OPEN ACCESS Journal of Environmental Science and Technology

ISSN 1994-7887
DOI: 10.3923/jest.2018.

Research Article
Effect of Fungal Glycolipids Produced by a Mixture of Sunflower Oil Cake and Pineapple Waste as Green Corrosion Inhibitors

[1]Amr Al-Kashef, [2]Samy Shaban, [1]Mohamed Nooman and [1]Mona Rashad

[1]Department of Biochemistry, Division of Genetic Engineering and Biotechnology, National Research Centre, 12622 Cairo, Egypt
[2]Department of Petrochemicals, Egyptian Petroleum Research Institute (EPRI), Cairo11727, Egypt

Abstract

Background and Objective: Agro-industrial wastes are one of the major environmental pollutants, in addition to steel corrosions, which is also an economic depleting problem for the steel industries. This work aimed mainly to produce fungal glycolipids (GLs) derived from the microbial conversion of sunflower oil cake and pineapple waste mixture as economic substrates and to evaluate their effectiveness as green corrosion inhibitors. **Materials and Methods:** Production was carried out by *Rhizopus oryzae* and *Fusarium oxysporum* under Solid State Fermentation (SSF) technique while, extraction of GLs achieved using methanol followed by re-extraction with a mixture of chloroform, methanol and water resulted in four glycolipid (GL) extracts. The produced GLs structure was proved by Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (NMR). Glycolipid extracts were evaluated as green corrosion inhibitors against steel corrosion at three different temperatures using weight loss method. **Results:** The four extracts showed good inhibition efficiency specially with increasing temperature as an indication for the chemical adsorption. The re-extracted GL from *R. oryzae* gave the highest level of corrosion inhibition at all the examined temperatures. The inhibition efficiency was confirmed electrically using two additional techniques; polarization and impedance spectroscopy. The four GL extracts exhibited good antimicrobial efficiency against the tested bio-corrosion bacterial strains. **Conclusion:** The obtained extracts had the ability to prevent corrosion in acidic media and inhibit the growths of the investigated bacteria responsible for the biocorrosion, thus opening up new potential applications in food, petroleum and steel industries.

Key words: Fungal glycolipids, agro industrial wastes, sunflower oil cake, pineapple waste, green corrosion inhibitor

Citation: Amr Al-Kashef, Samy Shaban, Mohamed Nooman and Mona Rashad, 2018. Effect of fungal glycolipids produced by a mixture of sunflower oil cake and pineapple waste as green corrosion inhibitors. J. Environ. Sci. Technol., CC: CC-CC.

Corresponding Author: Mohamed Nooman, Department of Biochemistry, Division of Genetic Engineering and Biotechnology Research, National Research Centre, Dokki, Cairo, Egypt Tel: +201223509897

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Biosurfactants are groups of amphiphilic compounds that reduce the energy of the liquid/liquid, liquid/solid or liquid/air immiscible systems, by replacing the high energy molecules at the contact surface[1]. They can be classified into glycolipids, lipopeptides and phospholipids. Glycolipids (GLs) are one of the most important classes of these compounds, which include sophorolipids, rhamnolipids and trehalolipids[2]. These natural surfactants have many advantages over chemical ones, such as low toxicity, biodegradability and ecological harmony. These compounds might also be used at extreme salt concentrations, temperature and acidic environments. However, they can be produced from economic, renewable resources[3].

Biosurfactants worldwide production was about USD 1,735.5 million in 2011 and expected to reach USD 2,210.5 million by 2018, with a rate of 3.5% annual growth[4]. Despite of these facts, the relatively high production costs, biosurfactants have not yet been employed properly in the industry[5]. This is particularly due to the high cost of the raw materials which accounts about 50% of the product final cost[6]. Thus, substrates from renewable sources, such as agro industrial wastes might be a reasonable solution. Pineapple waste, as an agro-industrial residue, accounts about 50% of the total fruit weight, also oil cakes which are derived from the industry of edible oils and fats generate a huge amount of waste. Both wastes represent a good source for bioconversion and production of bioactive materials due to their high contents of crude fiber and sugars[7].

Particularly, sunflower oil cake has been used previously for the production of GLs (sophorolipids) by *Candida bombicola*. However, many efforts have been reported to produce different types of GLs by utilizing agro-industrial residues in addition to maximize the production yield using different extraction techniques[5,8,9].

Since bacterial biosurfactants are well explored, fewer fungi are known to produce biosurfactants especially filamentous fungi as *Rhizopus* and *Fusarium* sp.[10-13]. However, to author's knowledge, no reports were published for their cultivation to produce biosurfactants using SSF technique which is generally preferable due to its high and concentrated productivity[14]. Microbial surfactants have several industrial, biotechnological and environmental applications[15-17]. However, very few studies have been devoted to biosurfactants considered as potential inhibitors for the steel corrosion[18].

Corrosion is the deterioration of a metal, as a result of chemical or electrochemical reactions at the metal/solution interface. It can be found where the metals are exposed to an unsuitable environment such as aqueous solutions, organic solvents, liquid and solid metals, alkaline, acids, gases and biofilms (metabolites) released by environmental attached bacteria. The corrosion caused by microorganisms is called biocorrosion[19]. The electrochemical process in nature is the most common and consists of oxidation-reduction irreversible reactions in many industries[20].

For the prevention of biocorrosion, different methods were applied, including physical processes, biocides, protective coatings and corrosion inhibitors. These methods commonly used combined to decrease or terminate the metal biocorrosion. Among bacterial species associated with biocorrosion, sulfate reducing bacteria (SRB) is the major source of biocorrosion, since it produces H_2S which is toxic and reactive corrosive agent[21-23].

Based on the above, agro-industrial wastes are real hazards to the environment, corrosion of steel is also an environmentally harmful factor and a waste of natural resources. To overcome these problems, this work was directed to produce fungal GLs using sunflower oil cake and pineapple waste mixture as economic substrates and examine their potential role as a green corrosion inhibitor.

MATERIALS AND METHODS

Microorganisms: *Rhizopus oryzae* ATCC 4858 and *Fusarium oxysporum* CCM F-358 were Obtained from Microbiological Resources Centre (MIRCEN), Faculty of Agriculture, Ain Shams University, Cairo, Egypt. *Desulfomonas pigra* (SRB) ATCC 29089; *Escherichia coli* ATCC 11775; *Pseudomonas aeruginosa* ATCC10145; *Aspergillus flavus* Link were obtained from Microbiology unit, Micro Analytical Center, Faculty of Science, Cairo University, Cairo, Egypt.

Fermentation substrates: Pineapple waste is a by-product of the pineapple processing industry and consists of the residual pulp, peels, skin, core and crown. It was provided from Juice extraction shops located in Cairo, Egypt, then collected freshly, sliced, crushed in a mixer and stored at -4°C till used.

Sunflower seeds (Giza 1) were obtained from the local market (Cairo, Egypt). The seeds were pressed with laboratory-type Carver hydraulic press under 10.000 lb^{-2} in pressure for 1 h at room temperature according to Ustun *et al.*[24] then the sunflower oil cake residue was collected, frozen and kept at -4°C until analysis. Crude soybean oil was obtained from the Food Technology Research Institute, Soy Processing Center, Agriculture Research Center, Giza, Egypt. All chemicals and reagents used were of analytical grade.

Inoculum preparation: *Rhizopus oryzae* and *Fusarium oxysporum* were inoculated on Potato Dextrose Agar (PDA) plates at 28-30°C and 1 mL of *Fusarium oxysporum* spore suspension in sterilized water (10^7 spores mL^{-1}) prepared for 7 days old plate was inoculated on the solid fermentation medium. While an inoculum of *Rhizopus oryzae* was prepared by making hyphal cubes (1 cm^3) and each cube was used to inoculate the same medium.

Fermentation medium: The SSF medium was prepared as follows: 1 mL of *Fusarium oxysporum* spore suspension (10^7 spores mL^{-1}) or hyphal cubes (1 cm^3) inoculum of *Rhizopus oryzae* were transferred to an Erlenmeyer flask (250 mL) containing a mixture of 7.5 g of sunflower oil cake, 7.5 g pineapple waste, 5 g of soybean oil, 10 mL of distilled water and 2 mL of nutrients[15] consisting of (g L^{-1}) NH_4NO_3 1.0; K_2HPO_4, 2.55; NaH_2PO_4, 0.15; $MgSO_4.7H_2O$, 0.5; $CaCl_2.2H_2O$, 0.1; $MnSO_4.H_2O$, 0.02; peptone, 1.0 to a final pH 7.8. Then, the cultures were grown for 14 days in a static incubator at 28-30°C.

Extraction of GLs

Extraction of GLs by methanol: The crude GL was isolated according to a modified method of Ohno *et al.*[25]. The cultures were ground in a blender, then 100 mL of methanol was added to one volume of the solid media and the mixture was shaken at 95 strokes min^{-1} for 60 min with a reciprocal shaker (New Brunswick Scientific, USA). The crude extract was then filtered through Whatman No. 2 filter paper. The methanol was evaporated by a rotary evaporator (BUCHI-ROTAVAPOR-R 110) to obtain the first extracts, *Fusarium* methanol extract (F 1) and *Rhizopus* methanol extract (R 1).

Re-extraction of GLs by solvent mixture: Re-extracting was carried out according to a modification of Rashad *et al.*[9]. The residual cultures remained after isolation of F 1 and R 1 were mixed with 100 mL mixture of chloroform, methanol and H_2O (65:15:20 mL, respectively) and shaking at 95 strokes min^{-1} for 60 min with a reciprocal shaker then filtered through Whatman No. 2 filter paper. Finally, the solvents were evaporated by the rotary evaporator to obtain the second extracts of Fusarium solvents mixture extract (F 2) and *Rhizopus* solvents mixture extract (R 2).

Characterization of GLs

Fourier transform infrared spectroscopy (FTIR): The infrared (IR) spectrum (from 400-4000 wave numbers, cm^{-1}) of GL extracts was recorded using a KBr pellet in Nicolet Impact 6100 FTIR spectrophotometer JASCO, USA.

Nuclear magnetic resonance spectra analysis (NMR): The NMR spectra have been recorded on a Varian Mercury VX-300 NMR spectrometer. The ^1H spectra were run at 300 MHz in deuterated chloroform ($CDCl_3$). Chemical shifts are quoted in δ and were related to those of the solvents.

Surface tension measurements (γ): The surface tension of the prepared extracts (F1, R1, F2 and R2) at three different temperatures 25, 40 and 60°C was measured using tensiometer-K6 Processor using the ring method (KrÜss Company, Germany). The critical micelle concentrations (CMC) were determined from the break point in surface tension (γ) versus the logarithm of concentrations (log c) plots of the prepared GL extracts. The effectiveness (π_{CMC}) represents the difference in the surface tension values of blank water (γ_o) and at critical micelle concentration (γ_{CMC}) was calculated utilizing Eq. 1 [26]:

$$\pi_{CMC} = \gamma_o - \gamma_{CMC} \quad (1)$$

The efficiency (C_{20}) is the concentration of the biosurfactant required to suppress the surface tension by 20 dyne cm^{-1} (mN m^{-1}).

The maximum surface excess (Γ_{max}) expressed as the concentration of the prepared biosurfactant compounds at interface per unit area and calculated utilizing Gibb's adsorption Eq. 2 [27]:

$$\Gamma_{max} = \left(\frac{1}{2.303\ RT}\right)\left(\frac{\delta\gamma}{\delta \log c}\right)T \quad (2)$$

where, R is the gas constant, $\delta\gamma/\delta$ log c is the surface pressure (slope at the premicellar region of surface tension-concentration curve) and T is the absolute temperature.

The average area (in square angstrom) occupied by each biosurfactant adsorbed at the system interface is known by the minimum surface area (A_{min}). It calculated at 25, 40 and 60°C utilizing Gibb's adsorption equation (Eq. 3), where N is Avogadro's number [28]:

$$A_{min} = \frac{10^{16}}{\Gamma_{max} N} \quad (3)$$

Corrosion measurements: The corrosion of carbon steel in the acidic solution (1.0 M HCl) has been monitored by various techniques in the presence of the prepared GL extracts. These techniques were weight loss and electrochemical measurements.

Weight loss technique: The steel coupons with a dimension of (2×6×0.3 cm) were applied to the weight loss method. Different concentration of the inhibited solution were prepared (100, 300, 500 and 700 ppm). The procedures are discussed briefly by Shaban[29]. The corrosion inhibition efficiency (η_w) and surface coverage (θ) of the prepared GL extracts have been obtained using the Eq. 4:

$$\eta_w = \theta \times 100 = \left(\frac{K^o - K}{K^o}\right) \times 100 \quad (4)$$

$$K = \frac{W}{St} \quad (5)$$

where, K^o and K are the corrosion rate of the carbon steel per unit area in the absence and presence of the prepared 4 extracts at an immersion time (t). The w and S in Eq. 5 represents the coupon weight loss and its area.

Electrochemical methodologies: The corrosion rate of the tested carbon steel in the absence and presence of the prepared GL extract (R2) was measured electrically at 25°C as an example using Voltalab 40 potentiostat PGZ 301. The working electrode was treated as mentioned previously in the weight loss method before each experiment.

Tafel curves were obtained by altering the electrode potential automatically from -800 to -200 mV with consideration of open circuit potential at a scan rate of 2 mV sec^{-1}. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) obtained by extrapolation the anodic and cathodic Tafel segments. The η_p and θ were calculated with the following Eq. 6 [30]:

$$\eta_p\% = \theta \times 100 = \left(\frac{i_{corr} - i^0_{corr}}{i_{corr}}\right) \times 100 \quad (6)$$

where, i_{corr} and i^0_{corr} are the corrosion current densities without and with the investigated cationic surfactant, respectively.

EIS experiments were performed AC signals with amplitude of 5 mV peak to peak at OCP in a range of 100 kHz to 50 mHz. The inhibition efficiency (η_{Eis}) obtained using Eq. 7 [31]:

$$\eta_{Eis} = \theta \times 100 = \left(\frac{R^o_{ct} - R_{ct}}{R^o_{ct}}\right) \times 100 \quad (7)$$

where, R_{ct} and R^o_{ct} are the charge transfer resistance in the absence and presence of the inhibitor, respectively.

Antimicrobial activity of GLs: The antimicrobial activity of the tested samples was determined using the disc diffusion technique[32]. The tested strains (100 µL) *Desulfomonas pigra* (SRB), *Escherichia coli*, *Pseudomonas aeuroginosa*, *Aspergillus flavus* were activated in 10 mL of fresh media (nutrient broth for bacteria and ISP for yeasts) until they reached a count of approximately 10^8 cells mL^{-1} for bacteria or 10^5 cells mL^{-1} for fungi.

Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated with 10 µL of dimethyl sulfoxide (DMSO) as a control and 10 µL of the tested GL samples (20 mg mL^{-1} in DMSO) then placed on agar plates inoculated with bacteria *Desulfomonas pigra* (SRB), *Escherichia coli*, *Pseudomonas aeuroginosa* and incubated at 35-37°C for 24-48 h, while plates inoculated with filamentous fungi (*Aspergillus flavus*) were incubated at 25°C for 48 h. For the disc diffusion, the zone diameters were measured in millimeters and mean values of inhibition zones were calculated from triple reading in each test.

Statistical analysis: The results are reported as Mean±Standard Error (SE) for experiments repeated at least four times. Statistical differences were analyzed according to the one way ANOVA test followed by the student's t-test wherein the differences were considered to be significant at $p<0.05$.

RESULTS AND DISCUSSION

Production of fungal GLs: This study was planned for the production of fungal GLs using two agro-industrial residues as economic substrate (Fig. 1). A mixture of sunflower oil cake and pineapple waste was fermented by each of *Rhizopus*

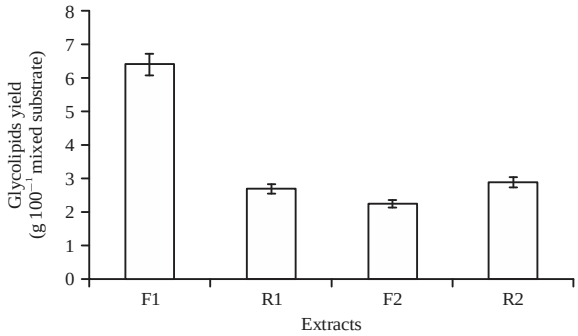

Fig. 1: Production of *R. oryzae* and *F. oxysporum* GLs under SSF using different extraction techniques
F1: *F. oxysporum* GL extracted by MeOH, F2: *F. oxysporum* GL extracted by solvent mixture, R1: *R. oryzae* GL extracted by MeOH, R2: *R. oryzae* GL extracted by solvent mixture

oryzae and *Fusarium oxysporum* using the SSF technique for 14 days. Extraction of the produced crude GLs was carried out using methanol as the first extraction solvent, which produced 6.4 and 2.7 g 100 g^{-1} mixed substrate for the fractions F1 and R1, respectively, while the re-extraction of the residual cultures by the solvent mixture gave GLs yield of 2.25 and 2.88 g 100 g^{-1} mixed substrate, for F2 and R2 extracts. Literatures that have been found for the production of biosurfactants from fungi (*Aspergillus fumigatus*, *Phialemonium* sp. and *Penicillium chrysogenum*) by SSF technique were mainly focusing on production using reactors or fermenter[33-35]. However, several studies were reported for the production of fungal biosurfactants using liquid or submerged fermentation techniques. Qazi *et al.*[12,13] recovered 5.25 and 1.2 g L^{-1} crude and pure *Fusarium* sp. BS-8 biosurfactant respectively, using ethyl acetate/methanol (5:1) mixture. Among the fungi used, *Rhizopus nigricans* was found to be suitable for maximum production of biosurfactant (3.47 g L^{-1})[10]. Silva *et al.*[11] used different mixture percentages of corn steep liquor and rice bran husks as nitrogen and energy sources and stated that the best result was obtained (9.10 g L^{-1}) from 8% corn steep liquor and 3% rice bran husks fermented by *Rhizopus arrhizus* under submerged fermentation.

Structural characterization of the isolated GLs

Fourier transform infrared spectroscopy (FTIR): The isolated GL compounds (F1, F2, R1 and R2 extracts) were identified and characterized by FTIR (Fig. 2). The broad bands at 3367 and 3436.5 cm^{-1} corresponded to the O-H stretching resulting from the OH groups of sugar in F1, F2. The IR spectra also revealed a broad band at 3389 cm^{-1} in the structure of R1 extract. Asymmetrical stretching (vas CH_2) and symmetrical stretching (vs CH_2) of methylene groups were observed at 2930 and 2860 cm^{-1} for F1 extract. However, the bands at 2925 and 2857 cm^{-1} were in F2 and R2 while, the band at 2937 cm^{-1} in R1 extract revealed the presence of asymmetrical stretching (vas CH_2) and the absence of symmetrical stretching (vs CH_2) in the compound. Absorption bands at 1739 and 1744 cm^{-1} were contributed to C=O stretching from lactone ester or acids in the structures of F2 and R2, respectively. The bands at 1455, 1458 and 1456 cm^{-1} corresponded to the C-O-H in plane binding of carboxylic acid (-COOH) appeared in the structure of F1, F2 and R2 extracts. The C=O absorption band from acetyl esters was observed at 1237, 1236 and 1243 cm^{-1}in F1, R1 and R2 extracts, respectively. While the stretch of C-O band of C(-O)-OC in lactones exists at 1165 cm^{-1} in F2 and at 1167 cm^{-1} in R2 fractions. However, the C-O stretch of C-O-H groups of sophorose moiety was observed at

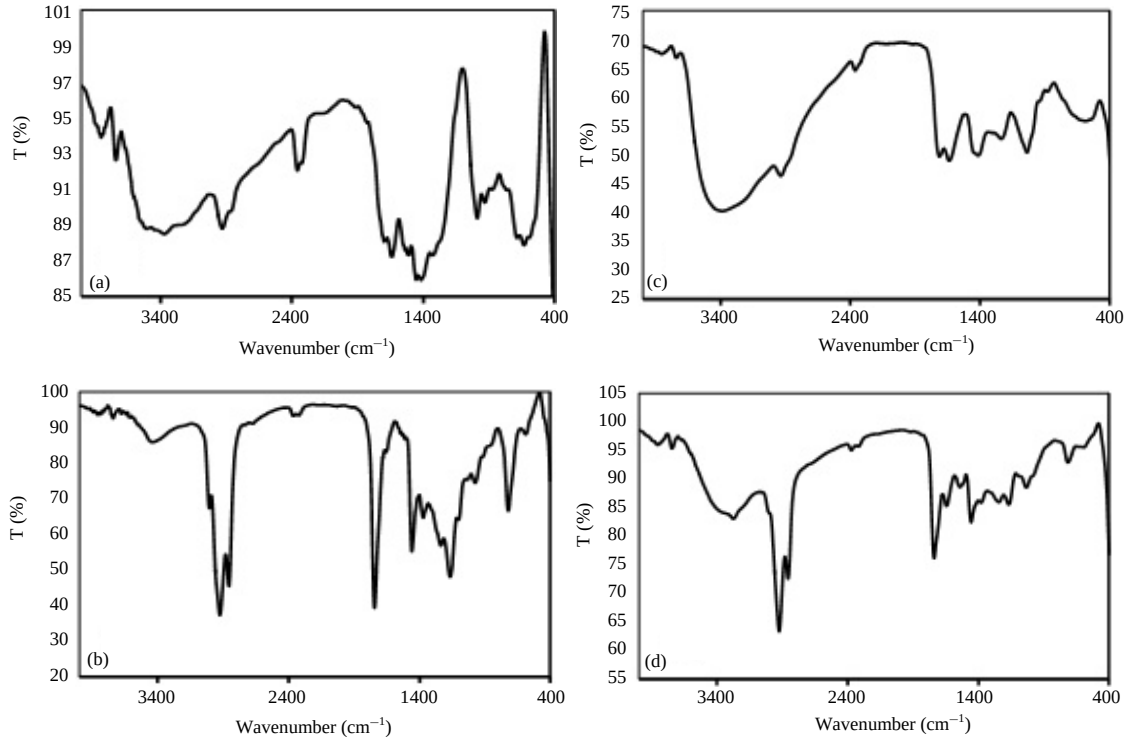

Fig. 2(a-d): FTIR spectra of the produced GLs compounds (a) F1, (b) F2, (c) R1 and (d) R2

F1: *F. oxysporum* GL extracted by MeOH, F2: *F. oxysporum* GL extracted by solvent mixture, R1: *R. oryzae* GL extracted by MeOH, R2: *R. oryzae* GL extracted by solvent mixture

1031, 1039 and 1032 cm^{-1} in F2, R1 and in R2 extracts. The absorption bands at 722 and 714.5 cm^{-1} indicated the existence of C=C in F 2 and in R 2 compounds, respectively.

Proton nuclear magnetic resonance (^{1}H NMR) analysis: The structure of the produced GL compounds (F1, F2, R1 and R2 extracts) was assigned to a typical glycolipid-type structure using proton nuclear magnetic resonance (^{1}H NMR) spectrum analysis. A resonance of two protons for glucose molecules was detected between 3.347~4.3 ppm in all extracts. The presence of -CO-CH_3 group in all structures was confirmed by the signals at 2.03~2.05 ppm in the spectra. The existence of fatty acid chain was confirmed by the multiple signals between 1.23 and 1.28 ppm in all extracts, while the signals from 5.32-5.33 gave the evidence for the existence of the vinyl group (-CH=CH-) in all extract.

According to the results assembled from the FTIR and ^{1}HNMR analyses, the Structural characterization studies gave the evidence for the existence of GL groups in isolated compounds which may be belonged to the sophorolipids either acidic or lactone ring form. So, further studies and identifications of these compounds will be needed to confirm their structures.

These results were found to be close to many reports[5,9,36-39], which confirmed that these products are sophorolipid compounds from different yeast strains. However, Qazi *et al.*[13] reported that the isolated *fusarium* sp. BS-8 biosurfactants from fermented media were a lipopeptide type of biosurfactant. Kiran *et al.*[40] found that the biosurfactant produced by a marine fungi *Aspergillus* sp. MSF1 was rhamnolipid in nature, which is belonging to the GL family.

Considering the results found in the ^{1}H NMR analysis, the existence of the biosurfactants GLs type in the analyzed compounds is confirmed, however, these results were in agreement with those obtained from yeast and fungi strains achieved by Rashad *et al.*[9], Daverey and Pakshirajan[36], Bajaj *et al.*[38], Rashad *et al.*[39], Kiran *et al.*[40] and Chen *et al.*[41].

Surface property studies: From the obtained results in Table 1, it was revealed that all the prepared GLs compounds have surface activity. The critical micelle concentrations (CMCs) of the 4 prepared GLs have been assessed by surface tension measurements at three different temperatures 25, 40 and 60°C and depicted in Table 1. By analyzing the obtained CMCs values, it can be revealed that the CMCs of F2 and R2 extracts were lower than the methanol extracted compounds (F1 and R1). These observations refer to that the re-extract GLs F2 and R2 are more hydrophobic[42,43].

Inspection data in Table 1 cleared that in general, the CMC of the obtained GLs decreased upon raising the solution temperature, which indicates that the effect of decreasing the hydration around the hydrophilic head of the prepared GLs is a dominant than the disruption of water structure around the hydrocarbon tail[44-46]. Earlier[13], found higher levels of CMC (4.45, 2.12, 0.25, 1.04 g %) for the biosurfactants produced by *Aspergillus niger*, *Aspergillus flavus*, *Fusarium* sp. and *Penicillium* sp., respectively. Andrade Silva *et al.*[47] also reported that the CMC of biosurfactant isolated from *Cunninghamella echinulate* was 2 g %.

The calculated maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) values of the 4 prepared compounds were compiled in Table 1. The experimental results refer that the Γ_{max} of the *Fusarium oxysporum* GL extract (F1) were higher than its re-extract F2 at 25, 40 and 60°C. While the Γ_{max} of the *Rhizopus oryzae* GL extract (R1) are lower than its re-extract (R2). The high concentration of the prepared GL extract (F1), induce the hydrophobic part to be oriented vertically and consequently, the area occupied by the GL molecules at the surface is lower compared to their re-extract (F2). On the contrary, the lower Γ_{max} values of R1

Table 1: The surface properties of the produced GLs at various temperatures

Sample	Temperature (°C)	CMC (%)	C_{20} (%)	π_{CMC} (mN m^{-1})	$\Gamma_{max} \times 10^{-10}$ (mol cm^{-2})	A_{min}/A^2	CMC/C_{20}
R1	25	0.023	0.0168	21.39	2.04	81.53	1.38
	40	0.020	0.0028	29.28	1.86	89.47	7.24
	60	0.014	0.0022	26.67	1.67	99.65	6.17
R2	25	0.022	0.0115	23.48	2.28	72.80	1.91
	40	0.011	0.0056	23.33	1.94	85.63	2.02
	60	0.010	0.0044	22.96	1.70	97.82	2.19
F1	25	0.029	0.0065	36.03	3.90	42.59	4.52
	40	0.025	0.0033	34.12	2.66	62.44	7.57
	60	0.020	0.0030	32.50	2.34	70.86	6.76
F2	25	0.021	0.0088	23.83	2.44	67.95	2.40
	40	0.017	0.0070	23.28	1.77	93.67	2.48
	60	0.012	0.0057	23.78	1.56	106.29	2.09

R1: *R. oryzae* GL extracted by MeOH, R2: *R. oryzae* GL extracted by solvent mixture, F1: *F. oxysporum* GL extracted by MeOH, F2: *F. oxysporum* GL extracted by solvent mixture

refer to their horizontal orientation (less perpendicular) at the surface and consequently the area occupied by the R1at surface are higher than R2 molecules.

The data revealed that upon elevating the solution temperature, the A_{min} increases while Γ_{max} decreases. The decreasing in the amount of accumulated GLs at the interface can be ascribed to decreasing the hydration around the hydrophilic head, which enhances the micellization process; hence, the GL molecules population at the interface decreases[48-50].

The effectiveness values (π_{CMC}) of the prepared GLs extracts at 25, 40 and 60°C, have been compiled in Table 1. The π_{CMC} values refer to the F1 extract, were more effective in reducing the surface tension at the surface at all tested temperature. The higher effectiveness value refers to the GLs form more condensed layer at the surface, while the lower π_{CMC} values refer that the formed layer at the surface is more expanded, which was similar to the results obtained in previous studies[51,52].

Weight loss: The effect of the extracted GLs (F1, F2, R1 and R2) on the steel corrosion in 1.0 M HCl has been carried out gravimetrically at the three different temperatures. Inspecting the obtained experimental results which depicted in Table 2, it was revealed that by increasing the GL concentration, the weight loss decreases as an indication of increasing the inhibition efficiency. The maximum inhibition efficiency reacted to 80-85% at room temperature (25°C). Increasing the inhibition efficiency with the incremental addition of the GL extracts refers to their ability to adsorb on the steel surface, which is directly proportional to the extract concentration. The presence of some functional groups in the GL extracts like carbonyl, hydroxyl and ether groups beside the sugar moiety enhances the adsorption process on the steel surface. The co-ordination bond between the vacant d-orbital (steel) and the rich electronic cloud in the GL extract (hydroxyl. Carbonyl, ether and sugar moiety) is responsible for the adsorption on the steel surface in the acidic environment[53-55].

Temperature effect: Raising the solution temperature of the extract, followed by increasing the inhibition efficiency, then it decreases at the higher temperature (Table 2). The maximum inhibition efficiency was found at temperature 45°C for all the extracted samples (F1, F2, R1 and R2). This behavior gives insight on the adsorption of the extract and its re-extract on the steel is a mixture of chemical and physical adsorption[56].

Activation parameters by gravimetric method: The apparent activation energy (E_a) for the 4 prepared GLs in 1.0 M HCl has been determined through the following Arrhenius equation (Eq. 8):

$$k = A\exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

where, k is the corrosion rate (Weight loss test), R is the gas constant (8.314 j moL^{-1}) and A is Arrhenius constant.

The relation between ln k and 1/T in the absence and presence of different concentrations from the prepared GL extract (R2) as an example was represented in Fig. 3. The calculated E_a for all the GLs extracts have been compiled in Table 3, which revealed that the E_a are lower than blank and it

Table 2: Corrosion rate, surface coverage and inhibition efficiency (%) of carbon steel in 1.0 M HCl at different temperatures

		25°C			45°C			60°C		
Sample	Inhibitor Conc., M	K (mg cm^{-2} h^{-1})	θ	η (%)	K (mg cm^{-2} h^{-1})	θ	η (%)	K (mg cm^{-2} h^{-1})	θ	η (%)
	0.00	0.1781	-	-	0.4897	-	-	1.1574	-	-
R1	100	0.0580	0.6745	67.45	0.1353	0.7236	72.36	0.3394	0.7068	70.68
	300	0.0495	0.722	72.2	0.1149	0.7653	76.53	0.2829	0.7556	75.56
	500	0.0411	0.769	76.9	0.0909	0.8144	81.44	0.2314	0.8001	80.01
	700	0.0348	0.8045	80.45	0.0729	0.8511	85.11	0.1790	0.8453	84.53
R2	100	0.0524	0.7055	70.55	0.1315	0.7315	73.15	359.6	0.7234	72.34
	300	0.0469	0.7365	73.65	0.1163	0.7625	76.25	319.5	0.7542	75.42
	500	0.0347	0.805	80.5	0.0789	0.8389	83.89	224.4	0.8274	82.74
	700	0.0260	0.854	85.4	0.0525	0.8927	89.27	164.6	0.8734	87.34
F1	100	0.1204	0.662	66.2	0.2692	0.7251	72.51	0.7682	0.6682	66.82
	300	0.0482	0.7295	72.95	0.1106	0.7742	77.42	0.2753	0.7423	74.23
	500	0.0374	0.79	79	0.0781	0.8405	84.05	0.1993	0.8135	81.35
	700	0.0327	0.8165	81.65	0.0621	0.8733	87.33	0.1687	0.8421	84.21
F2	100	0.0848	0.762	76.2	0.1927	0.8033	80.33	0.5011	0.7835	78.35
	300	0.0687	0.807	80.7	0.1514	0.8455	84.55	0.3962	0.8288	82.88
	500	0.0572	0.8395	83.95	0.1122	0.8855	88.55	0.3139	0.8644	86.44

R1: *R. oryzae* GL extracted by MeOH, F1: *F. oxysporum* GL extracted by MeOH, R2: *R. oryzae* GL extracted by solvent mixture, F2: *F. oxysporum* GL extracted by solvent mixture

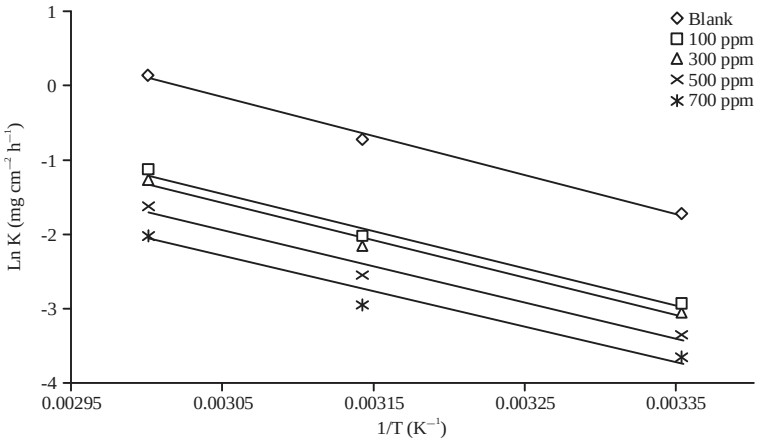

Fig. 3: Arrhenius plots for carbon steel dissolution in absence and presence of different concentrations of the produced GL (R2) in 1M HCl solution

R2: *R. oryzae* GL extracted by solvent mixture

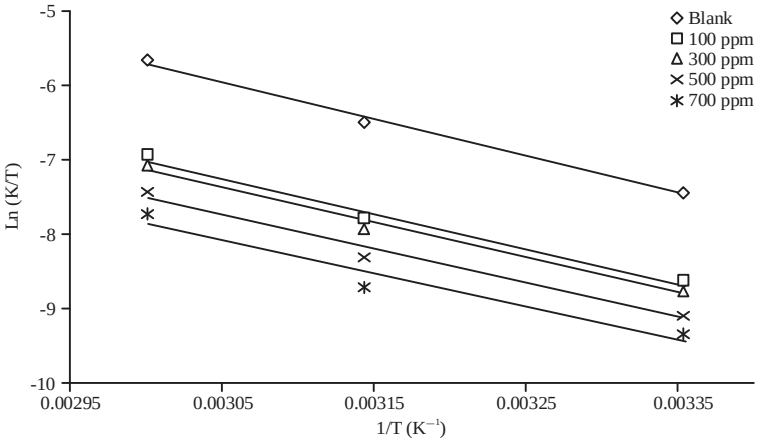

Fig. 4: Relationship between Ln (K/T) and the reciprocal of the absolute temperature in absence and presence of different concentrations of prepared GL (R2) in 1M HCl solution

R2: *R. oryzae* GL extracted by solvent mixture

Table 3: Activation parameters values for carbon steel in 1.0 M HCl of different concentrations of the produced extracts (F1, F2, R1 and R2)

Inhibitor name	Conc. of inhibitor (M)	E_a (kJ moL^{-1})	ΔH* (kJ moL^{-1})	ΔS* (J moL^{-1} K^{-1})
	0.00	43.83	41.22	-121.24
R1	100	41.06	38.45	-140.09
	300	40.51	37.90	-143.23
	500	40.02	37.41	-146.50
	700	37.91	35.29	-154.98
R2	100	42.19	39.57	-137.04
	300	42.00	39.39	-138.62
	500	40.60	37.98	-145.95
	700	39.79	37.18	-151.29
F1	100	42.80	40.19	-128.39
	300	40.48	37.87	-143.58
	500	38.67	36.05	-151.89
	700	37.69	35.08	-156.45
F2	100	41.19	38.57	-136.58
	300	40.54	37.93	-140.53
	500	39.14	36.52	-146.97

R1: *R. oryzae* GL extracted by MeOH, R2: *R. oryzae* GL extracted by solvent mixture, F1: *F. oxysporum* GL extracted by MeOH, F2: *F. oxysporum* GL extracted by solvent mixture

decreases with increasing the concentration of the 4 prepared GL extracts. The lower E_a refers to the chemisorption onto the metal surface/solution interface.

The change in enthalpy and entropy of activation values (ΔH*, ΔS*) was estimated through transition state theory as shown in Eq. 9:

$$\ln\left(\frac{k}{T}\right)=\left(\ln\left(\frac{R}{N_A h}\right)+\left(\frac{\Delta S^*}{R}\right)\right)-\frac{\Delta H^*}{RT} \quad (9)$$

where, h is the Plank constant (6.63×10^{-34} j.s) and N_A is the Avogadro's numbers (6.02×10^{23}). Figure 4 represents a plot of log (k/T) vs. 1/T with a slope equal to (ΔH*/R) and intercept equal to ($R/N_A h$) for the extract (R2).

The positive signs of ΔH* (Table 3) reflect the endothermic nature of the steel corrosion process in 1.0 M HCl in case of all the prepared extracts, while the negative sign of ΔS* either in the absence or presence of the prepared inhibitors refers to decreasing the entropy upon achieving the transition state[57,58].

Electrochemical measurements: Figure 5 shows the polarization curves of the tested mild steel immersed in the aggressive medium in the presence and absence of the extracted R2 as an example and the obtained results have been depicted in Table 4. Inspection data in Table 4, it can observe that by increasing the R2 concentration, the corrosion current density decreases as an indication for increasing the inhibiting effect of the compound. Upon addition of 700 ppm of R2, the corrosion current density (i_{corr}), decreased to 0.0747 mA cm^{-2} compared to the blank solution without the inhibitor (0.4326 mA cm^{-2}), so the maximum inhibition efficiency against the steel corrosion reached to 82.37%.

Table 4: Potentiodynamic polarization and impedance parameters for corrosion of carbon steel in 1.0 M HCl of GL R2 at 25°C

	Tafel					EIS			
Conc. (ppm)	E_{corr} mV	I_{corr} mA (cm^{-2})	β_a mV (dec^{-1})	β_c mV (dec^{-1})	η_p (%)	Rs (ohm cm^2)	R_{ct} (ohm cm^2)	C_{dl} (μF cm^{-2})	η_Z (%)
0.00	-555.6	0.4326	188.8	-168.3	-	2.86	135.3	94.09	-
100	-571.0	0.1105	311.9	-169.1	74.46	1.56	542.3	29.34	75.05
300	-560.7	0.0957	240.1	-156.7	77.88	0.912	602.1	26.42	77.53
500	-570.4	0.0926	350.0	-135.0	78.60	0.321	688.6	16.45	80.35
700	-585.4	0.0747	326.7	-141.4	82.37	1.012	809.7	15.72	83.29

R2: *R. oryzae* GL extracted by solvent mixture

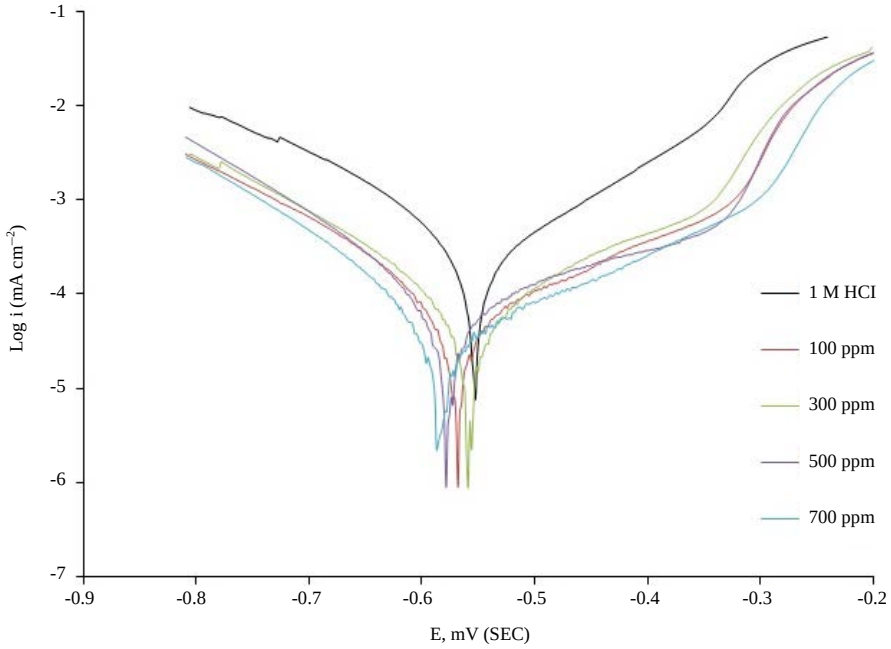

Fig. 5: Potentiodynamic polarization curves for the carbon steel in 1 M HCl in the absence and presence of different concentrations of the produced GL R2 at scanning rate 2 mV sec^{-1}

R2: *R. oryzae* GL extracted by solvent mixture

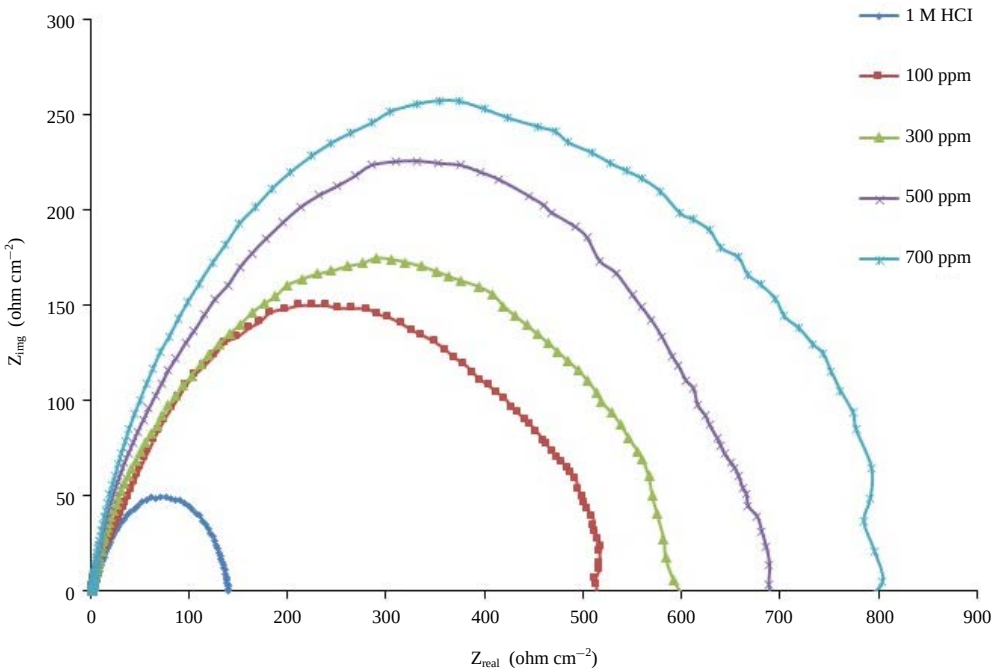

Fig. 6: Nyquist plots for the carbon steel in 1 M HCl in the absence and presence of different concentrations of GL R2 extract
R2: *R. oryzae* GL extracted by solvent mixture

From the results in Table 4, inferred that the corrosion potential E_{corr} of the inhibited re-extract solution (R2) shifted to the more negative direction (maximum potential displacement doesn't exceed 30 mV). This behavior refers that the GL R2 acts as a mixed-type inhibitor with a predominantly cathodic reaction[59].

Figure 6 represents a typical Nyquist plot for the prepared GL extract (R2) solution at 25°C. The Nyquist diagram shows a single depressed and non-perfect semicircle, which refers that the charge transfer process occurs at the working electrode/solution interface. The non-ideality semicircle returns to the homogeneousness and roughness in of the corroded mild steel electrode surface.

Data in Table 4, revealed that increasing the inhibition efficiency (η_Z) upon increasing the concentration of the re-extract (R2). Increasing the inhibitor concentration followed by increasing the diameter of the semicircle. R^o_{ct} and R_{ct} are charge transfer resistance values of inhibited and uninhibited solution respectively[60].

Antimicrobial activity of the produced GIs: Microbially Influenced Corrosion (MIC) refers to the influence of microorganisms on the kinetics of corrosion processes of metals. Therefore, the antimicrobial effect of the four extracts (F1, F2, R1 and R2) was evaluated using disc diffusion method. In this study three strains of bacteria (*P. aeruginosa*, *E. coli* and *D. pigra* (SRB)) and one fungal strain (*A. flavus*) were examined as an example of microorganisms involved in biocorrosion process.

The results showed that F2 extract exhibited the highest effect against the bacterial strains with a clear zone diameter of 15 mm for the three tested strains, this was followed by R1 extract which gave a clear hallow diameter of 14 mm for *P. aeruginosa* and 13 mm for both *D. pigra* (SRB)and *E. coli*. However, R2 extract revealed a clear zone diameter (13 mm) for the three bacterial strains, while, F1 extract showed only inhibition effects (13 mm) on both *E. coli* and *D. pigra* (SRB) and has no effect on *P. aeruginosa* strain. On the other hand, none of the four extracts exhibited antifungal effect against *A. flavus*.

Gautam *et al.*[35] produced a lipopeptide biosurfactant from a fungal strain (*Penicillium chrysogenum* SNP5) and tested against pathogenic bacteria *S. aureus* and *P. aeruginosa*. The obtained results indicated the antimicrobial activity of the examined compound against *S. aureus* (mean values 16.7 mm) and *P. aeruginosa* (mean values 19.3 mm). While, a glycolipid surfactant from *Aspergillus* sp. MSF1 has demonstrated a broad spectrum of antimicrobial activity against different species of bacteria and yeast strains[40].

The Sulfate Reducing Bacteria (SRB) is the major cause of bio-corrosion. These strains can release H_2S, toxic and corrosive agents during their growth, causing a serious damage for many industries[61]. In this context, Korenblum *et al.*[62] found that a surfactin-like molecule

produced by *Bacillus* sp. H_2O-1 has an antimicrobial activity against *Desulfovibrio alaskensis* NCIMB 13491 and they suggested that this biosurfactant is a potential alternative to the chemical biocides currently used to prevent corrosion caused by SRB in petroleum industries.

CONCLUSION

In this study, four fungal economic eco-friendly glycolipids were produced by using a mixture of residues, which considered as environmental polluting materials. The obtained compounds were found to have the ability to prevent corrosion in acidic media. They were also able to inhibit the growths of the tested bacterial strains involved in the biocorrosion process, thus opening up a new application area in the food industry, in addition to the possibility of their potential interventions in the fields of petroleum and steel industries.

SIGNIFICANCE STATEMENT

This study discovered that new fungal glycolipids could be produced by using agro-industrial wastes, which is considered as environmental pollutants. The new fungal glycolipids can be beneficial as new safe green anticorrosion agents. They are also able to inhibit the growths of some bacterial strains involved in the biocorrosion process. This will help the researchers to continue studying and identifying the structure of this new fungal glycolipids and its potential admittance in many industrial fields such as food, pharmaceuticals, petroleum and steels.

ACKNOWLEDGMENTS

The authors appreciatively expressed their gratitude for the financial support presented by the National Research Centre, Egypt (Project No.10130105). They would also like to express their gratitude to the Egyptian Petroleum Research Institute for participation in this study.

REFERENCES

1. Shukla, A. and R. Bhandari, 2015. Biosurfactants from fungi and its application: A review. J. Basic Applied Mycol., 11: 14-18.
2. Desai, J.D. and I.M. Banat, 1997. Microbial production of surfactants and their commercial potential. Microbiol. Mol. Biol. Rev., 61: 47-64.
3. Santos, D.K., R.D. Rufino, J.M. Luna, V.A. Santos, A.A. Salgueiro and L.A. Sarubbo, 2013. Synthesis and evaluation of biosurfactant produced by *Candida lipolytica* using animal fat and corn steep liquor. J. Petroleum Sci. Eng., 105: 43-50.
4. Sekhon, K.K., S. Khanna and S.S. Cameotra, 2012. Biosurfactant production and potential correlation with esterase activity. J. Pet. Environ. Biotechnol., Vol. 3. 10.4172/2157-7463.1000133.
5. Parekh, V.J., V.B. Patravale and A.B. Pandit, 2012. Mango kernel fat: A novel lipid source for the fermentative production of sophorolipid biosurfactant using *Starmerella bombicola* NRRL-Y 17069. Ann. Biol. Res., 3: 1798-1803.
6. Rufino, R.D., J.M. de Luna, G.M. de Campos Takaki and L.A. Sarubbo, 2014. Characterization and properties of the biosurfactant produced by *Candida lipolytica* UCP 0988. Electron. J. Biotechnol., 17: 34-38.
7. Rashad, M.M., A.E. Mahmoud, M.M. Ali, M.U. Nooman and A.S. Al-Kashef, 2015. Antioxidant and anticancer agents produced from pineapple waste by solid state fermentation. Int. J. Toxicol. Pharmacol. Res., 7: 287-296.
8. Fontes, G.C., N.M. Ramo, P.F. Amaral, M. Nele and M.A.Z. Coelho, 2012. Renewable resources for biosurfactant production by *Yarrowia lipolytica*. Brazl. J. Chem. Eng., 29: 483-493.
9. Rashad, M.M., M.U. Nooman, M.M. Ali, A.S. Al-Kashef and A.E. Mahmoud, 2014. Production, characterization and anticancer activity of *Candida bombicola* sophorolipids by means of solid state fermentation of sunflower oil cake and soybean oil. Grasas Aceites, Vol. 65. 10.3989/gya.098413.
10. Aulwar, U., B. Patlolla and R.S. Awasthi, 2009. Biosurfactant production in deproteinised juice (dpj) of eucalyptus by *Rhizopus nigricans*. Proceedings of the 6th International Symposium on Recent Advances in Environmental Health Research, Poster session A, September 13-16, 2009, USA.
11. Silva, M.C., P.M. Souza, A.A. Antunes, A. Cardoso and C.I.M. Lins *et al*., 2012. Biosurfactant Production by *Rhizopus arrhizus* using Agro Industrials Substrates as Alternative Medium. In: Microbes in Applied Research: Current Advantages and Challenges, Mendez-Vilas, A. (Ed.)., World Scientific, Singapore, pp: 353-357.
12. Qazi, M.A., M. Subhan, N. Fatima, M.I. Ali and S. Ahmed, 2013. Role of biosurfactant produced by *Fusarium* sp. BS-8 in Enhanced Oil Recovery (EOR) through sand pack column. Int. J. Biosci. Biochem. Bioinform., 3: 598-604.
13. Qazi, M.A., T. Kanwal, M. Jadoon, S. Ahmed and N. Fatima, 2014. Isolation and characterization of a biosurfactant producing *Fusarium* sp. BS-8 from oil contaminated soil. Biotechnol. Prog., 30: 1065-1075.
14. Ashokkumar, B., N. Kyalvizhi and P. Gunasekaran, 2001. Optimization of media for β-fructofuranosidase production by *Aspergillus niger* in submerged and solid state fermentation. Process Biochem., 37: 331-338.

15. Kosaric, N., C.N. Mulligan and B.F. Gibbs, 1993. Biosurfactants, Production, Properties, Applications. Marcel Dekker, New York, USA., pp: 329-371.
16. Rodrigues, L., I.M. Banat, J. Teixeira and R. Oliveira, 2006. Biosurfactants: Potential applications in medicine. J. Antimicrobial Chemotherapy, 57: 609-618.
17. Luna, J.M., A.S. Santos Filho, R.D. Rufino and L.A. Sarubbo, 2016. Production of biosurfactant from *Candida bombicola* URM 3718 for environmental applications. Chem. Eng., 49: 583-588.
18. Dagbert, C., T. Meylheuc and M.N. Bellon-Fontaine, 2006. Corrosion behaviour of AISI 304 stainless steel in presence of a biosurfactant produced by *Pseudomonas fluorescens*. Electrochim. Acta, 51: 5221-5227.
19. Shi, X., N. Xie and J. Gong, 2011. Recent progress in the research on microbially influenced corrosion: A bird's eye view through the engineering lens. Recent Patents Corrosion Sci., 1: 118-131.
20. Ghali, E., 2010. Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance and Testing. John Wiley and Sons, Inc., Canada.
21. Videla, H.A. and L.K. Herrera, 2005. Microbiologically influenced corrosion: Looking to the future. Int. Microbiol., 8: 169-180.
22. Rajasekar, A., S. Maruthamuthu, N. Palaniswamy and A. Rajendran, 2007. Biodegradation of corrosion inhibitors and their influence on petroleum product pipeline. Microbiol. Res., 162: 355-368.
23. Muyzer, G. and A.J.M. Stams, 2008. The ecology and biotechnology of sulphate-reducing bacteria. Nat. Rev. Microbiol., 6: 441-454.
24. Ustun, G., L. Kent, N. Cekin and H. Civelekoglu, 1990. Investigation of the technological properties of *Nigella sativa* (Black Cumin) seed oil. J. Am. Oil Chem. Soc., 67: 958-960.
25. Ohno, A., T. Ano and M. Shoda, 1995. Production of a lipopeptide antibiotic, surfactin, by recombinant *Bacillus subtilis* in solid state fermentation. Biotechnol. Bioeng., 47: 209-214.
26. Shaban, S.M., A.S. Fouda, S.M. Rashwan, H.E. Ibrahim and M.F. El-Bhrawy, 2016. Synthesis and characterization of newly cationic surfactants based on 2-(2-(dimethylamino) ethoxy) ethanol: Physiochemical, thermodynamic and evaluation as biocide. J. Mol. Liquids, 221: 224-234.
27. Bhadani, A., R.G. Shrestha, S. Koura, T. Endo, K. Sakai, M. Abe and H. Sakai, 2014. Self-aggregation properties of new ester-based gemini surfactants and their rheological behavior in the presence of cosurfactant-monolaurin. Colloids Surfaces A: Physicochem. Eng. Aspects, 461: 258-266.
28. Rosen, M.J., 1989. Surfactants and Interfacial Phenomena. John Wiley and Sons, New York, USA., pp: 28.
29. Shaban, S.M., 2016. N-(3-(Dimethyl benzyl ammonio) propyl) alkanamide chloride derivatives as corrosion inhibitors for mild steel in 1 M HCl solution: Experimental and theoretical investigation. RSC Adv., 6: 39784-39800.
30. Bentiss, F., M. Lebrini and M. Lagrenee, 2005. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2, 5-bis (n-thienyl)-1, 3, 4-thiadiazoles/hydrochloric acid system. Corrosion Sci., 47: 2915-2931.
31. Dinodi, N. and A.N. Shetty, 2014. Alkyl carboxylates as efficient and green inhibitors of magnesium alloy ZE41 corrosion in aqueous salt solution. Corrosion Sci., 85: 411-427.
32. British Pharmacopoeia, 1968. Biological Assay of Antibiotics. The Pharmaceutical Press, London, pp: 1313-1317.
33. Martins, V.G., S.J. Kalil, T.E. Elit and J.A.V. Costa, 2006. Solid state biosurfactant production in a fixed-bed column bioreactor. Zeitschrift Naturforschung C, 61: 721-726.
34. Castiglioni, G.L., T.E. Bertolin and J.A.V. Costa, 2009. Solid-state biosurfactant production by *Aspergillus fumigates* using agricultural residues as substrate. Quimica Nova, 32: 292-295.
35. Gautam, G., V. Mishra, P. Verma, A.K. Pandey and S. Negi, 2014. A cost effective strategy for production of bio-surfactant from locally isolated *Penicillium chrysogenum* SNP5 and its applications. J. Bioprocess Biotech., Vol. 4. 10.4172/2155-9821.1000177.
36. Daverey, A. and K. Pakshirajan, 2009. Production, characterization and properties of sophorolipids from the yeast *Candida bombicola* using a low-cost fermentative medium. Applied Biochem. Biotechnol., 158: 663-674.
37. Ma, X.J., H. Li, L.J. Shao, J. Shen and X. Song, 2011. Effects of nitrogen sources on production and composition of sophorolipids by *Wickerhamiella domercqiae* var. sophorolipid CGMCC 1576. Applied Microbiol. Biotechnol., 91: 1623-1632.
38. Bajaj, V., A. Tilay and U. Annapure, 2012. Enhanced production of bioactive sophorolipids by *Starmerella bombicola* NRRL Y-17069 by design of experiment approach with successive purification and characterization. J. Oleo Sci., 61: 377-386.
39. Rashad, M.M., A.S. Al-Kashef, M.U. Nooman and A.E. El-Din Mahmoud, 2014. Co-utilization of motor oil waste and sunflower oil cake on the production of new sophorolipids by *Candida bombicola* NRRL Y-17069. Res. J. Pharmaceut. Biol. Chem. Sci., 5: 1515-1528.
40. Kiran, G.S., N. Thajuddin, T.A. Hema, A. Idhayadhulla, R.S. Kumar and J. Selvin, 2010. Optimization and characterization of rhamnolipid biosurfactant from sponge associated marine fungi *Aspergillus* sp. MSF1. Desalin. Water Treat., 24: 257-265.

41. Chen, J., X. Song, H. Zhang, Y.B. Qu and J.Y. Miao, 2006. Sophorolipid produced from the new yeast strain *Wickerhamiella domercqiae* induces apoptosis in H7402 human liver cancer cells. Applied Microbiol. Biotechnol., 72: 52-59.
42. Ahmad, I., P. Patial, C. Kaur and S. Kaur, 2014. Cationic imidazolium monomeric surfactants: Their synthesis and surface active properties. J. Surfactants Detergents, 17: 269-277.
43. Shaban, S.M., I. Aiad and A.R. Ismail, 2016. Surface parameters and biological activity of *N*-(3-(Dimethyl Benzyl Ammonio) Propyl) alkanamide chloride cationic surfactants. J. Surfact. Deterg., 19: 501-510.
44. Patial, P., A. Shaheen and I. Ahmad, 2014. Gemini pyridinium surfactants: Synthesis and their surface active properties. J. Surfactants Detergents, 17: 929-935.
45. Zhong, X., J. Guo, L. Feng, X. Xu and D. Zhu, 2014. Cationic Gemini surfactants based on adamantane: Synthesis, surface activity and aggregation properties. Colloids Surfaces A: Physicochem. Eng. Aspects, 441: 572-580.
46. Shaban, S.M., I. Aiad, H.Y. Moustafa and A. Hamed, 2015. Amidoamine gemini surfactants based dimethylamino propyl amine: Preparation, characterization and evaluation as biocide. J. Mol. Liquids, 212: 907-914.
47. Andrade Silva, N.R., M.A. Luna, A.L. Santiago, L.O. Franco and G.K. Silva *et al*., 2014. Biosurfactant-and-bioemulsifier produced by a promising *Cunninghamella echinulata* isolated from caatinga soil in the northeast of Brazil. Int. J. Mol. Sci., 15: 15377-15395.
48. Mousli, R. and A. Tazerouti, 2011. Synthesis and some surface properties of glycine-based surfactants. J. Surfactants Detergents, 14: 65-72.
49. Shaban, S.M. and A.A. Abd-Elaal, 2017. Studying the silver nanoparticles influence on thermodynamic behavior and antimicrobial activities of novel amide Gemini cationic surfactants. Mater. Sci. Eng.: C, 76: 871-885.
50. Ye, Z., F. Zhang, L. Han, P. Luo, J. Yang and H. Chen, 2008. The effect of temperature on the interfacial tension between crude oil and gemini surfactant solution. Colloids Surfaces A: Physicochem. Eng. Aspects, 322: 138-141.
51. Li, H., C. Yu, R. Chen, J. Li and J. Li, 2012. Novel ionic liquid-type Gemini surfactants: Synthesis, surface property and antimicrobial activity. Colloids Surfaces A: Physicochem. Eng. Aspects, 395: 116-124.
52. Shaban, S.M., I. Aiad, H.A. Fetouh and A. Maher, 2015. Amidoamine double tailed cationic surfactant based on dimethylaminopropylamine: Synthesis, characterization and evaluation as biocide. J. Mol. Liquids, 212: 699-707.
53. Hegazy, M.A. and I. Aiad, 2015. 1-Dodecyl-4-(((3-morpholinopropyl) imino) methyl) pyridin-1-ium bromide as a novel corrosion inhibitor for carbon steel during phosphoric acid production. J. Ind. Eng. Chem., 31: 91-99.
54. Dehdab, M., Z. Yavari, M. Darijani and A. Bargahi, 2016. The inhibition of carbon-steel corrosion in seawater by streptomycin and tetracycline antibiotics: An experimental and theoretical study. Desalination, 400: 7-17.
55. Verma, D.K. and F. Khan, 2016. Green approach to corrosion inhibition of mild steel in hydrochloric acid medium using extract of spirogyra algae. Green Chem. Lett. Rev., 9: 52-60.
56. Popova, A., E. Sokolova, S. Raicheva and M. Christov, 2003. AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives. Corrosion Sci., 45: 33-58.
57. Amin, M.A., M.A. Ahmed, H.A. Arida, T. Arslan, M. Saracoglu and F. Kandemirli, 2011. Monitoring corrosion and corrosion control of iron in HCl by non-ionic surfactants of the TRITON-X series-Part II. Temperature effect, activation energies and thermodynamics of adsorption. Corrosion Sci., 53: 540-548.
58. Shaban, S.M., A.A. Abd-Elaal and S.M. Tawfik, 2016. Gravimetric and electrochemical evaluation of three nonionic dithiol surfactants as corrosion inhibitors for mild steel in 1 M HCl solution. J. Mol. Liquids, 216: 392-400.
59. Aljourani, J., K. Raeissi and M.A. Golozar, 2009. Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution. Corros. Sci., 51: 1836-1843.
60. Zhang, Q.B. and Y.X. Hua, 2009. Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. Electrochim. Acta, 54: 1881-1887.
61. Neria-Gonzalez, I., E.T. Wang, F. Ramirez, J.M. Romero and C. Hernandez-Rodriguez, 2006. Characterization of bacterial community associated to biofilms of corroded oil pipelines from the southeast of Mexico. Anaerobe, 12: 122-133.
62. Korenblum, E., L.V. de Araujo, C.R. Guimaraes, L.M. De Souza and G. Sassaki *et al*., 2012. Purification and characterization of a surfactin-like molecule produced by *Bacillus* sp. H2O-1 and its antagonistic effect against sulfate reducing bacteria. BMC Microbiol., Vol. 12. 10.1186/1471-2180-12-252.