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Effect of surfactants adsorption on the structure of bentonite-based sorbents

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4–8 May 2020
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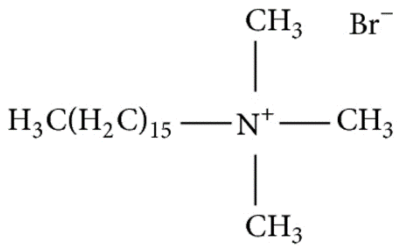
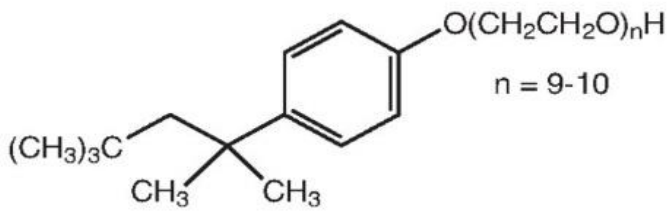
Modification process

hexadecyltrimethylammonium bromide (HDTMA)

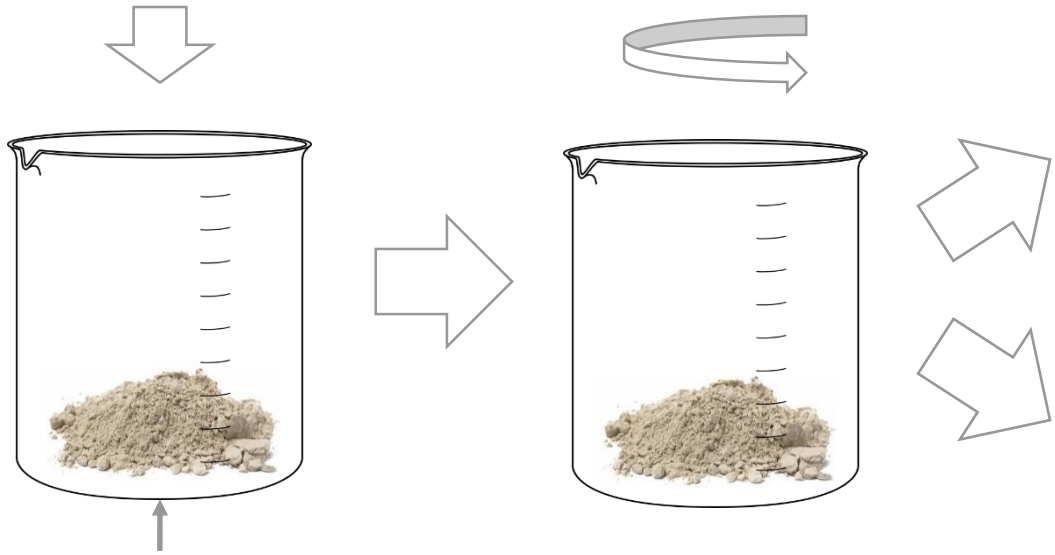


t-octylphenoxypolyethoxyethanol (Triton X-100; TX100)



HDTMA **or** TX-100
48 mmol/100 g

40 °C; 24 h



bentonite

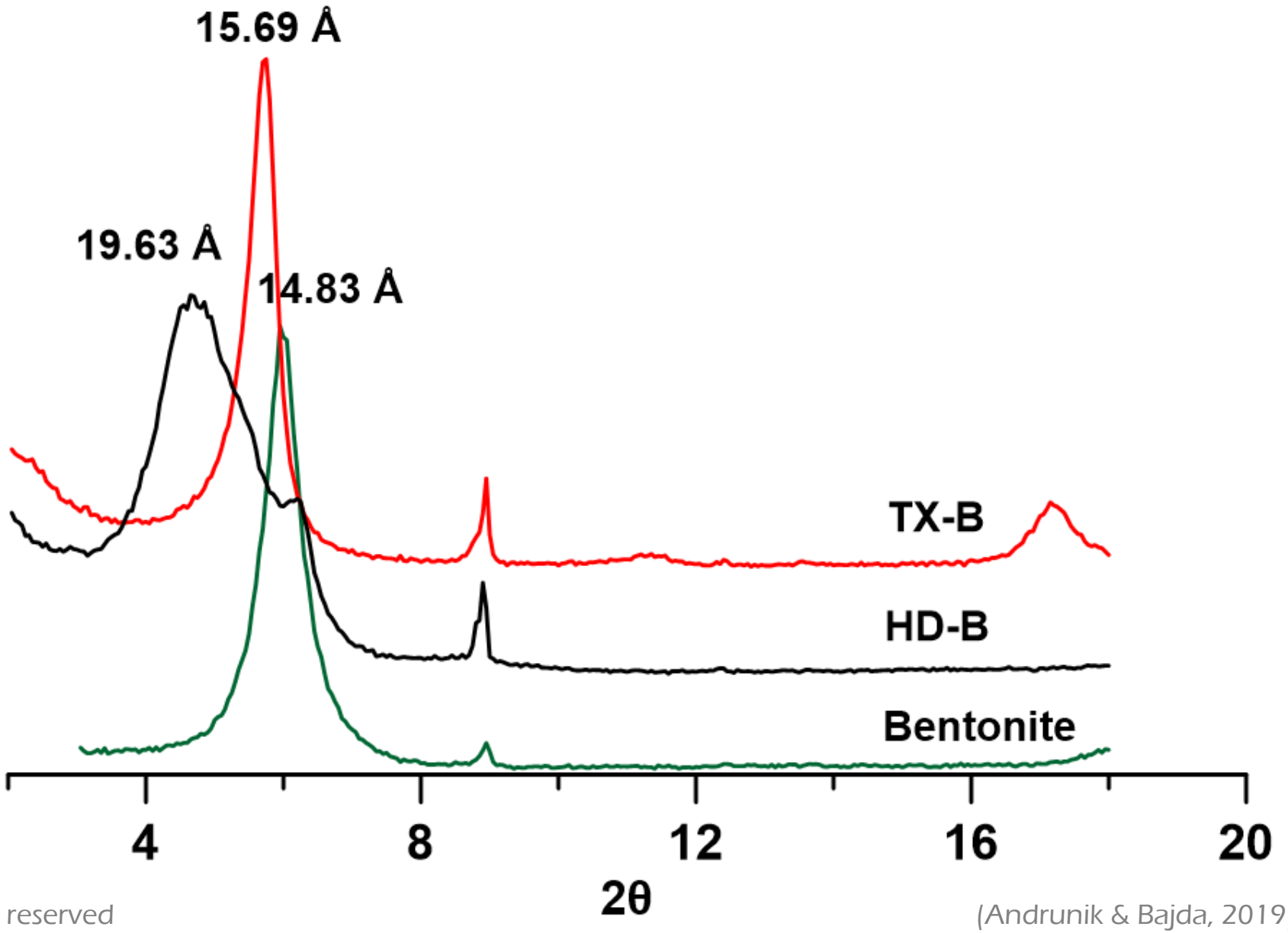
Sample: HD-B

HDTMA +

Sample: TX-B

TX-100 +

XRD results



(Andrunik & Bajda, 2019)

XRD results

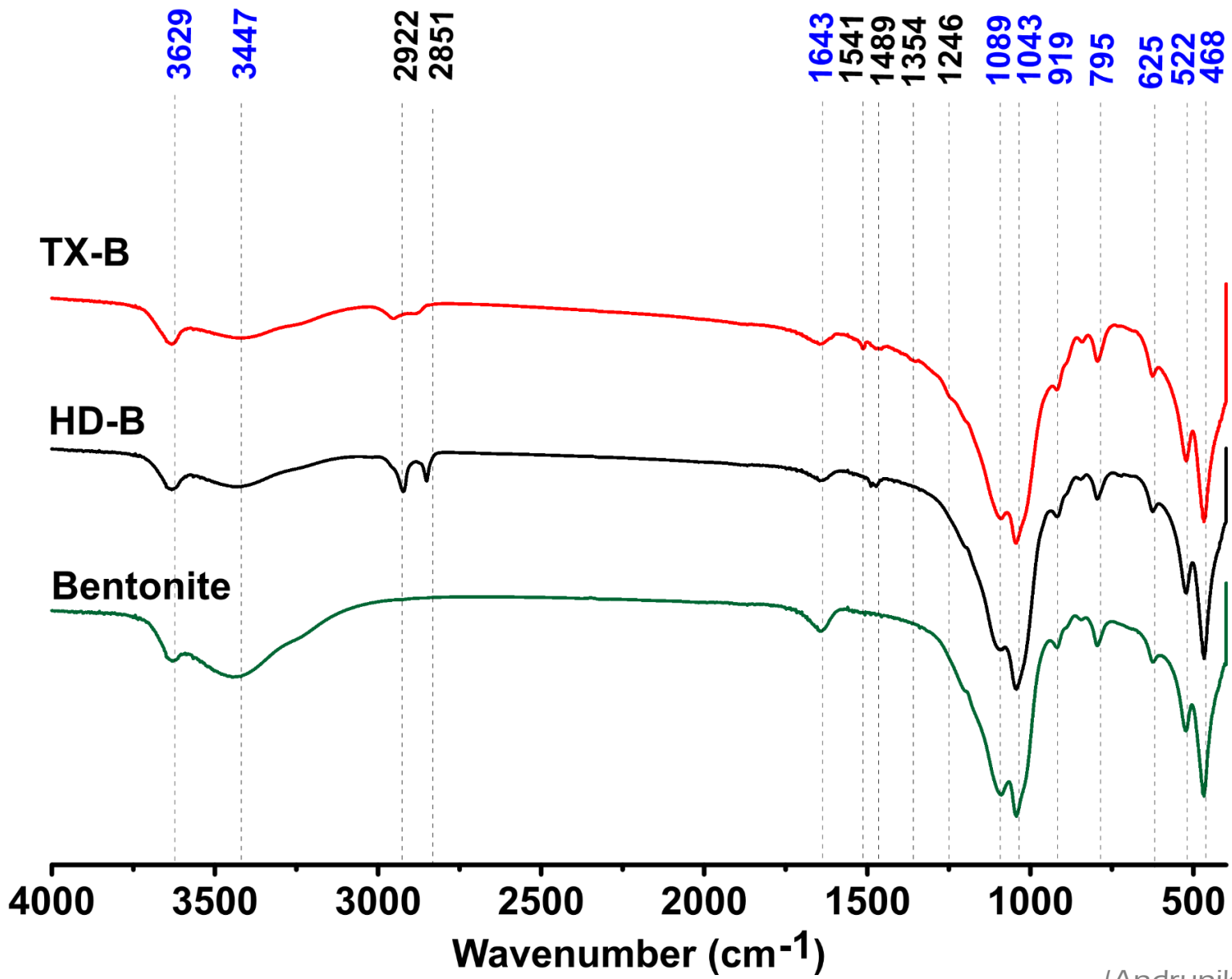
The modification of bentonite with HDTMA (sample HD-B):

- the interlayer space increased to 19.63 Å – the main peak (001) from smectite shifted toward higher interlayer distances
- basal spacing corresponds to bilayer coverage

The modification of bentonite with TX-100 (sample TX-B):

- the interlayer space of smectite expanded slightly – TX100 molecules are too big and cannot intercalate into interlayer space of smectite
- the modification of bentonite with TX100 was seen mostly on the surface

FTIR spectra



blue values—bands derived from natural bentonite;
black values—bands that appear after adsorption of the surfactants

(Andrunik & Bajda, 2019)

FTIR spectra

Position of bands on FTIR spectrum of bentonite:

- 3629 cm^{-1} – stretching vibrations of structural OH groups of bentonite
- 3447 cm^{-1} and 1643 cm^{-1} – H–O–H vibration tensile and deformation vibrations in water
- 1089, 1043, and 468 cm^{-1} – vibration of Si–O–Si
- 522 cm^{-1} – Si–O–Al bridges
- 919 cm^{-1} – deformation vibrations of the Al–Al–O bond
- 795 cm^{-1} and 625 cm^{-1} – stretching vibrations of Si–O bonds.
- 625 cm^{-1} – deformation and bending modes of Si–O and Al–O bonds.
- 795 cm^{-1} – quartz admixture in the sample

FTIR spectra

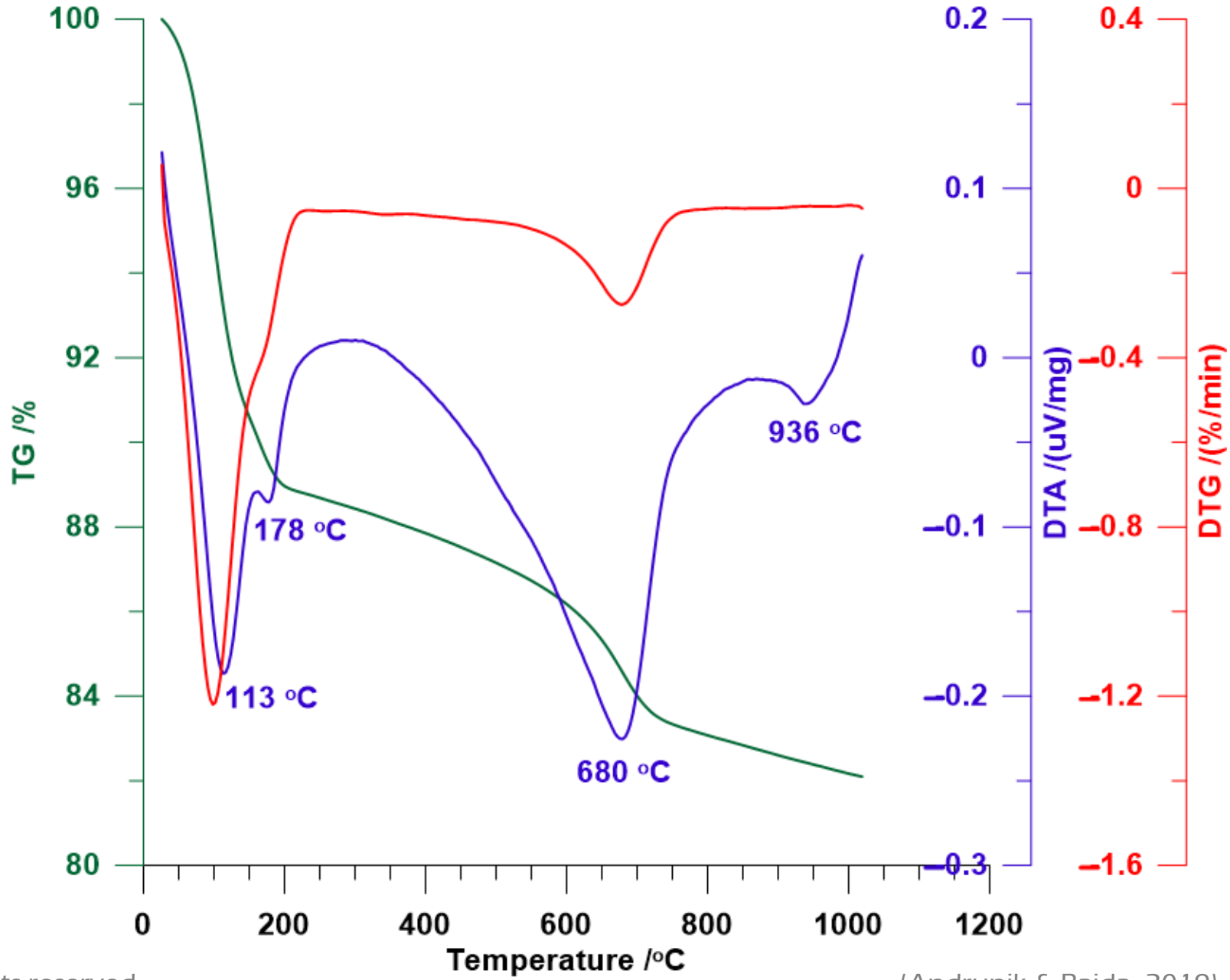
Position of bands on FTIR spectrum of HD-B:

- 3000 to 2800 cm^{-1} – anti-symmetric and symmetric tensile vibrations of methylene groups ($-CH_2$) of the hydrocarbon tails of the surfactants
- 1489 cm^{-1} – bending vibrations of C–H.
- 3447 cm^{-1} and 1643 cm^{-1} – the occurrence of the bands corresponding to the adsorbed water indicate that not all the water has been replaced by surfactant molecules

Position of bands on FTIR spectrum of TX-B:

- new bands are similar to those that occur on the spectra of bentonite modified with HDTMA—all bands characteristic for HDTMA can also be the evidence of the presence of TX100.
- 2922–2851 cm^{-1} – methylene groups ($-CH_2$);
- 1541 cm^{-1}, 1354 cm^{-1}, and 1246 cm^{-1} – CH stretching and bending and CO and OH bending vibrations of TX100 molecules
- 1643 cm^{-1} – C–C bonds of phenyl rings.

TG/DTA curves - bentonite



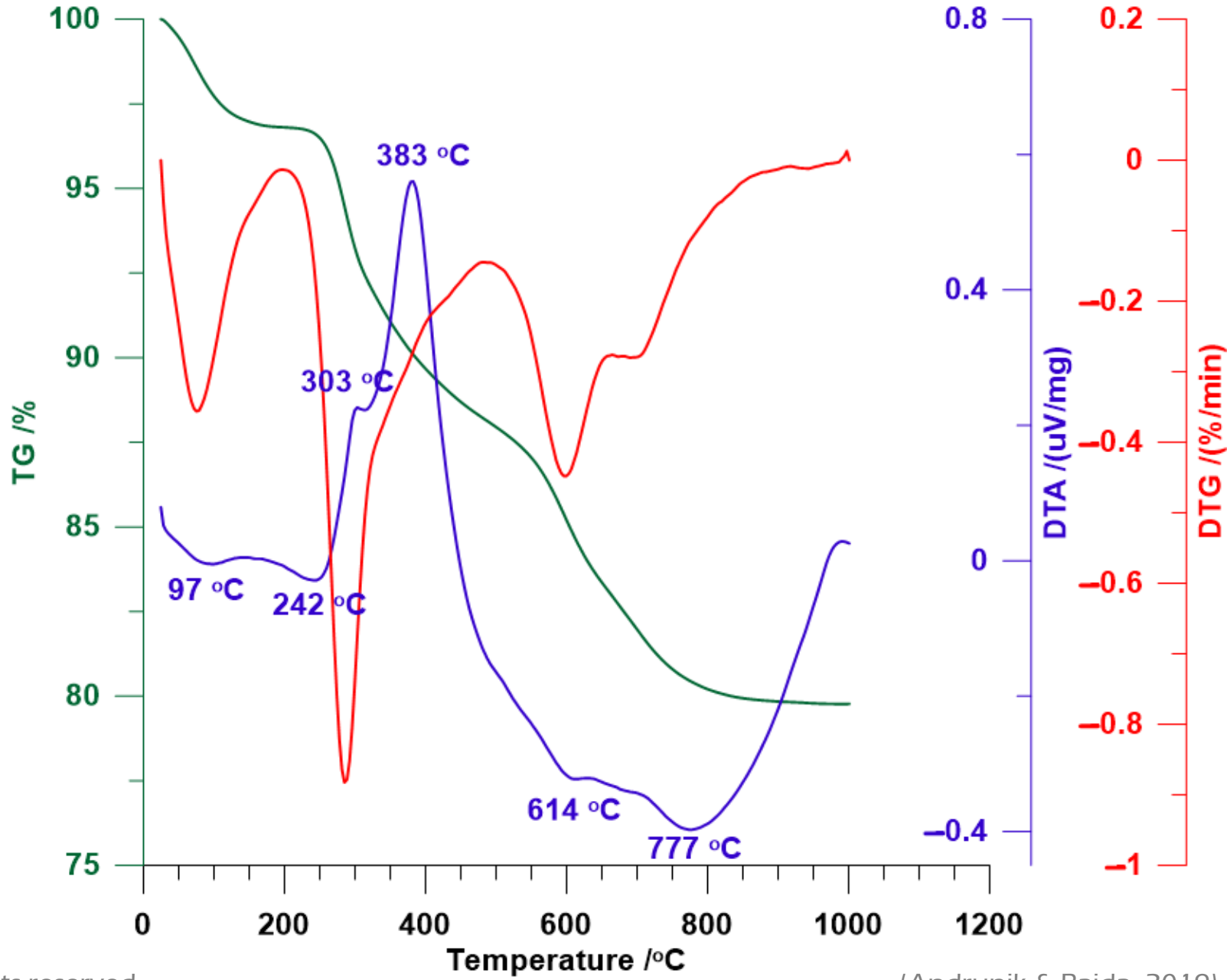
(Andrunik & Bajda, 2019)

TG/DTA curves - bentonite

- 113°C – removal of water molecules physically adsorbed onto the surface of bentonite
- 178°C – the removal of water molecules from interlayer space of montmorillonite—the primary component of bentonite. The shape and the position of the peaks are the effects of dehydratation of Ca-montmorillonite.
- 680°C – dehydroxylation of clay OH units and probable formation of an amorphous meta-montmorillonite phase,
- 936°C – the structural breakdown of bentonite

- 11% loss of mass at 100–200°C – the dehydratation process
- 5–6% loss of mass at 600–1000°C – dehydroxylation and structural breakdown

TG/DTA curves – HD-B



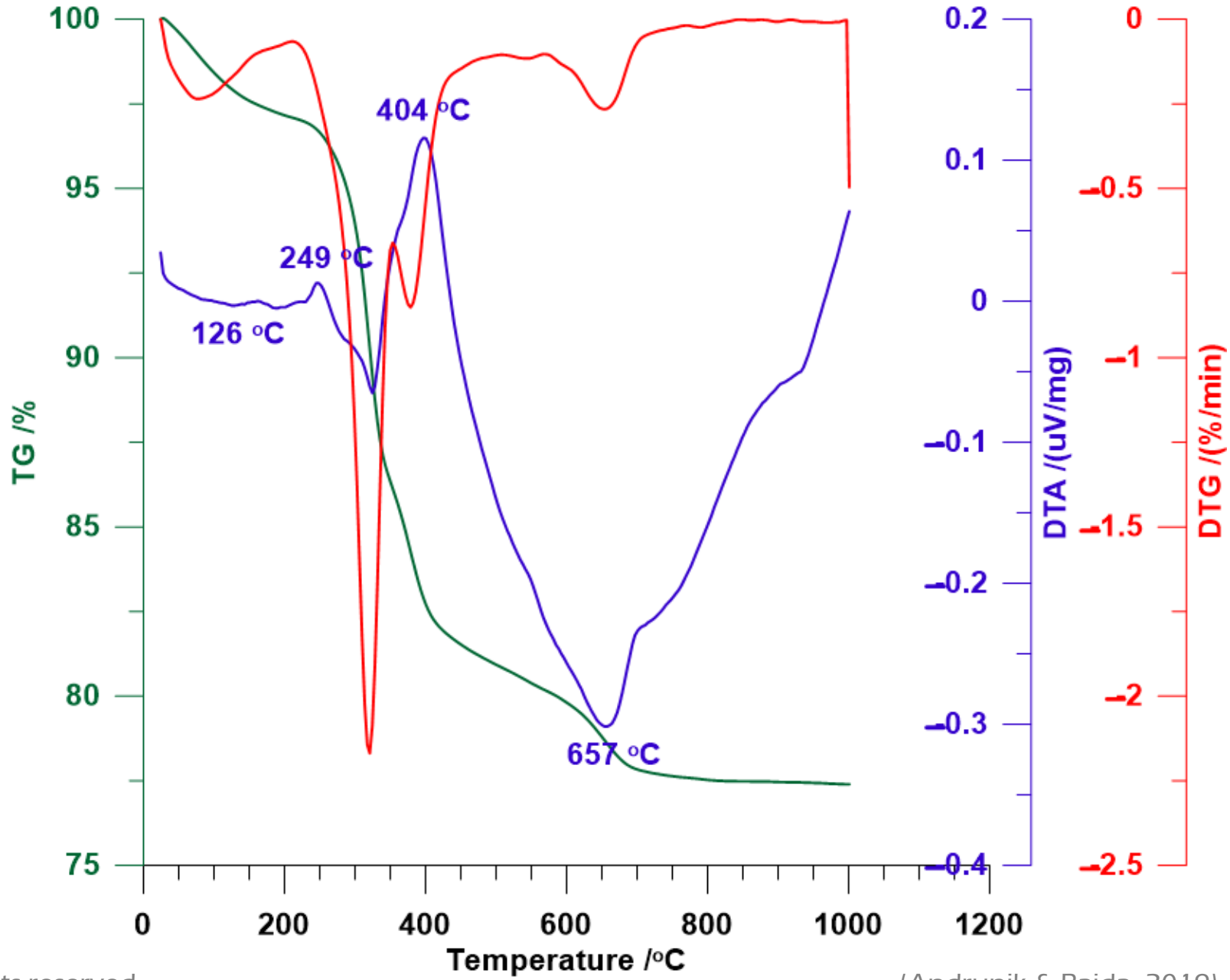
(Andrunik & Bajda, 2019)

TG/DTA curves – HD-B

- 97°C – dehydratation of bentonite
- 303–383°C – the combustion and loss of the surfactant molecules from the surface and from the interlayer space. HDTMA molecules are either decomposed or combusted at ~210°C. The fact that the surfactant molecules are not lost until almost 400°C indicates that the surfactant molecules are strongly bonded in the interlayer of smectite.
- above 600°C – the dehydroxylation and breakdown of the mineral structure. Temperatures of dehydroxylation and breakdown are lower than for natural bentonite—this suggests bonding of the methyl groups of the surfactant with the siloxane layer.

- 20% loss in total mass – decomposition of adsorbed surfactant

TG/DTA curves – TX-B



(Andrunik & Bajda, 2019)

TG/DTA curves – TX-B

- The decomposition of TX100 molecule, with 9.5 ethoxylate groups and one OH group consists of two steps: first, rupture of C–OH and ethoxylate part and C–C alkyl part and second, is the process of combustion. Moreover, oxidation reaction of the organic material derived from a surfactant also usually takes place in two steps. At temperatures ranging from 200 to 500°C, oxidation of organic hydrogen and formation of water and charcoal occurs, whereas at temperatures ranging from 400 to 750°C, oxidation of charcoal and the formation of CO_2 takes place.

- 249°C and 404°C – the decomposition or combustion of TX100 and first step of oxidation. Pure TX100 is decomposed or combusted at a temperature of ~310°C. The interaction of surfactant with the mineral minimizes the disintegration of the surfactant, which occurs at a temperature higher than that is required to disintegrate pure TX100.
- ~400 to 650°C – dehydroxylation processes but also probably oxidation of charcoal originating from the decomposition of surfactants.

- ~23% loss in total mass - decomposition of adsorbed surfactant

Conclusions

- XRD analysis of the surfactants–bentonite systems revealed that nonionic surfactants cause only slight expansion of the interlayer space of smectite. This suggests that the modification of bentonite with TX100 occurs mostly on the surface.
- FTIR spectra showed that the presence of OH vibration bands in samples with adsorbed TX100 suggests interaction of surfactant molecules with the silicate through the functional groups of surfactant and the water coordinated to the exchangeable cations of clay minerals by ion-dipole or hydrogen bonding.
- The analysis of TG/DTA curves indicates that intercalation of surfactants increased the structural and thermal stability of organo-bentonites.

For more detailed information please refer to:

Andrunik, M.; Bajda, T. Modification of Bentonite with Cationic and Nonionic Surfactants: Structural and Textural Features. Materials 2019, 12, 22, doi:10.3390/ma12223772.

Thank you for your attention!