



## Research article

## Could petroleum work as lubricant oil on slippery lubricated surfaces to prevent inorganic scaling?



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## ABSTRACT

The use of nucleation and growth inhibitors at offshore oil industry to avoid inorganic scaling could be replaced by both physical and chemical modifications at surfaces to prevent the scaling. In that way, the slippery lubricated surfaces have been showing promising results as scaling preventers, notably when the lubricants are per-fluorinated oils, which are immiscible with almost every kind of compound. Nonetheless, the requirement of periodically refilling these lubricant oils is disadvantageous, especially when dealing with deep sea facilities. Using petroleum as the lubricant oil could skip the refilling step, since it is always present in the extraction medium. So, this work tests the effectiveness of petroleum as the lubricant oil in functionalized textured poly-aniline applied as anti-scaling material in conditions that simulate the medium of offshore operation. As result, petroleum as lubricant oil presents effective anti-scaling capacity and works perfectly in slippery lubricated surfaces.

## 1. Introduction

Industrial activity in high salinity medium, as occurs at offshore oil industry, suffers with inorganic scaling onto walls of pipelines, valves and other equipment of platform. Aiming to prevent this type of scaling, nucleation and growth inhibitors are used. For calcium carbonate and barium and strontium sulfates, the major inorganic scales at this production, phosphonate and carboxylate compounds and polyacrylate based polymers are used as inhibitors (Sousa et al., 2016). Besides the costs of constant reinjection, the use of inhibitors causes negative environmental impact because these compounds disperse over surroundings and change the local sea ecosystem.

A way of reducing, or even completely replacing, the use of inorganic scale inhibitors is physically and chemically modifying the surfaces of equipment exposed to scaling brines during the offshore oil production to prevent, for themselves, the formation and adhesion of salts onto their walls. Such modifications can be performed by exploring the interfacial tensions of the system and the topography of the surfaces.

The interfacial tension,  $\gamma_{AB}$ , is a thermodynamic property of the interface between phases A and B. It is defined as the work to change the interfacial area at constant temperature, volume, pressure and number of mols. At a molecular level it is related to the difference of the

intermolecular interactions at the interfaces when compared with the ones in the bulk of each phase (Adamson and Gast, 1997).

From the thermodynamics point of view, interfacial tensions are the responsible for the wettability of surfaces by liquids, and for the adhesion between materials. As stated by Thomas Young (Young, 1805) a droplet of a liquid deposited over a flat and homogeneous solid surface shall, at equilibrium, present a contact angle,  $\theta$ , at the three-point phase contact, which depends on the interfacial tensions between the phases of the system (Figure 1a). For surfaces that present  $\theta > 90^\circ$  with water droplets, the interfacial area between solid and liquid phases is reduced; these surfaces are called hydrophobic (Figure 1b). In the opposite way, when  $\theta < 90^\circ$ , the interfacial area between solid and liquid phases is increased, and the surfaces are called hydrophilic (Figure 1c).

The Young's equation is given by Eq. (1):

$$\gamma_{la} \cos \theta = \gamma_{sa} - \gamma_{sl} \quad [1]$$

in which  $\gamma_{la}$  is the interfacial tension between liquid and air,  $\gamma_{sa}$  is the interfacial tension between solid and air,  $\gamma_{sl}$  is the interfacial tension between solid and liquid, and  $\theta$  is the contact angle between the solid surface and the tangent of the sessile droplet profile at the three-phase contact point.

The Young statement is valid for perfect flat and homogeneous interfaces, which are ideal systems. To add roughness to the model, Wenzel

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(Wenzel, 1936) considers a surface where the liquid infiltrates into the reentrances of the rough topography, filling all the space over the solid (Figure 1d). In this case, the contact area of solid and liquid is increased and then, the hydrophobicity or hydrophilicity of the flat surface is augmented by the roughness, leading to an apparent contact angle,  $\theta_a$ . Thus, for flat surfaces presenting  $\theta > 90^\circ$ ,  $\theta_a > \theta$ , and for flat surfaces presenting  $\theta < 90^\circ$ ,  $\theta_a < \theta$ .

The Wenzel state is given by Eq. (2):

$$\gamma_{la} \cos \theta_a = f_r (\gamma_{sa} - \gamma_{sl}) \quad [2]$$

in which  $\theta_a$  is the apparent contact angle and  $f_r$  is the roughness factor that corrects the contact area.

There is another possibility of wetting rough surfaces, the Cassie-Baxter state (Cassie and Baxter, 1944). If the liquid doesn't fill all the space over the surface, there will be air pockets remaining between the solid and the liquid phase (Figure 1e). In this situation the contact area between solid and liquid decreases and the contact area of these phases with air increases. For that, if the Cassie-Baxter state occurs, the apparent contact angle always increases when compared with the ideal flat surfaces, no matter if their nature is hydrophobic or hydrophilic. The Cassie-Baxter model can also be used for heterogeneous surfaces.

The Cassie-Baxter state is given by Eq. (3):

$$\gamma_{sl} \cos \theta_a = \sigma_{sl} (\gamma_{sa} - \gamma_{sl}) + \sigma_{la} (\gamma_{la}) \quad [3]$$

in which  $\sigma_{sl}$  and  $\sigma_{la}$  are, respectively, the interfacial contact area between solid and liquid, and liquid and air phases.

As the roughness can significantly change the contact angles of a material, it is possible to achieve, by physical modification, superhydrophobic or superhydrophilic surfaces, which present  $\theta_a > 150^\circ$  or  $\theta_a < 10^\circ$  respectively.

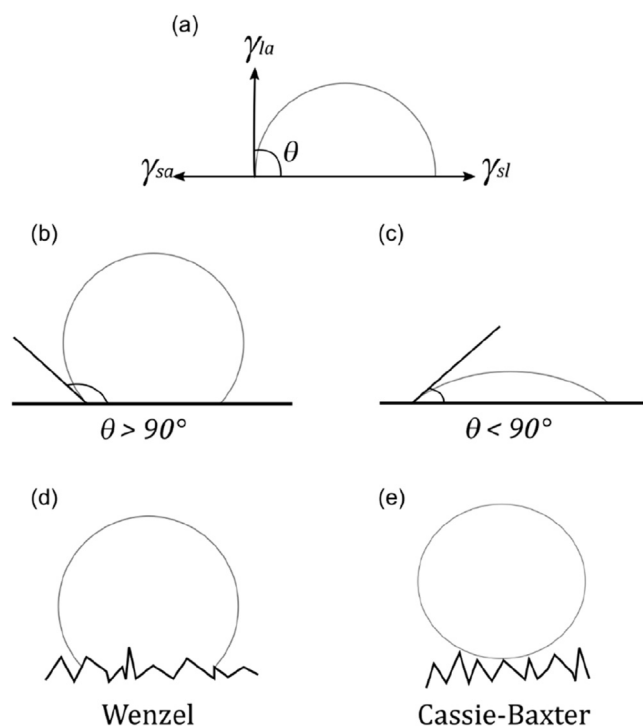
Works on literature show that superhydrophobic surfaces can prevent adhesion of contaminants (Barthlott and Neinhuis, 1997; Lejars et al., 2012; Bixler et al., 2014; Schmüser et al., 2016) but are not efficient when dealing with inorganic scaling process (Signorelli et al., 2019). On

the other hand, slippery lubricated surfaces, which are surfaces covered by an oil attached to their rough structure, work well not only preventing adhesion onto them (Wong et al., 2011; Shillingford et al., 2014) but also avoiding heterogeneous nucleation over the surfaces, such as occurs in inorganic scaling (Grinthal and Aizenberg, 2014; Subramanyam et al., 2014; Charpentier et al., 2015; Sousa et al., 2017; Signorelli et al., 2019).

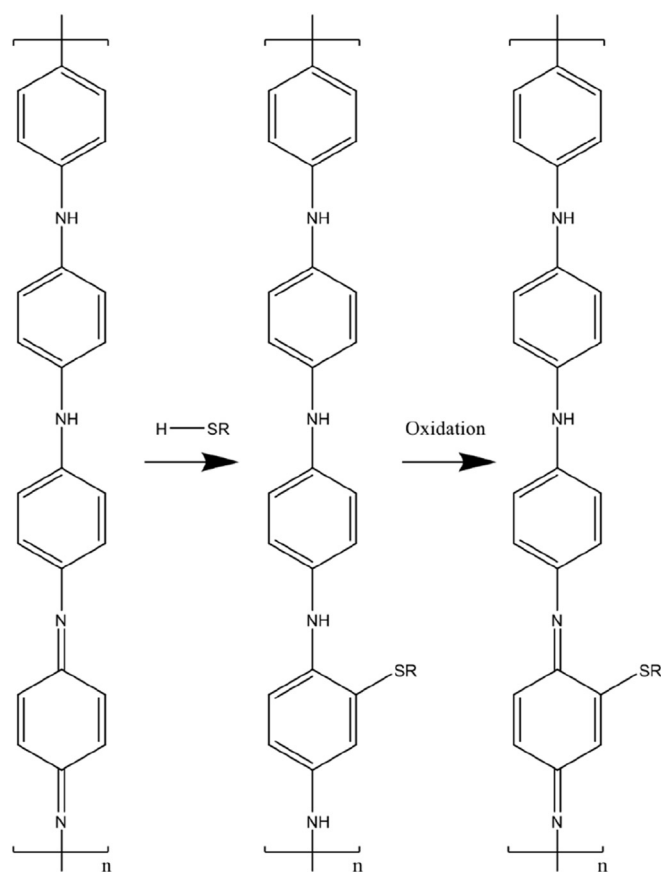
Perfluorinated oils are widely used as lubricant oil in many works in the literature about slippery lubricated surfaces (Wong et al., 2011; Charpentier et al., 2015; Gao and Guo, 2018; Signorelli et al., 2019) because of the low polarizability provided by the fluorine atoms in the molecular structure, which results in their well-known immiscibility with water as well as with hydrocarbons (Wong et al., 2011).

Despite their qualities, slippery lubricated surfaces suffer with the depletion of oil during their use (Baumli et al., 2019). Thus, aiming at offshore oil production application, the need of lubricant oil replenishment is disadvantageous, for it would mean the stop of production and/or replacement of equipment. Alternatively, it would be possible to use the very own petroleum as lubricant oil, since it is available in the medium and could refill the surface, maintaining its lubrication.

For this purpose, the objective of this work is to assess if petroleum, in spite of its complexity, presents the inorganic anti-scaling property that is known of perfluorinated oils, in terms of the anti-scaling capacity itself and also its stability in such system. For that, polyaniline surfaces were used as substrates for scaling tests. They had their topography assessed by electron microscopy and their interfacial tension with brine varied by functionalization with thiol. The scaling tests were carried out in still and flow conditions for petroleum-lubricated samples and non-lubricated ones. The amount of scaling was assessed after the jar test by optical microscopy.



**Figure 1.** Two-dimensional representation of (a) a droplet and a flat surface, showing the interfacial tensions and the contact angle, as stated by Young; (b) hydrophobic and (c) hydrophilic surfaces; and (d) Wenzel and (e) Cassie-Baxter models at rough surfaces.



**Figure 2.** Mechanism of the functionalization of the polyaniline by a thiol group, which resists after oxidation (Bergman and Hanks, 2000).

**Table 1.** Composition of the Brazilian petroleum used in his work. The percentages are given in weight.

$^{\circ}$ API	Saturated	Aromatics	Resins	Asphaltenes	Asphaltenes C51/IP143/84
27.9	53%	24%	21%	2.2%	3.6%

## 2. Materials and methods

Disks and cylinders made of 316 stainless steel, polished with 1600 mesh sandpaper, were used as work electrodes onto which the electropolymerization of polyaniline took place in a galvanostatic method of three-electrode cell. A platinum plate was used as counter electrode and Ag/AgCl (6.0726.100 Metrohm) was used as reference electrode. The electropolymerization was conducted in a 4% (v/v) aqueous solution of aniline (Sigma-Aldrich Brazil, 99% purity, distilled twice) and a 1 mol/L  $H_2SO_4$  (Synth Brazil, PA - ACS) with current set at 1 mA by a potentiostat/galvanostat Metrohm Autolab PGSTAT128N. The electrochemical reaction was carried out for 10 min for the disks and 1 h for the cylindrical substrates. The disks were exposed to solution with one round face, sizing 1.26 cm<sup>2</sup> of area, by the meniscus method. The cylinders were sunk into water and had their inferior base and all the round side exposed to the solution, sizing 7.82 cm<sup>2</sup> of area. After the reaction was concluded, the samples were gently washed in deionized water followed by sinking in ethanol to remove unbound oligomers (Guo and Zhou, 2007).

The surface morphology of the polyaniline was assessed by field emission scanning electron microscopy (FESEM) with a FEI Quanta FEG 250 microscope. The samples were assessed with 10 kV of acceleration voltage and no metallization.

The polyaniline surfaces were functionalized by nucleophilic attack of thiol group (Figure 2) (Bergman and Hanks, 2000). For that, the sample surfaces were sunk into a 5 mmol/L solution of 1-dodecanethiol (Sigma-Aldrich Brazil, 98% purity) in isopropyl alcohol. The surfaces were assessed, before and after the functionalization, by static contact angle measurements, made with 10  $\mu$ L droplets of deionized water and carried out in a DSA100 Krüss goniometer with Teflon needle and Advance software.

For lubrication with oil, a 50  $\mu$ L droplet of petroleum, enough to exceed the capacity of the functionalized surface, was dropped over it. The surface was completely covered and impregnated by capillarity. The petroleum was provided and had its composition determined by PETROBRAS, using the SARA methodology for  $^{\circ}$ API, saturated, aromatic, resins and asphaltene contents and the IP143/84 methodology (IP 143/84, 1988) for the asphaltene precipitated with n-pentane (C51). The petroleum composition is shown in Table 1.

The scaling tests were performed in an aqueous media that simulates the composition of the formation water from pre-salt region in Brazilian offshore oil wells, in which the mainly scaling salts are calcium, barium and strontium sulfates and carbonates. Two brines were prepared, one containing the cations chlorides of the scaling salts and other containing the sodium anions of the scaling salts. Table 2 reports the compositions of

**Table 2.** Composition of brines used in scaling test.

Salts	Cations chlorides brine (g L <sup>-1</sup> )	Sodium anions brine (g L <sup>-1</sup> )
Na <sub>2</sub> SO <sub>4</sub>	—	0.0414
NaCl	180.8250	228.0267
KCl	9.4228	—
CaCl <sub>2</sub> ·2H <sub>2</sub> O	84.6521	—
MgCl <sub>2</sub> ·6H <sub>2</sub> O	28.0756	—
BaCl <sub>2</sub> ·2H <sub>2</sub> O	0.5598	—
SrCl <sub>2</sub> ·6H <sub>2</sub> O	16.3241	—
NaHCO <sub>3</sub>	—	1.5484
NaBr	—	2.6372
CH <sub>3</sub> COONa	—	0.3068

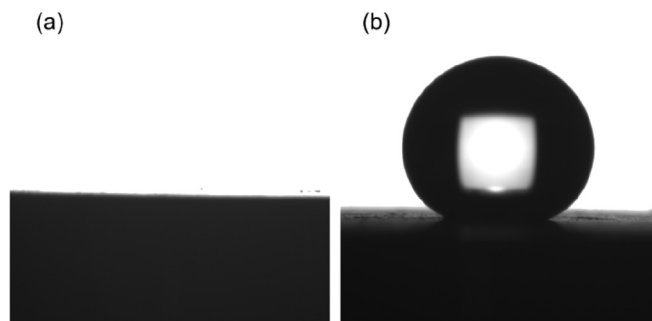
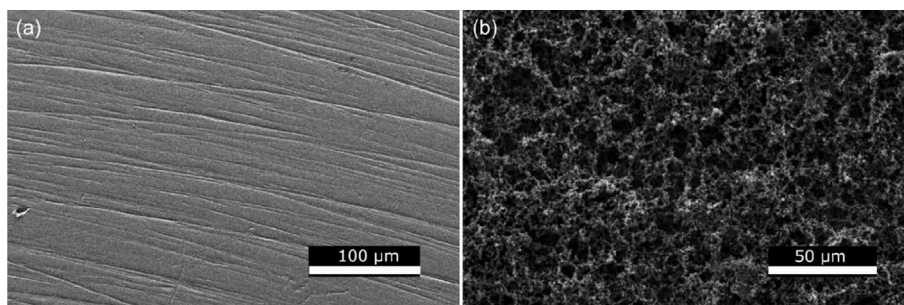
the brines. The test was conducted at 56 °C by mixing 60 mL of each brine at once in a jar test, producing a supersaturated solution that starts precipitation and scaling processes.

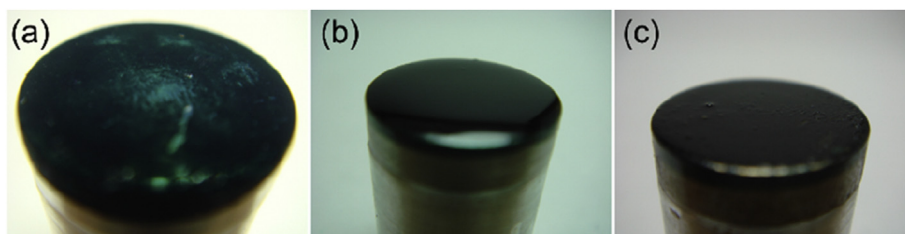
The disk samples coated with functionalized polyaniline, both lubricated and non-lubricated, were exposed to the scaling test, sunken perpendicularly to the water surface, for 16 h. The cylinder samples were exposed to the test, also perpendicularly to the water surface, for 90 min while connected to a rotor at 2000 rpm to simulate flux condition. In this case, only the lubricated surfaces were tested.

The results of the scaling tests were evaluated by optical reflectance microscopy with a Microtonal microscope.

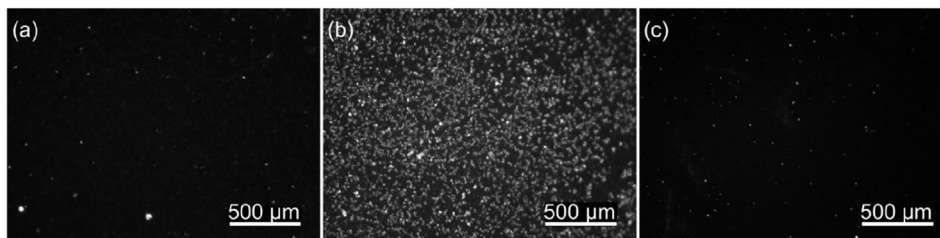
## 3. Results and discussion

For a lubricant oil to stay impregnated over a surface, two requirements shall be fulfilled: the topography of the surface needs to present a hollowed structure where the oil could permeate, preferably with an intricate roughness, such as in hierarchical structures, that leads to a higher contact area between the solid and oil, increasing their

**Figure 4.** Static contact angle measurements of deionized water droplet onto electropolymerized polyaniline (a) before and (b) after functionalization with 1-dodecanethiol.**Figure 3.** FESEM image of (a) stainless steel 316 substrate and (b) polyaniline electropolymerized onto the stainless steel 316.



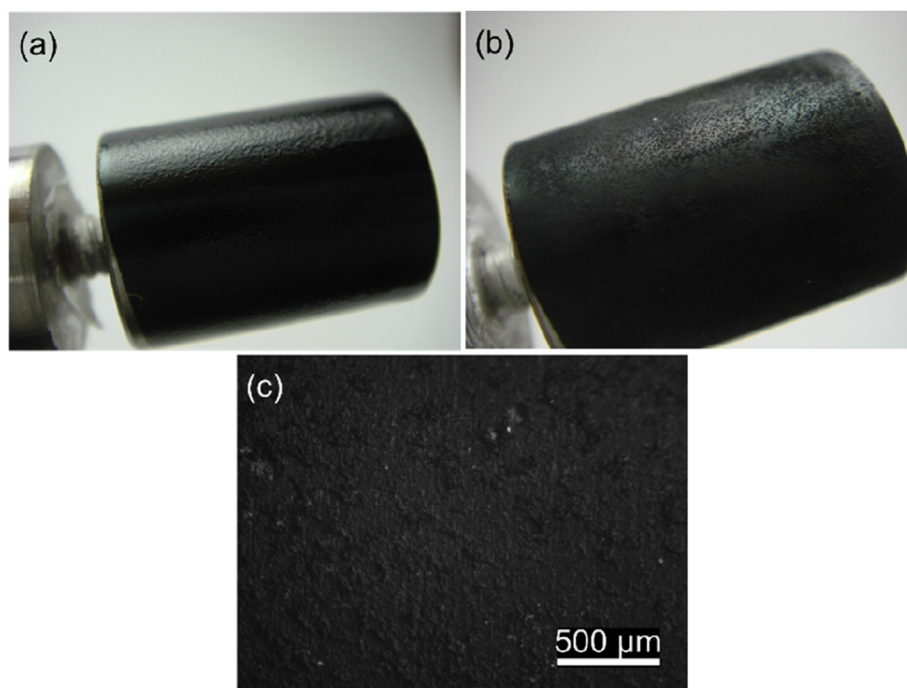
**Figure 5.** Photographs of 316 stainless steel disk samples coated with electropolymerized polyaniline (a) before the scaling test and non-lubricated, (b) before the scaling test and lubricated and (c) after the scaling test and lubricated.



**Figure 6.** Images of optical reflectance microscopy of the functionalized polyaniline (a) lubricated and before the scaling test, (b) non-lubricated and after the scaling test and (c) lubricated and after the scaling test.

interaction and thus, reducing the fraction of oil disposable to the aqueous medium; and the chemical properties of the surface must promote favorable interaction with the lubricant oil in order to increase its adhesion onto the high surface area of the hierarchical structure (Nosonovsky, 2011). The electropolymerization of polyaniline onto flat 316 stainless steel leads to an intensely textured surface with interconnected hollows, as can be seen in the FESEM micrograph (Figure 3b). This morphology fits to the purpose of being filled with a lubricant oil to produce a slippery surface and works as a good substrate to test the petroleum effectiveness on such application. Moreover, the polyaniline has the advantage of being easily functionalized by thiol groups (Bergman and Hanks, 2000), that can be used to change the chemical affinity of the surface.

The functionalization of polyaniline with 1-dodecanethiol has as objective changing the hydrophilic property of the surface to a hydrophobic one because of its low polarity hydrocarbon chain. This is an important step to keep the lubricant oil wetting the surface instead of being replaced by water. The functionalization was confirmed by static contact angle tests. Before the functionalization, the surface completely absorbs the droplet of water into its hollows (Figure 4a). After the functionalization, the droplet does not stick onto the surface, remaining adhered to the needle and rolling off the surface if dropped over it which clearly shows a superhydrophobic behavior. Using a Teflon needle and spotting the droplet onto a defect point, we could measure a contact angle of  $147,3^\circ$  (Figure 4b).



**Figure 7.** Photographs of 316 stainless steel cylindrical samples coated with electropolymerized polyaniline, functionalized and lubricated with petroleum (a) before the scaling test and (b) after the scaling test, and (c) optical reflectance micrograph of this surface after scaling test.



The scaling tests were performed with an excess of petroleum in the beginning of the experiment (Figure 5b). After its conclusion, it is possible to see that the excess of oil is lost during the test, but the surface remains lubricated (Figure 5c).

The results of optical reflectance microscopy show no scaling onto the lubricated surface after the test (Figure 6c), which looks just like before the test (Figure 6a). Furthermore, when compared with the functionalized non-lubricated sample, the anti-scaling property of the former is conspicuous, since the latter presents crystals scaled over the whole surface (Figure 6b).

The inorganic scaling process occurs in the non-lubricated surface because the Cassie-Baxter wetting state, which grants the superhydrophobicity of the surface (Cassie and Baxter, 1944), cannot suppress heterogeneous nucleation onto its sharp relief. Since the contact area between solid and liquid is reduced in the Cassie-Baxter state (Figure 1e), these small points of contact acts like seeds for heterogeneous nucleation (Mullin, 2001). Moreover, the increasing of scale amount is a consequence of the high energy interface between the functionalized polyaniline and the brine (Signorelli et al., 2019).

However, the oily interface with the brine mechanically prevents the heterogeneous nucleation onto the lubricated solid surface and the adhesion of particles from homogeneous nucleation because the liquid/liquid interface offers no spot for solid particles to stick.

Additionally to the results observed in the scaling test, which show that the petroleum lubricated surfaces effectively prevent scaling, the assessment of the maintenance of the oil in flux condition is required.

The results obtained testing the cylindrical surface coupled to a rotor show that this system is also effective against scale formation. Even though some loss of oil was visible after the test (Figure 7b), the remaining amount was enough to prevent the crystals adhesion over the surface (Figure 7c).

These results show that petroleum works as a good lubricant oil for slippery lubricant surfaces in anti-scaling systems such as the perfluorinated oil does (Signorelli et al., 2019) and can be an option for future applications.

#### 4. Conclusions

The slippery lubricated surfaces, that were prepared on 316 stainless steel, covered with electropolymerized polyaniline functionalized with 1-dodecanethiol and lubricated with petroleum, present effective anti-scaling behavior at highly saline medium that simulates offshore facilities condition.

Moreover, scaling tests were made with rotation of the surface samples to add the flux condition of the system. The petroleum remained impregnated at the surface during the experiment time. In such conditions, the slippery surface also presents an effective anti-scaling behavior.

Further studies considering the development of abrasion resistant surface and the flow effect of the lubrication with water onto the surface should be performed. This work presents a first approach of a possible use for petroleum at scaling prevention, which has the advantages of dismissing the use of inhibitors, along with their cost and environmental impact, and might be self-refilled as surface lubricant by the oily medium during the extraction.

#### Declarations

##### Author contribution statement

Filipe Signorelli: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Celso Aparecido Bertran: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

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