

Anti-friction and Anti-wear Surfactant-assisted Nano-onions Stable Formulations for Lubricants

Maria Sarno^{a,b}, Claudia Cirillo^{a,*}, Adolfo Senatore^{b,c}

^aDepartment of Physics "E.R. Caianiello", University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.

^bNANO_MATES, Research Centre for Nanomaterials and Nanotechnology at the University of Salerno, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.

^cDepartment of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.

ccirillo@unisa.it

Carbon nano-onions (CNOs) have been synthesized by the catalytic decomposition of methane at atmospheric pressure. The catalyst was prepared by a reduction-substitution method. The produced CNOs have a regular shape with concentric carbon layers with an external diameter of about 50 nm. A systematic study of their stability in Group I and III base oils, with and without low amounts of dispersant/surfactants, was performed, revealing the effectiveness of the synergistic combination of SDBS and Tween 80. Tribological tests showed a significant reduction of friction coefficient and wear scar diameter up to 23 % and 20 %.

1. Introduction

Carbon nanomaterials are widely studied and used in a range of applications, including electronics, energy storage, tribology,... However, two kinds of carbon nanoparticles, nanodiamond (Mochalin et al., 2012) and carbon onions (Butenko et al., 2013), discovered before fullerenes and nanotubes, stayed for a long time in the shadow of more popular and better-investigated nanocarbons. However, both of them have become increasingly studied in recent years. Carbon onions, also called carbon nano-onions (CNOs) or onion-like carbon (OLC), consist of spherical closed carbon shells and owe their name to the concentric layered structure resembling that of an onion. Carbon nano-onions present a structure similar to inorganic MoS₂ fullerenes, but they are exclusively made of carbon, and they are not hollow in the center. Thus, we may expect that this carbon species also can present interesting tribological properties, as already suggested in the literature (Matsumoto et al., 2007; Joly-Pottuz et al., 2008).

Lubricating oils are of fundamental relevance in order to ensure proper operation of machines by protecting them from damages caused by wear, friction, and heat, but the current lubricants have achieved their performance limits. However, control at the nanoscale has been recently recognized as a key factor for further improvement of additive formulation in terms of wear and friction reduction, as well as of energy efficiency and environmental sustainability. To guarantee good tribological performance, leading to a reduction of friction and wear even under heavy load conditions and long-time operations, nano-additives such as carbon nano-onions, thanks to their inert structure, can be used.

For nano-additives stability improvement, two approaches can be followed: either the use of a dispersant or a surface modification by surfactants. A lot of research has been performed around the possibility of using surfactants in a wide range of applications, also other than lubrication, such as oil and impurities recovery, dehydration (or hydration), detergents processes, for pharmaceuticals, etc. (Sharma and Mahajan, 2012; Biswal and Paria, 2014; Posocco et al., 2016, Von Rybinski and Schuwuger, 1986). Mixtures of surfactants can have a potentially improved possibility to modify interfacial properties (Bera et al., 2013; Mohammad et al., 2013). The presence of the synergistic combination of surfactants generally shows more easily the formation of micelles and surface modifications (Zhang and Zhu, 2010). The simultaneous use, for instance, of two surfactants, thanks to the interactions between the two different species with different synergistic properties, can more easily lead to the formation of micelles, i.e., overcome either repulsion forces, typical for ionic molecules, or steric hindrances, as in the case of non-ionic molecules. Moreover, different functionalities can

contribute to generating multi-contact points on mixed behavior surfaces, favoring interaction and dispersibility (Sheikh and ud-Din, 2011; Gharibi et al., 2000; Razavizadeh et al., 2004; Sohrabi et al., 2008; Rosen and Zhou, 2001). In this study, mineral oil-based lubricants, such as polyalphaolefins (PAO) and Group III base oils were chosen because they are typically used for industrial gears and widely adopted in the automotive field in manual and automatic transmissions. In particular, to enhance tribological properties of lubricating oils by adopting stable nano-additives and without substantially modifying oil rheological properties, carbon nano-onions were synthesized through simple and scalable processes. Afterward, a systematic study of their stability in Group I and III base oils, with and without low amounts of dispersant/surfactants, was performed, revealing the effectiveness of the synergistic combination of SDBS and Tween 80. Tribological tests showed a significant reduction of friction coefficient and wear scar diameter up to 23 % and 20 %, respectively. Moreover, a substantial reduction in the surface roughness was also recorded, both at ambient temperature and 80 °C, due to the addition of the 0.1 wt. % of carbon nano-onions.

2. Experimental

2.1 Materials and Methods

Iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), sodium borohydride (NaBH_4), ethanol, and dilute hydrochloric acid (0.5 mol/L HCl) were purchased from Sigma-Aldrich. All the chemicals are of analytical grade and used as received. Cylinder gases (99.998 pure methane, 99.999 pure nitrogen, and 99.9990 pure hydrogen) were purchased from SOL Spa.

2.2 Lubricant Bases and surfactants/dispersants

Two different bases were chosen for this study:

- ETRO IV (Group III) base, whose family commercial name after the addition of further additives, for fully formulated oil, is SYNPLUS by RILUB SPA, named as SYNPLUS in the following study.
- SN150 and BS150 mixture (Group I), whose family commercial name after the addition of further additives, for fully formulated oil, is EUBUSH by RILUB SPA, named as EUBUSH in the following study.

The synthesized carbon nano-onions were dispersed in SYNPLUS both with and without dispersants/surfactants, whereas stability in EUBUSH was quite high (see Table 1); therefore no further dispersants were added into the latter oil.

The adopted dispersants are the following ones: 1,8 diamionaphthalene, sodium dodecylbenzenesulfonate (SDBS), Tween 80, and a commercial dispersant (HiTEC@646E Performance Additive - Polyisobutylene Succinimides), in the following called PS. According to the type of dispersant/surfactant adopted, four groups of samples have been prepared: i) A mixture of CNOs and 1,8 diamionaphthalene in 100 mL of water with a weight ratio of 1:8 was prepared, followed by sonication for 20 minutes and drying at 80 °C. ii) A mixture of CNOs and SDBS was prepared in 100 mL of bidistilled water with a weight ratio of 1:10, followed by a 20 minutes sonication at 45 °C, drying under air for 24 hours, centrifugation for 30 minutes at 7500 rpm, and eventually drying at 80 °C. iii) A mixture of CNOs, SDBS, and Tween 80 was prepared with a weight ratio of 1:5:5 in 100 mL of bi-distilled water, followed by sonication for 20 minutes at 45 °C, drying under air for 24 hours, centrifugation for 30 minutes at 7500 rpm and finally drying at 80 °C. iv) A mixture of CNOs at different percentages (0.05 wt. %, 0.1 wt. % and 1 wt. %) and 2 wt. % of PS was prepared.

After this preliminary procedure, mixtures of the base oils and the as-obtained nanomaterials at three weight percentages (0.05 wt. %, 0.1 wt. %, and 1 wt. %) were prepared through sonication and homogenization.

In order to test dispersion stability in SYNPLUS, UV-Vis spectroscopy and periodic centrifugation were performed. After nanomaterials had been dispersed into the base oil through a homogenizer, the dispersions were precipitated through centrifugation carried out at 1000 rpm for 30 minutes, and the resulting supernatant was tested with a UV-Vis spectrophotometer. Eventually, the absorbance ratio between the absorbance before and after centrifugation (named as A ratio in the present study) was evaluated, taking advantage of the proportionality between absorbance and concentration.

2.3 Catalyst preparation

In a typical procedure, 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ powder was dissolved in 500 ml distilled water with constant stirring until the solution became transparent. Then NaBH_4 aqueous solution (0.03 M) was dropped into the FeCl_3 solution to reduce Fe^{3+} to elementary Fe precipitate. After the reducing reaction, the black iron precipitate was washed using HCl (0.5 mol/L) to eliminate boron hydroxide and filtered with distilled water three times. 0.05 M NiCl_2 ethanol solution was then dropped gradually onto iron precipitates, during which Ni^{2+} were reduced to nickel nanoparticles coating on the iron nanoparticles due to the substitution reaction. Thus, the Ni-Fe bimetallic particles formed. Ultimately, the as-prepared Ni-Fe bimetallic particles were filtered and dried in the air in order to be employed in the subsequent growth of carbon nano-onions.

2.4 Carbon nano-onions preparation

The synthesis of CNOs was carried out by the catalytic decomposition of methane (Sarno et al., 2012; Ciambelli et al., 2004; Sarno et al., 2014; Sarno et al., 2016) over the as-prepared Ni–Fe catalyst. In a typical synthesis, 500 mg of catalysts were placed in a quartz boat placed inside a horizontal tubular quartz furnace. Prior to the catalytic decomposition reaction, the catalyst was pre-reduced at 400 °C h in hydrogen flow for 1.5 h to reduce the oxides generated in the drying process. Successively, the synthesis of CNOs was conducted using a mixture of methane and nitrogen, with a flow rate ratio of 20/100 ml, at the temperature of 850 °C for 1 h. After the reaction, the samples were cooled to room temperature in a nitrogen atmosphere.

2.5 Catalyst and carbon nano onions characterization

The catalyst and the obtained carbon nano-onions were characterized by using several techniques. XRD measurements were performed with a Bruker D8 Advance X-ray diffractometer using CuK α radiation. TEM images were acquired using a FEI Tecnai electron microscope, operating at 200 kV with a LaB6 filament as the source of electrons, equipped with an energy-dispersive X-ray spectroscopy (EDX) probe. For the preparation of the TEM sample, drops of CNOs suspension in ethanol were deposited on carbon-coated electron microscope grids. Raman spectra were obtained at room temperature with a micro-Raman spectrometer Renishaw inVia with a 514 nm excitation wavelength (laser power 30 mW). A Leica DMLM optical microscope connected on-line with the instrument allowed collecting optical images. In order to test dispersion stability, tests with a UV-vis spectrophotometer (Thermo Fisher, Evolution 60S) were performed.

2.6 Tribological tests description

The tribometer adopted in this study is a Ducom TR-BIO-282 with a setup for performing reciprocating sliding tests in both dry and lubricated contacts, with specimens of several shapes/sizes in order to enable application of a broad range of contact pressures. The investigated tribopair is made up of an upper X45Cr13 steel ball (diameter of 6 mm, 52–54 HRC), with a reciprocating motion, and a lower X210Cr12 steel disc (thickness of 6 mm, a diameter of 25 mm, roughness Ra of 0.30 μ m, 60 HRC), immersed in a lubricant bath with electrical resistances as a heating source. The sliding motion, characterized by a triangular speed profile, was set up with a frequency of 10 Hz, a stroke of 5 mm, as well as a maximum and a mean sliding speed for each stroke of 240 mm/s and 120 mm/s respectively. As for the evaluation of the coefficient of friction and the wear scar diameter, the error of each value was determined as the average of the errors over 3 tests.

The normal load produced through a dead weight-based lever system was 19 N, and the corresponding average Hertzian pressure at the tribopair interface was 1.17 GPa. Experiments were carried out at both ambient temperature and 80 °C, and the mean lubricant temperature was kept constant by means of a temperature-based feedback control system. The data reported in the following refers to the ones obtained at ambient temperature unless otherwise indicated.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the as-prepared catalyst and carbon nano-onions are shown in Figure 1a e 1b. In Figure 1a, the peak at $2\theta = 35.3^\circ$ is attributed to nickel ferrite phase (NiFe₂O₄) (Menzel et al., 2001) formed in the surface layer of the catalyst due to the oxidizing reaction of nickel and iron during the drying process, while the peak at $2\theta = 44.4^\circ$, is attributed to α -Fe(Ni) alloy, also called kamacite.

In Figure 1b, the peak at $2\theta = 26.9^\circ$ can be assigned to the graphite (0 0 2), indicating the formation of the high crystalline graphite during the growth (Guadagno et al., 2015). It can also see peaks at 44.5° due to kamacite and peaks at $2\theta = 43.6^\circ$, 50.7° and 74.4° due to γ -Fe(Ni) alloy, also called taenite.

Figure 2a and Figure 2b show, respectively, the Raman spectrum of the synthesized CNOs and the optical image where the measurement was performed. There are two broad peaks, D band centered at around 1343 cm^{-1} and G band centered at around 1575 cm^{-1} , respectively. The D band indicates the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite, while the G band represents the vibrations in all sp² bonded carbon atoms in a two-dimensional hexagonal lattice (Flahaut et al., 2012). For the produced CNOs, the I_D/I_G ratio, which implies the degree of crystalline perfection, is 0.82, revealing that our CNOs have high crystallinity. Figure 2c shows high magnification TEM images of the produced CNOs. The carbon nano-onions have a quasi-spherical shape with concentric carbon layers having external diameter of about 50 nm. The obtained CNOs are of high purity, and no other carbon nanostructures such as carbon nanotubes (CNTs) are present.

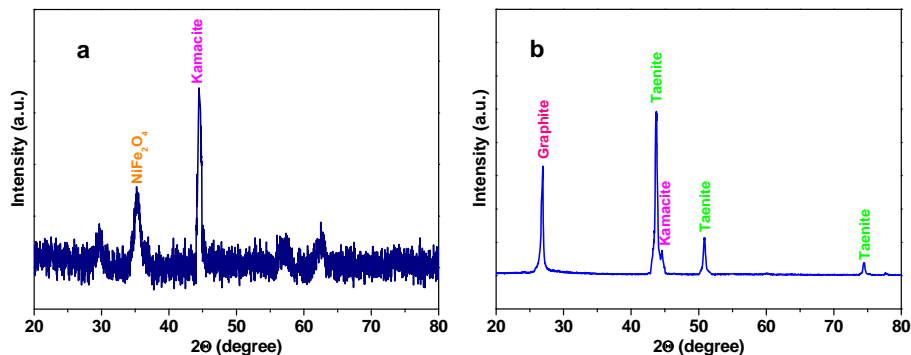


Figure 1: XRD patterns of as-prepared catalyst and prepared carbon nano-onions

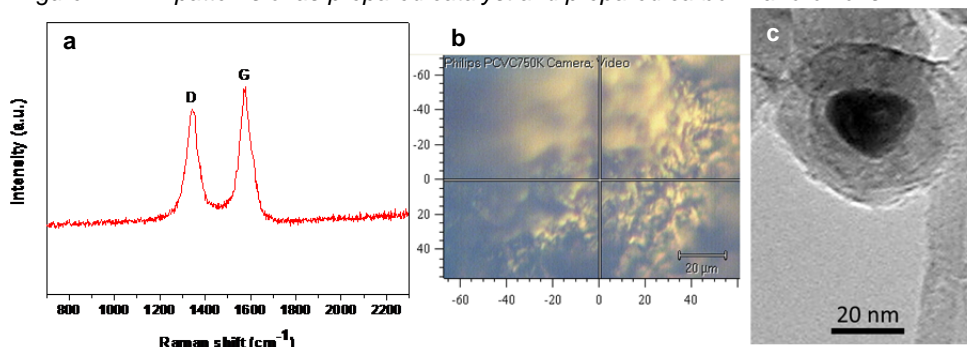


Figure 2: Raman spectrum (a), optical image (b) and TEM image (c) of the synthesized CNOs

4. Stability dispersion tests

The stability in SYNPLUS was analyzed in the presence of different surfactant/dispersant agents, while the stability in EUBUSH was found very high. In particular, the A ratio, obtained under UV-Vis, with different concentrations of CNOs, were reported in Table 2.

Table 1: Stability of free formulations in EUBUSH.

CNOs concentrations (wt.%)	Surfactant/dispersant	A ratio
0.05	/	0.87
0.1	/	0.89
1	/	0.75

Table 2: Stability of surfactant/dispersant-assisted and free formulations in SYNPLUS.

CNOs concentrations (wt.%)	Surfactant/dispersant	A ratio
0.05	/	0.43
0.05	1,8 diamionaphthalene	0.72
0.1	1,8 diamionaphthalene	0.53
1	1,8 diamionaphthalene	0.12
0.05	SDBS	0.75
0.1	SDBS	0.63
1	SDBS	0.34
0.05	SDBS & Tween 80	0.91
0.1	SDBS & Tween 80	0.92
1	SDBS & Tween 80	0.53
0.05	PS	0.90
0.1	PS	0.91
1	PS	0.38

In the case of the presence of SDBS +Tween 80 surfactants and PS dispersants, the stability is strongly dependent on concentration. The combination of the two surfactants ensures higher stability for all the time of the investigation.

5. Tribological characterization

The results of the tribological tests performed on SYNPLUS are summarized in Table 3. Reduction of Coefficient of Friction (CoF) and Wear Scar Diameter (WSD) was recorded for the synthesized dispersant and surfactants-enhanced CNOs in SYNPLUS at three different concentrations (0.05 wt. %, 0.1 wt. %, and 1 wt. %). As shown in Table 3, CNOs, with a concentration at 0.1 wt.%, exhibit the best tribological performance, showing a mean reduction during 160 min operation of CoF and WSD, at ambient temperature, of 23 % and 20 %, respectively. At 80 °C the reductions are 21 % and 19 %, respectively, at an optimum concentration of 0.1 wt. %. This highlights the role of the nano-additive, which, indeed, at higher temperatures where the base viscosity decreases, locally precipitates on the metal surfaces in contact by protecting them. At higher concentration, the tribological performance are reduced. This is probably due to the fact the CNOs come closer to each other and tend to agglomerate. In Table 4, the results of the tribological tests performed on EUBUSH are also reported. A comparison between the two CNOs loaded oil at 0.1 wt. % was reported in Figure 3. The reductions are rather similar, highlighting the role of the additive.

Table 3: COF (%) and mean wear scar diameter reduction (%) for different formulations in SYNPLUS after 160 min of operation.

CNOs Concentration (wt. %)	Surfactant/dispersant	COF reduction (%)	Mean wear scar diameter reduction (%)
0.05	SDBS & Tween 80	18.0±1.3	8.4±1.0
0.1	SDBS & Tween 80	23.0±0.9	20.0±0.9
1	SDBS & Tween 80	5.3±0.3	8.0±0.4
0.05	PS	16.0±0.9	12.1±1.3
0.1	PS	14.0±1.2	13.1±1.9
1	PS	12.2±1.3	10.0±0.8

Table 4: COF (%) and mean wear scar diameter reduction (%) for different formulations in EUBUSH after 160 min of operation.

CNOs Concentration (wt. %)	Surfactant/dispersant	COF reduction (%)	Mean wear scar diameter reduction (%)
0.05	/	13.0±1.4	10.3±0.9
0.1	/	15.0±0.7	11.1±0.2
1	/	7.0±0.6	6.3±0.5

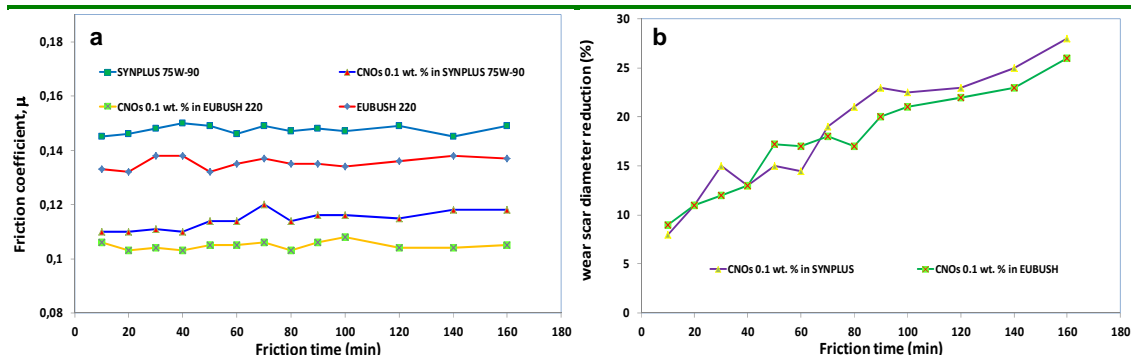


Figure 3. For SYNPLUS alone, EUBUSH alone, and both oils with CNOs at 0.1 wt. %, evolution over friction time of wear scar diameter reduction % (a), and friction coefficient (b). SDBS + Tween 80 surfactant mixture was added to the samples in SYNPLUS.

6. Conclusions

Carbon nano-onions have been prepared by catalytic chemical vapor deposition in the presence of methane at atmospheric pressure on a Ni-Fe catalyst at 850°C. The synthesized CNOs have an external diameter of about 50 nm. Tribological tests showed a significant reduction in both base oils of CoF and WSD, especially for the 0.1 wt. % (up to 23 % and 20 % in SYNPLUS).

References

Bera A., Ojha K., Mandal A., 2013, Synergistic Effect of Mixed Surfactant Systems on Foam Behavior and Surface Tension, Journal of Surfactants and Detergents, 16, 621–630.

- Biswal N.R., Paria S., 2014, Interfacial and wetting behavior of natural–synthetic mixed surfactant systems, *RSC Advance*, 4, 9182–9188.
- Butenko Yu.V., Siller L., Hunt M.R.C., 2013, in *Carbon Nanomaterials*, 2nd edition, Y. Gogotsi, V. Presser, Eds., CRC Press, 279–231.
- Ciambelli P., Sannino D., Sarno M., Fonseca A., Nagy J.B., 2004, Hydrocarbon decomposition in alumina membrane: an effective way to produce carbon nanotubes bundles, *Journal of Nanoscience and Nanotechnology*, 4, 779–787.
- Flahaut E., Agnoli F., Sloan J., O'Connor C., Green M.L.H., 2002, CCVD synthesis and characterization of cobalt-encapsulated nanoparticles, *Chemistry of Materials*, 14, 2553–2558.
- Friction and Wear, *Lubricants*, 8, 13.
- Gharibi H., Razavizadeh B.M., Hashemianzaheh M., 2000, New approach for the studies of physicochemical parameters of interaction of Triton X-100 with cationic surfactants, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 174, 375–386.
- Guadagno L., Sarno M., Vietri U., Raimondo M., Cirillo C., Ciambelli P., 2015, Graphene-based structural adhesive to enhance adhesion performance, *RSC Advance*, 5, 27874–27886.
- Joly-Pottuz L., Vacher B., Ohmae N., Martin J.M., Epicier T., 2008, Anti-wear and Friction Reducing Mechanisms of Carbon Nano-onions as Lubricant Additives, *Tribology Letters*, 30, 69–80.
- Matsumoto N., Joly-Pottuz L., Kinoshita H., Ohmae N., 2007, Application of onion-like carbon to micro and nanotribology, *Diamond & Related Materials*, 16, 1227–1230.
- Menzel M., Sepelak V., Becker K.D., 2001, Mechanochemical reduction of nickel ferrite, *Solid State Ionics* 141–142, 663–669.
- Mochalin V. N., Shenderova O., Ho D., Gogotsi Y., 2012, The properties and applications of nanodiamonds, *Nature Nanotechnology*, 7, 11–23.
- Mohammad D.E., Negm N.A., Mishrif M.R., 2013, Micellization and Interfacial Interaction Behaviors of Gemini Cationic Surfactants–CTAB Mixed Surfactant Systems, *Journal of Surfactants and Detergents*, 16, 723–731.
- Posocco P., Perazzo A., Preziosi V., Laurini E., Prici S., Guido S., 2016, Interfacial tension of oil/water emulsions with mixed non-ionic surfactants: comparison between experiments and molecular simulations, *RSC Advance*, 6, 4723–4729.
- Razavizadeh B.M., Mousavi-Khoshdel M., Gharibi H., Behjatmanesh-Ardakani R., Javadian S., Sohrabi B., 2004, Thermodynamic studies of mixed ionic/nonionic surfactant systems, *Journal of Colloid and Interface Science*, 276, 197–207.
- Rosen M.J., Zhou Q., 2001, Surfactant–Surfactant Interactions in Mixed Monolayer and Mixed Micelle Formation, *Langmuir*, 17, 3532–3537.
- Sarno M., Sannino D., Leone C., Ciambelli P., 2012, Evaluating the effects of operating conditions on the quantity, quality and catalyzed growth mechanisms of CNTs, *Journal of Molecular Catalysis A: Chemical*, 357, 26–38.
- Sarno M., Cirillo C., Ciambelli P., 2014, Selective graphene covering of monodispersed magnetic nanoparticles, *Chemical Engineering Journal*, 246, 27–38.
- Sarno M., Cirillo C., Scudieri C., Polichetti M., Ciambelli P., 2016, Electrochemical Applications of Magnetic Core–Shell Graphene Coated FeCo Nanoparticles, *Industrial & Engineering Chemistry Research*, 55, 3157–3166.
- Sharma R., Mahajan R.K., 2012, An investigation of binding ability of ionic surfactants with trifluoperazine dihydrochloride: insights from surface tension, electronic absorption and fluorescence measurements, *RSC Advance*, 2, 9571–9583.
- Sheikh M.S., ud-Din K., 2011, Synergistic interaction of Gemini surfactant pentanediyl-1,5-bis(dimethylcetylammmonium bromide) with conventional (ionic and nonionic) surfactants and its impact on the solubilisation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 378, 60–66.
- Sohrabi B., Gharibi H., Tajik B., Javadian S., Hashemianzadeh M., 2008, Molecular Interactions of Cationic and Anionic Surfactants in Mixed Monolayers and Aggregates, *Journal of Physical Chemistry B*, 112, 14869–14876.
- Von Rybinski W., Schuwuger M.J., 1986, Adsorption of surfactant mixtures in froth flotation, *Langmuir* 2, 639–643.
- Zhang M., Zhu L., 2010, Effect of SDBS–Tween 80 mixed surfactants on the distribution of polycyclic aromatic hydrocarbons in soil–water system, *Journal of Soils and Sediments*, 10, 1123–1130.