

## INTRODUCTION

Acid activation is a useful method to modify the catalytic behavior, enhance clay properties, mainly their sorptive properties of clay minerals. Thus, acid treatment is commonly required when clays are used in industry, for example, as catalysts or catalyst supports in alkylation, dimerisation and polymerisation reactions and as a component in carbonless copying papers (Fahn and Fenderl, 1983). Probably the most widely used acid-activated clays are the bleaching earths (Anderson and Williams, 1962; Gates et al., 2002), which are capable of removing colour, odour and other impurities from cooking oils of vegetable and animal origin.

The focus of this study was to prepare clay materials by acid attack and determine the effect of acid treatment on the physicochemical and mineralogical properties of the new products obtained.

## ACID ACTIVATION

Samples of 10 g were dispersed in 100 ml of 0.0, 0.5, 0.7, 1.0 and 4.0 N H<sub>2</sub>SO<sub>4</sub> (prepared from H<sub>2</sub>SO<sub>4</sub> 96% p.a, Fischer), the slurry was stirred for 2H at 80°C. At the end of each run, suspensions were filtered and the remaining solid phases were washed several times with pure water (MilliQ ultra filtration) to remove any unspent acid until the filtrates were neutral (test of 5% BaCl<sub>2</sub>). The obtained activated clays were then dried at 110°C, gently ground in an agate mortar. The clay samples thus prepared are designed as BN-0.0, BN-0.5, BN-0.7, BN-1.0 and BN-4.0; S-0.0, S-0.5, S-0.7, S-1.0 and S-4.0 with the suffix indicating the concentration of H<sub>2</sub>SO<sub>4</sub> used during the treatment. The acid treated samples were stored in the plastic bottles closed tightly for uses to the analytical methods.

## ANALYTICAL METHODS

### Structural modification

- X-ray diffraction (XRD)
- Fourier transform infrared spectroscopy (FTIR)
- Thermal analyses (DTA/TGA)
- Scanning electron microscopy (SEM)

### Physicochemical properties

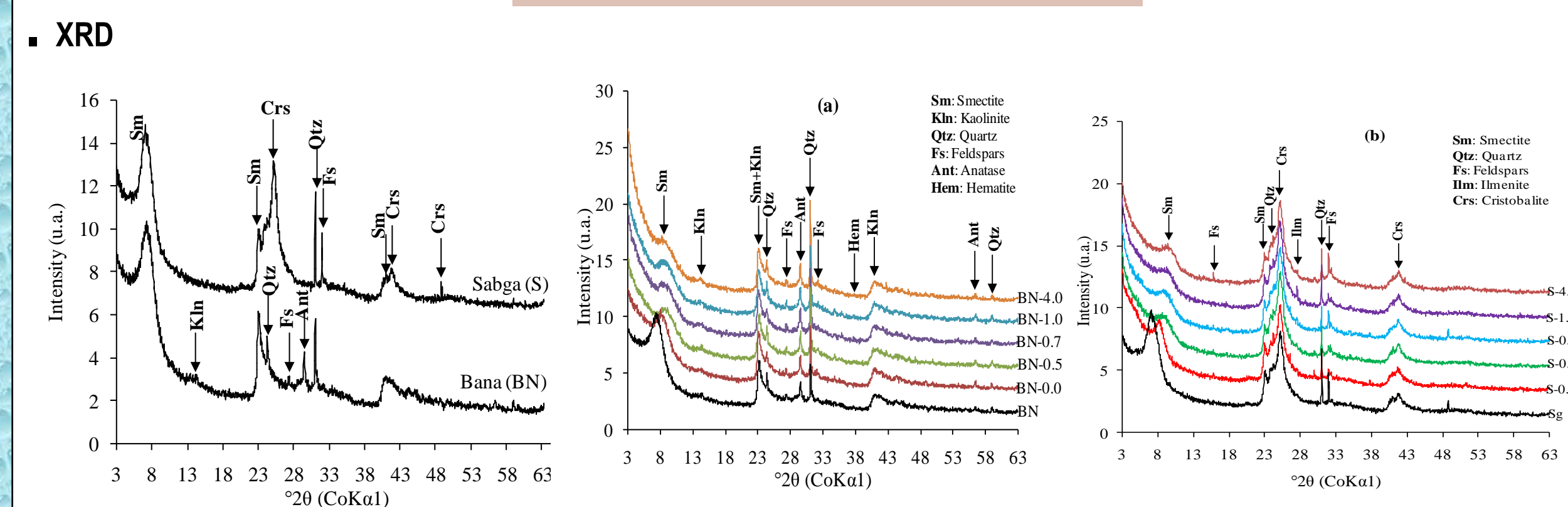
- Nitrogen adsorption – desorption isotherm (BET): for specific surface determination
- Cation exchange capacity (CEC)
- Cations dissolution
- Particle size distribution

## CONCLUSION

The results of this investigation show that the acid activation has caused remarkable change on the structure of smectite phase, the non-clay minerals like cristobalite, quartz and anatase remain unchanged during acid treatment. The specific surface area of activated clays increase, however the cation exchange capacity of clays decreases with increasing acid concentration.

## RESULTS

### 1. Structural modification



The main clay minerals are smectites associated with kaolinite; the non clay minerals are cristobalite (Crs), feldspars (Fps), anatase (Ant) and quartz (Qtz).  
Smectite : montmorillonite

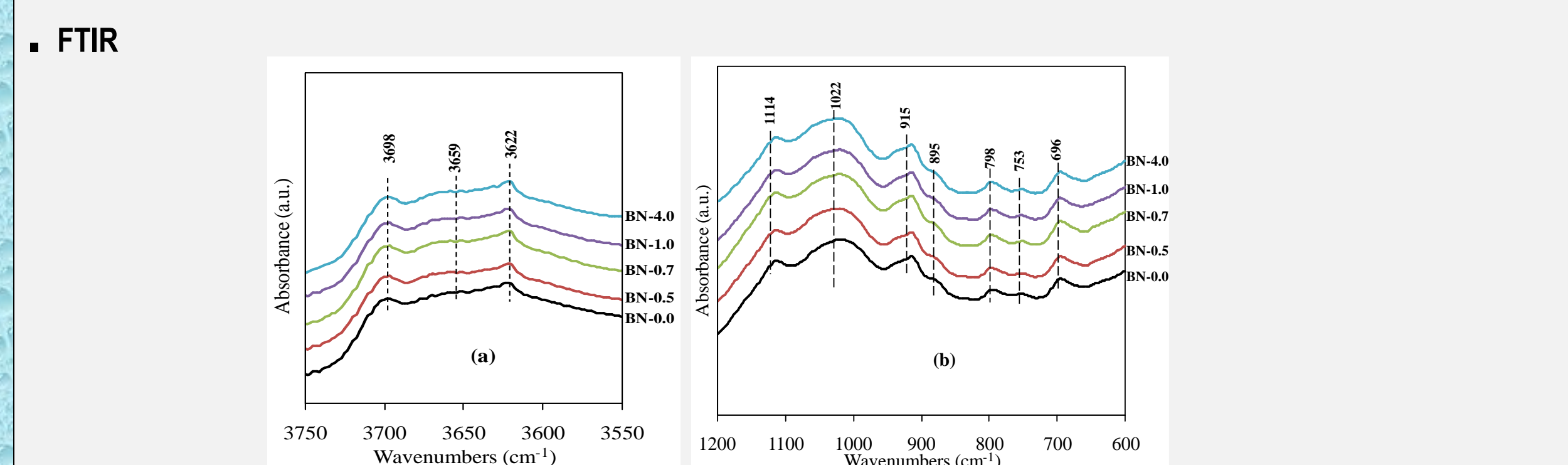


Fig.3. FTIR spectra of natural and activated Bana clay: (a) OH stretching domain (b) Si-O stretching domain

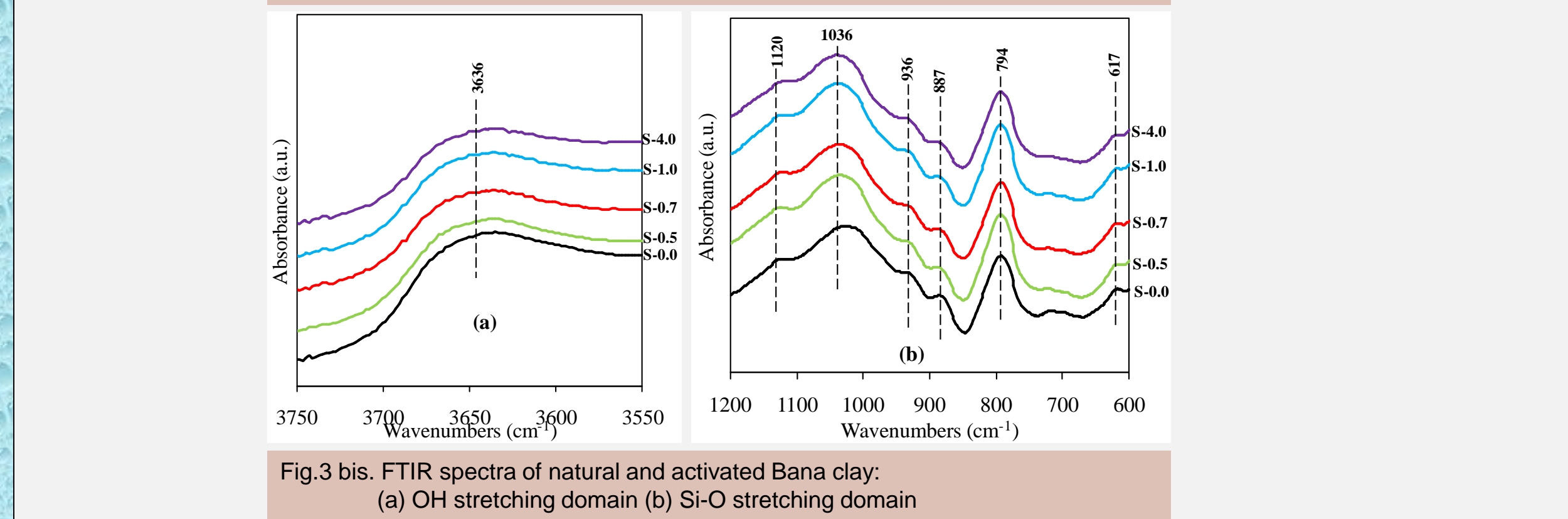


Fig.3 bis. FTIR spectra of natural and activated Bana clay: (a) OH stretching domain (b) Si-O stretching domain

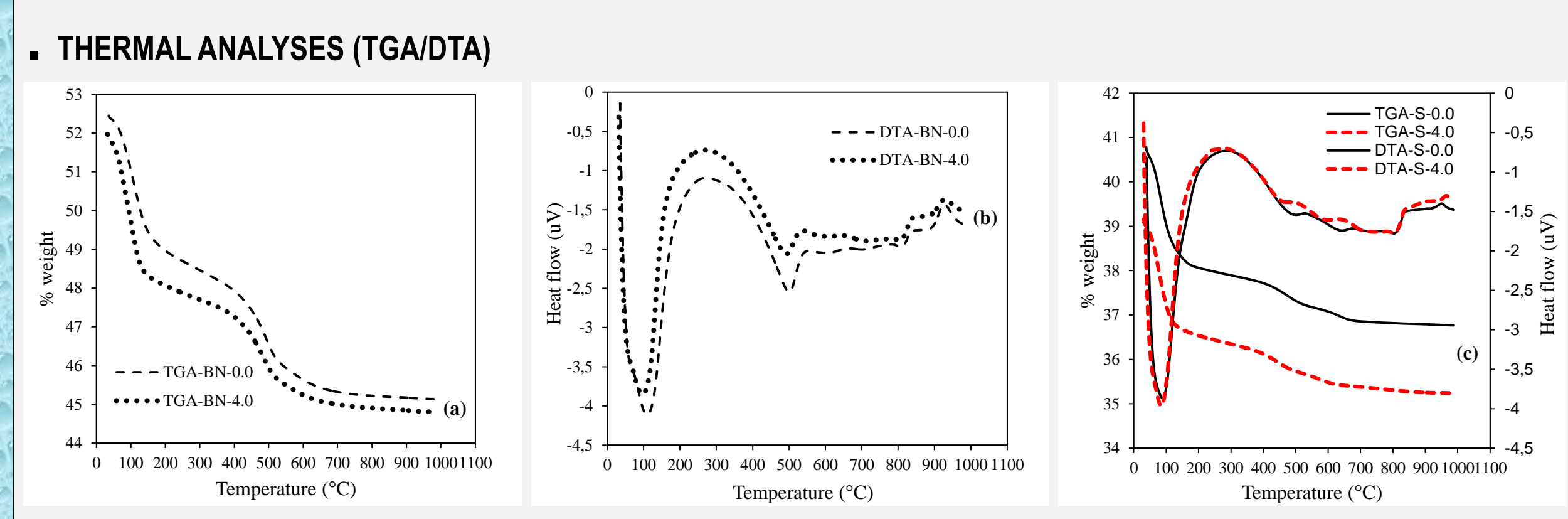


Fig. 4. (a) TGA curves of untreated and treated BN sample, (b) DTA curves of untreated and treated BN sample, (c) DTA-TGA curves of untreated and treated S sample

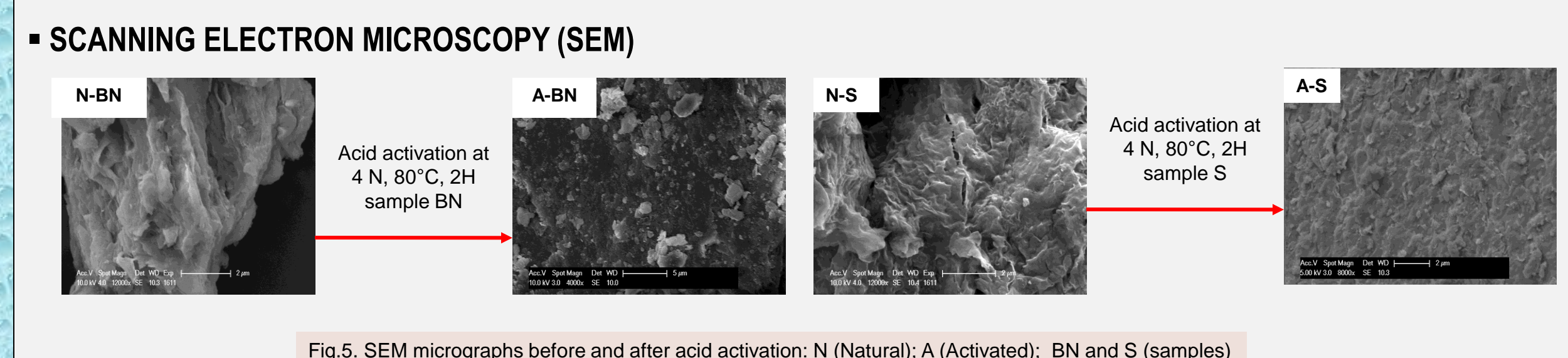


Fig.5. SEM micrographs before and after acid activation: N (Natural); A (Activated); BN and S (samples)

### 2. Physicochemical properties of acid activated clays

- **Particle size distribution:**  
Natural clay (1-10µm): 26.9%; Activated clay: 48.09% (sample BN)  
Natural clay (10-20µm): 19.65%; Activated clay: 26.06% (sample BN)
- **CEC:** Cation exchange capacity decreases continuously with acid concentration (56 to 46 meq/100g for BN and 36 to 25 meq/100g for sample S)
- **Specific surface area (S<sub>BET</sub>):** Specific surface area of acid-activated samples increased with the acid concentration, such that acid activation at 4 N gave rise to a specific surface area 134 m<sup>2</sup>/g and 84 m<sup>2</sup>/g, respectively for BN and S clay samples, whereas in the untreated samples it was 65 m<sup>2</sup>/g and 74 m<sup>2</sup>/g
- **Cations dissolution:** Increase of H<sub>2</sub>SO<sub>4</sub> concentration up to 4 N caused increase of cation dissolution (Ca, K, Mg, Na, Al, Fe and Si), and no amount of titanium is dissolved during acid treatment, indicating that anatase is not destroyed.

#### References:

1. Anderson, A.J.C., Williams, P.N., 1962. Refining of Oils and Fats for Edible Purposes. Pergamon, New York.
2. Fahn, R., Fenderl, K., 1983. Reaction products of organic dye molecules with acid-treated montmorillonites. Clay Minerals. 18, 447– 458.
3. Gates, W.P., Anderson, J.S., Raven, M.D., Churchman G.J., 2002. Mineralogy of a bentonite from Miles, Queensland, Australia and characterization of its acid activation products, Applied Clay Science. 20 189–197.