieved by low polar phytochemicals extracted by ethanol compared to that extracted in aqueous solution. Ethanolic extract of *Sargassum latifolium* can be considered as acceptable inhibitor for scale formation in industrial purpose especially in food factories and desalination processes where the use of non-toxic inhibitors is an important issue. Moreover, preserving the phytochemicals extracted by ethanol in solid form can control the biodegradation of the extract and prolongs its shelf time.

References

- Abdel-Gaber, A. M., Abd-El-Nabey, B. A., Khamis, E. & Abd-El-Khalek, D. E. (2008). Investigation of fig leaf extract as a novel environmentally friendly antiscalent for CaCO₃ calcareous deposits. *Desalination*, 230 (1–3), 314–328.
- Abd-El-Khalek, D. E. & Abd-El-Nabey, B. A. (2013). Evaluation of sodium hexametaphosphate as scale and corrosion inhibitor in cooling water using electrochemical techniques. *Desalination*, 311, 227–233.
- Amjad Z. (2012). Investigations on the evaluation of polymeric calcium sulfate dihydrate (gypsum) scale inhibitors in the presence of phosphonates. *Desalin. Water Treat*, 37 (1–3), 268–276.
- Ay Ç., Özcan A., Erdogan Y., Özcan A., (2012) Characterization of Punica granatum L. peels and quantitatively determination of its biosorption behavior towards lead(II) ions and Acid Blue 40", *Colloids and Surfaces B: Biointerfaces*, 100, 197–204.
- Bose D.S., Fatima L., Mereyala H.B. (2003) Green chemistry approaches to the synthesis of 5-alkoxycarbonyl-4-aryl-3, 4-dihydropyrimidin-2 (1 H)-ones by a three-component coupling of one pot condensation reaction: comparison of ethanol, water, and solvent-free conditions, *J. Organomet. Chem.* 68 587–590.
- Bouyahia C., Slaoui M., Al D. AL-Sharabi H., EL Bakraoui H., El Hajjaji S. (2022) Sawdust Essential Oil of Cedrus Atlantica as Eco-Friendly inhibitor against mild steel corrosion in 1M HCl solution, *Mor. J. Chem.* 10(4) 738-751.
- Bunghez F., Socaciu C., Zagrean F., Maria Pop R., Ranga F., Romanciuc F. (2013), Characterisation of an Aromatic Plant-based Formula using UV-Vis Spectroscopy, LC–ESI(+)QTOF-MS and HPLC-DAD Analysis, *Bulletin UASVM Food Science and Technology*, 70(1), 16-24
- Chen, S. F., Yu, S. H., Jiang, J., Li, F. Q., & Liu, Y. K. (2006). Polymorph discrimination of CaCO₃ mineral in an ethanol/water solution: Formation of complex vaterite superstructures and aragonite rods. *Chem. Mater.*, 18, 115–122.
- Duan H., Wang D., Li Y., (2015) Green chemistry for nanoparticle synthesis, *Chem. Soc. Rev.* 44, 5778–5792.
- Edison T., Sethuraman M., (2013), Biogenic robust synthesis of silver nanoparticles using Punica granatum peel and its application as a green catalyst for the reduction of an anthropogenic pollutant 4-nitrophenol, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 104, 262–264.
- El bastrioui M., Haboubi K., Chetouani A., Hammouti B., Nandiyanto A. B. D. (2022), Phytochemical study of four leaves extracts of Chamærops humilis L. from the region of Al-Hoceima, Morocco, *Mor. J. Chem.* 10 (4) 851-860.
- Franca J., Deluca M., Ribeiro T. (2014), Propolis - based chitosan varnish: drug delivery, controlled release and antimicrobial activity against oral pathogen bacteria", *BMC Complementary and*

Alternative Medicine, 14:4781-11.

Horner, O., Cheap-Charpentier, H., Cachet, X., Perrot, H., Lédion, J., Gelus, D., & Pécou, N., (2017). Antiscalant properties of *Herniaria glabra* aqueous solution. *Desalination*, 409, 157–162.

Hssaini L., Razouk R. and Bouslihim Y. (2022), Rapid Prediction of Fig Phenolic Acids and Flavonoids Using Mid-Infrared Spectroscopy Combined With Partial Least Square Regression, *Frontiers in Plant Science*, 13, Article 782159.

Husna, U. Z., Elraies, K. A., Shuhili, J. A. B. M., & Elryes, A. A. (2021). A review: the utilization potency of biopolymer as an eco-friendly scale inhibitors. *J. Pet. Explor. Prod. Technol.*, <https://doi.org/10.1007/s13202-021-01370-4>

Jafar Mazumder, M. A. (2020). A review of green scale inhibitors: Process, types, mechanism and properties. *Coatings*, 10 (10), 1–29.

Konopacka-Łyskawa, D., Czaplicka, N., Łapiński, M., Kościelska, B., & Bray, R. (2020). Precipitation and transformation of vaterite calcium carbonate in the presence of some organic solvents. *Materials (Basel)*, 13 (12), 1–14.

Lai W. H., Su Y. H., Teoh L. G. & Hon M. H. (2008), Commercial and natural dyes as photosensitizers for a water-based dye-sensitized solar cell loaded with gold nanoparticles, *J. Photochem. Photobiol.*, A (195), 307.

Legrand, L., & Leroy, P. (1990). Prevention of Corrosion and Scaling in Water Supply Systems (Ellis Horwood Series in Water and Wastewater Technology), Prevention.; New York: Ellis Horwood Ltd.

Li H. Y., Ma, W., Wang, L., Liu, R., Wei, L. S., Wang, Q. (2006). Inhibition of calcium and magnesium-containing scale by a new antiscalant polymer in laboratory tests and a field trial. *Desalination*, 196 (1–3), 237–247.

Manev, Z., Iliev, A., & Vachkova, V., (2013). Chemical characterization of brown seaweed - *Cystoseira barbata*. *Bulg. J. Agric. Sci.*, 19 (SUPPL. 1), 12–15.

Manoli, F. & Dalas, E. (2000). Spontaneous precipitation of calcium carbonate in the presence of ethanol, isopropanol and diethylene glycol. *J. Cryst. Growth*, 218 (2), 359–364.

Martinod A., Neville, A., Euvrad, M. & Sorbie, K. (2009). Electrodeposition of a calcareous layer: Effects of green inhibitors. *Chem. Eng. Sci.*, 64 (10), 2413–2421.

Martinod A., Euvrad M., Foissy, A., & Neville, A. (2008). Progressing the understanding of chemical inhibition of mineral scale by green inhibitors. *Desalination*, 220 (1–3), 345–352.

Nunes R., Maurício O., Mancini C., Cabral F., de Oliveira S., Marques T., Brid P., Rossana Q., Mara da Silva Moreira, Garrett Th., McGuinness B.(2016), FTIR analysis and quantification of phenols and flavonoids of five commercially available plants extracts used in wound healing, *Matéria (Rio J.)* 21 (03), 767-779.

Obluchinskaia ED. (2008). Comparative chemical composition of the Barents Sea brown algae. *Prikl*

Biokhim Mikrobiol., 44(3), 337–42.

Pontaza-Liconaa Y. S., Ramos-Jacquesb A.L., Cervantes-Chavezc J.A., Luis Lopez-Mirandad J., Alvaro de Jesus Ruiz-Baltazare, Maya-Cornejod J., Rodriguez-Moralesd A. L., Esparzad, M Estevezd R., Perezf R., Hernandez-Martinezd A.R. (2019), Alcoholic extracts from *Paulownia tomentosa* leaves for silver nanoparticles Synthesis, *Results in Physics* 12 ,1670–1679.

Rushdi, M. I., Abdel-Rahman, I. A. M., Saber, H., Attia, E. Z., Abdelraheem, W. M., Madkour, H. A. & Hassan, H. M. (2020). Pharmacological and natural products diversity of the brown algae genus: *Sargassum*. *RSC Adv.*, 10 (42), 24951–24972.

Saeed, A., Sharif, M., & Iqbal, M. (2010). Application potential of grapefruit peel as dye sorbent : Kinetics , equilibrium and mechanism of crystal violet adsorption. *J. Hazard. Mater.*, 179 (1–3), 564–572; Elsevier B.V.

Sand, K. K., Rodriguez-Blanco, J. D., Makovicky, E., & Benning, L. G. (2012). Crystallization of CaCO_3 in Water–Alcohol Mixtures: Spherulitic Growth, Polymorph Stabilization, and Morphology Change, *Cryst. Growth Des.*, 12, 842–853.

Schwanninger M., Rodrigues J. C., Pereira H. and Hinterstoisser B. (2004), Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib. Spectrosc.* 36, 23–40. doi: 10.1016/j.vibspec.2004.02.003.

Seo, K. S., Han, C., Wee, J. H., Park, J. K., & Ahn, J. W. (2005). Synthesis of calcium carbonate in a pure ethanol and aqueous ethanol solution as the solvent. *J. Cryst. Growth*, 276 (3–4), 680–687.

Sharghi H., Khalifeh R., Doroodmand M.M. (2009), Copper nanoparticles on charcoal for multicomponent catalytic synthesis of 1, 2, 3-triazole derivatives from benzyl halides or alkyl halides, terminal alkynes and sodium Azide in water as a “green” solvent, *Adv. Synth. Catal.* 351, 207–218.

Shevchenko, N. M., Anastyuk, S. D., Gerasimenko, N. I., Dmitrenok, P. S., Isakov, V. V., & Zvyagintseva, T. N. (2007). Polysaccharide and lipid composition of the brown seaweed *Laminaria gurganovae*. *Russ. J. Bioorganic Chem.*, 33 (1), 88–98.

Vardin H., Tay A., Ozen B., Mauer L. (2008), Authentication of pomegranate juice concentrate using FTIR spectroscopy and chemometrics, *Food Chemistry*, 108(2), 742-748.

Varma R.S. (2016), Greener and sustainable trends in synthesis of organics and nanomaterials, ACS publications, *ACS Sustain. Chem. Eng.*, 4, 5866–5878.

Venkateswarlu S., Kumar B., Prathima B., (2014), A novel green synthesis of Fe_3O_4 magnetic nanorods using *Punica granatum* rind extract and its application for removal of Pb(II) from aqueous environment, *Arabian Journal of Chemistry*, 1-9,.

Verma, C., Ebenso, E. E., Bahadur, I., & Quraishi, M. A. (2018). An overview on plant extracts as

environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media. *J. Mol. Liq.*, 266, 577–590; Elsevier B.V. Retrieved from <https://doi.org/10.1016/j.molliq.2018.06.110>

Vongsvivut J., Heraud P., Gupta A., Puri M., McNaughton D., and Barrow C. J. (2013) , FTIR microspectroscopy for rapid screening and monitoring of polyunsaturated fatty acid production in commercially valuable marine yeasts and protists. *Analyst*, 138, 6016–6031. doi: 10.1039/c3an00485f.

Wang, H., Liu, G., Huang, J., Zhou, Y., Yao, Q., Ma, S., & Cao, K. (2015). Performance of an environmentally friendly anti-scalant in CaSO₄ scale inhibition. *Desalin. Water Treat.*, 53 (1), 8–14.

Zhou, Y., Wang, J., Fang, Y. (2021), Green and high effective scale inhibitor based on ring-opening graft modification of polyaspartic acid. *Catalysts* , 11 (7), 1-9.

(2023) ; <https://revues.imist.ma/index.php/morjchem/index>